

Solid State Chemistry

An introduction

SECOND EDITION

Lesley Smart and Elaine Moore



Springer-Science+Business Media, B.V.

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Second edition

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Dedicated to
Graham, Sam, Rosemary and Laura

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Preface to the second edition

We were very pleased to be asked to prepare a second edition of this book. When we tried to decide on the changes (apart from updating) to be made, the advice from our editor was ‘if it ain’t broke, don’t fix it’. However, the results of a survey of our users requested about five new subjects but with the provisos that nothing was taken out, that the book didn’t get much longer and above all that it didn’t increase in price! So what you see here is an attempt to do the impossible, and we hope that we have satisfied some, if not all, of the requests.

The main changes from the first edition are two new chapters – Chapter 2 on X-ray diffraction and Chapter 3 on preparative methods. A short discussion of symmetry elements has been included in Chapter 1. Other additions include an introduction to ALPOs and to clay minerals in Chapter 7 and to ferroelectrics in Chapter 9. We decided that there simply was not enough room to cover the Phase Rule properly and for that we refer you to the excellent standard physical chemistry texts such as Atkins. We hope that the book now covers most of the basic undergraduate teaching material on solid state chemistry.

We are indebted to Professor Tony Cheetham for kindling our interest in this subject with his lectures at Oxford University and the beautifully illustrated articles that he and his collaborators have published over the years. Our thanks are also due to Dr Paul Raithby for commenting on part of the manuscript.

As always, we thank our colleagues at the Open University for all their support and especially the members of the lunch club, who not only keep us sane, but keep us laughing. Finally, thanks go to our families for putting up with us and in particular to our children for coping admirably with two increasingly distracted academic mothers – our book is dedicated to them.

Lesley E. Smart and Elaine A. Moore
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Preface to the first edition

The idea for this book originated with our involvement in an Open University inorganic chemistry course (S343: Inorganic Chemistry). When the Course Team met to decide the contents of this course, we felt that solid state chemistry had become an interesting and important area that must be included. It was also apparent that this area was playing a larger role in the undergraduate syllabus at many universities, due to the exciting new developments in the field.

Despite the growing importance of solid state chemistry, however, we found that there were few textbooks that tackled solid state theory from a chemist's rather than a physicist's viewpoint. Of those that did most, if not all, were aimed at final year undergraduates and postgraduates. We felt there was a need for a book written from a chemist's viewpoint that was accessible to undergraduates earlier in their degree programme. This book is an attempt to provide such a text.

Because a book of this size could not cover all topics in solid state chemistry, we have chosen to concentrate on structures and bonding in solids, and on the interplay between crystal and electronic structure in determining their properties. Examples of solid state devices are used throughout the book to show how the choice of a particular solid for a particular device is determined by the properties of that solid.

Chapter 1 is an introduction to crystal structures and the ionic model. It introduces many of the crystal structures that appear in later chapters and discusses the concepts of ionic radii and lattice energies. Ideas such as close-packed structures and tetrahedral and octahedral holes are covered here; these are used later to explain a number of solid state properties.

Chapter 2 introduces the band theory of solids. The main approach is via the tight binding model, seen as an extension of the molecular orbital theory familiar to chemists. Physicists more often develop the band model via the free electron theory, which is included here for completeness. This chapter also discusses electronic conductivity in solids and in particular properties and applications of semiconductors.

Chapter 3 is concerned with solids that are not perfect. The types of

defect that occur and the way they are organized in solids forms the main subject matter. Defects lead to interesting and exploitable properties and several examples of this appear in this chapter, including photography and solid state batteries.

The remaining chapters each deal with a property or a special class of solid. Chapter 4 covers low-dimensional solids, the properties of which are not isotropic. Chapter 5 deals with zeolites, an interesting class of compounds used extensively in industry (as catalysts for example), the properties of which strongly reflect their structure. Chapter 6 deals with optical properties and Chapter 7 with magnetic properties of solids. Finally, Chapter 8 explores the exciting field of superconductors, in particular the relatively recently discovered high-temperature superconductors.

The approach adopted is deliberately non-mathematical, and assumes only the chemical ideas that a first year undergraduate would have. For example, differential calculus is used on only one or two pages and non-familiarity with this would not hamper an understanding of the rest of the book; topics such as ligand field theory are not assumed.

As this book originated with an Open University text, it is only right that we should acknowledge the help and support of our colleagues on the Course Team, in particular Dr David Johnson and Dr Kiki Warr. We are also grateful to Dr Joan Mason who read and commented on much of the script and to the anonymous reviewer to whom Chapman & Hall sent the original manuscript and who provided very thorough and useful comments.

The authors have been sustained through the inevitable drudgery of writing, by an enthusiasm for this fascinating subject. We hope that some of this transmits itself to the student.

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OU, Walton Hall, Milton Keynes

Basic SI units

<i>Physical quantity (and symbol)</i>	<i>Name of SI unit</i>	<i>Symbol for unit</i>
Length (l)	metre	m
Mass (m)	kilogram	kg
Time (t)	second	s
Electric current (I)	ampere	A
Thermodynamic temperature (T)	kelvin	K
Amount of substance (n)	mole	mol
Luminous intensity (I_v)	candela	cd

Derived SI units having special names and symbols

<i>Physical quantity (and symbol)</i>	<i>Name of SI unit</i>	<i>Symbol for SI derived unit and definition of unit</i>
Frequency (ν)	hertz	Hz ($= \text{s}^{-1}$)
Energy (U), enthalpy (H)	joule	J ($= \text{kg m}^2 \text{s}^{-2}$)
Force	newton	N ($= \text{kg m s}^{-2} = \text{J m}^{-1}$)
Power	watt	W ($= \text{kg m}^2 \text{s}^{-3} = \text{J s}^{-1}$)
Pressure (p)	pascal	Pa ($= \text{kg m}^{-1} \text{s}^{-2} = \text{N m}^{-2} = \text{J m}^{-3}$)
Electric charge (Q)	coulomb	C ($= \text{A s}$)
Electric potential difference (V)	volt	V ($= \text{kg m}^2 \text{s}^{-3} \text{A}^{-1} = \text{J A}^{-1} \text{s}^{-1}$)
Capacitance (c)	farad	F ($= \text{A}^2 \text{s}^4 \text{kg}^{-1} \text{m}^{-2} =$ $\text{A s V}^{-1} = \text{A}^2 \text{s}^2 \text{J}^{-1}$)
Resistance (R)	ohm	Ω ($= \text{V A}^{-1}$)
Conductance (G)	siemen	S ($= \text{A V}^{-1}$)
Magnetic flux density (B)	tesla	T ($= \text{V s m}^{-2} = \text{J C}^{-1} \text{s m}^{-2}$)

SI prefixes

10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^3	10^6	10^9	10^{12}
femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga	tera
f	p	n	μ	m	c	d	k	M	G	T

Fundamental constants

<i>Constant</i>	<i>Symbol</i>	<i>Value</i>
Speed of light in a vacuum	c	$2.997925 \times 10^8 \text{ m s}^{-1}$
Charge of proton	e	$1.602189 \times 10^{-19} \text{ C}$
Charge of electron	$-e$	
Avogadro constant	N_{A}	$6.022045 \times 10^{23} \text{ mol}^{-1}$
Boltzmann constant	k	$1.380662 \times 10^{-23} \text{ J K}^{-1}$
Gas constant	$R = N_{\text{A}}k$	$8.31441 \text{ J K}^{-1} \text{ mol}^{-1}$
Faraday constant	$F = N_{\text{A}}e$	$9.648456 \times 10^4 \text{ C mol}^{-1}$
Planck constant	h	$6.626176 \times 10^{-34} \text{ J s}$
	$\hbar = \frac{h}{2\pi}$	$1.05457 \times 10^{-34} \text{ J s}$
Vacuum permittivity	ϵ_0	$8.854 \times 10^{-12} \text{ F m}^{-1}$
Vacuum permeability	μ_0	$4\pi \times 10^{-7} \text{ J s}^2 \text{ C}^{-2} \text{ m}^{-1}$
Bohr magneton	μ_{B}	$9.27402 \times 10^{-24} \text{ J T}^{-1}$
Electron g value	g_{e}	2.00232

Miscellaneous physical quantities

<i>Name of physical quantity</i>	<i>Symbol</i>	<i>SI unit</i>
Enthalpy	H	J
Entropy	S	J K^{-1}
Gibbs function	G	J
Standard change of molar enthalpy	$\Delta H_{\text{m}}^{\ominus}$	J mol^{-1}
Standard change of molar entropy	$\Delta S_{\text{m}}^{\ominus}$	$\text{J K}^{-1} \text{mol}^{-1}$
Standard change of molar Gibbs function	$\Delta G_{\text{m}}^{\ominus}$	J mol^{-1}
Wavenumber	$\sigma \left(= \frac{1}{\lambda} \right)$	cm^{-1}
Atomic number	Z	dimensionless
Conductivity	σ	S m^{-1}
Density	ρ	kg m^{-3}
Molar bond dissociation energy	D_{m}	J mol^{-1}
Molar mass	$M \left(= \frac{m}{n} \right)$	kg mol^{-1}

Periodic classification of the elements

Group	I	II																
1st Period																		¹ H
2nd Period	³ Li	⁴ Be																
3rd Period	¹¹ Na	¹² Mg																
4th Period	¹⁹ K	²⁰ Ca																
5th Period	³⁷ Rb	³⁸ Sr	lanthanides															
6th Period	⁵⁵ Cs	⁵⁶ Ba	⁵⁷ La	⁵⁸ Ce	⁵⁹ Pr	⁶⁰ Nd	⁶¹ Pm	⁶² Sm	⁶³ Eu	⁶⁴ Gd	⁶⁵ Tb	⁶⁶ Dy	⁶⁷ Ho	⁶⁸ Er	⁶⁹ Tm	⁷⁰ Yb		
7th Period	⁸⁷ Fr	⁸⁸ Ra	⁸⁹ Ac	⁹⁰ Th	⁹¹ Pa	⁹² U	⁹³ Np	⁹⁴ Pu	⁹⁵ Am	⁹⁶ Cm	⁹⁷ Bk	⁹⁸ Cf	⁹⁹ Es	¹⁰⁰ Fm	¹⁰¹ Md	¹⁰² No		
			actinides															
			typical elements															

										III	IV	V	VI	VII	0
															² He
										5 B	6 C	7 N	8 O	9 F	10 Ne
										13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
103 Lr	104	105	106												

transition elements

The Greek alphabet

alpha	Α	α	nu	Ν	ν
beta	Β	β	xi	Ξ	ξ
gamma	Γ	γ	omicron	Ο	ο
delta	Δ	δ	pi	Π	π
epsilon	Ε	ε	rho	Ρ	ρ
zeta	Ζ	ζ	sigma	Σ	σ
eta	Η	η	tau	Τ	τ
theta	Θ	θ	upsilon	Υ	υ
iota	Ι	ι	phi	Φ	φ
kappa	Κ	κ	chi	Χ	χ
lambda	Λ	λ	psi	Ψ	ψ
mu	Μ	μ	omega	Ω	ω

An introduction to simple crystal structures

1

1.1 INTRODUCTION

All substances, except helium, if cooled sufficiently form a solid phase; the vast majority form one or more **crystalline** phases, where the atoms, molecules or ions pack together to form a regular repeating array. This book is concerned mostly with the structure of metals and solids which do not contain discrete molecules as such, but comprise extended arrays of atoms or ions. We try to show how the properties of the solid depend on the structure.

Crystal structures are usually determined by the technique of **X-ray crystallography**. This technique relies on the fact that the atomic spacings in crystals are of the same order of magnitude as the wavelength of X-rays (of the order of $1 \text{ \AA}$ or 100 pm): a crystal thus acts as a three-dimensional diffraction grating to a beam of X-rays. The resulting diffraction pattern can be interpreted to give the internal positions of the atoms in the crystal very precisely. Chapter 2 discusses this technique in some detail, but we refer you to the further reading lists at the end of each chapter for references to suitable texts or articles on other physical techniques.

The structures of many inorganic solids can be discussed in terms of the simple packing of spheres, so it is at this point we will start, before moving on to the more formal classification of crystals.

1.2 CLOSE PACKING

Think for the moment of an atom as a small hard sphere. Figure 1.1 shows two possible arrangements for a layer of such identical atoms. On squeezing the square layer in Figure 1.1a, the spheres would move to the positions in Figure 1.1b so that the layer takes up less space. The layer in Figure 1.1b (layer A) is called **close-packed**.

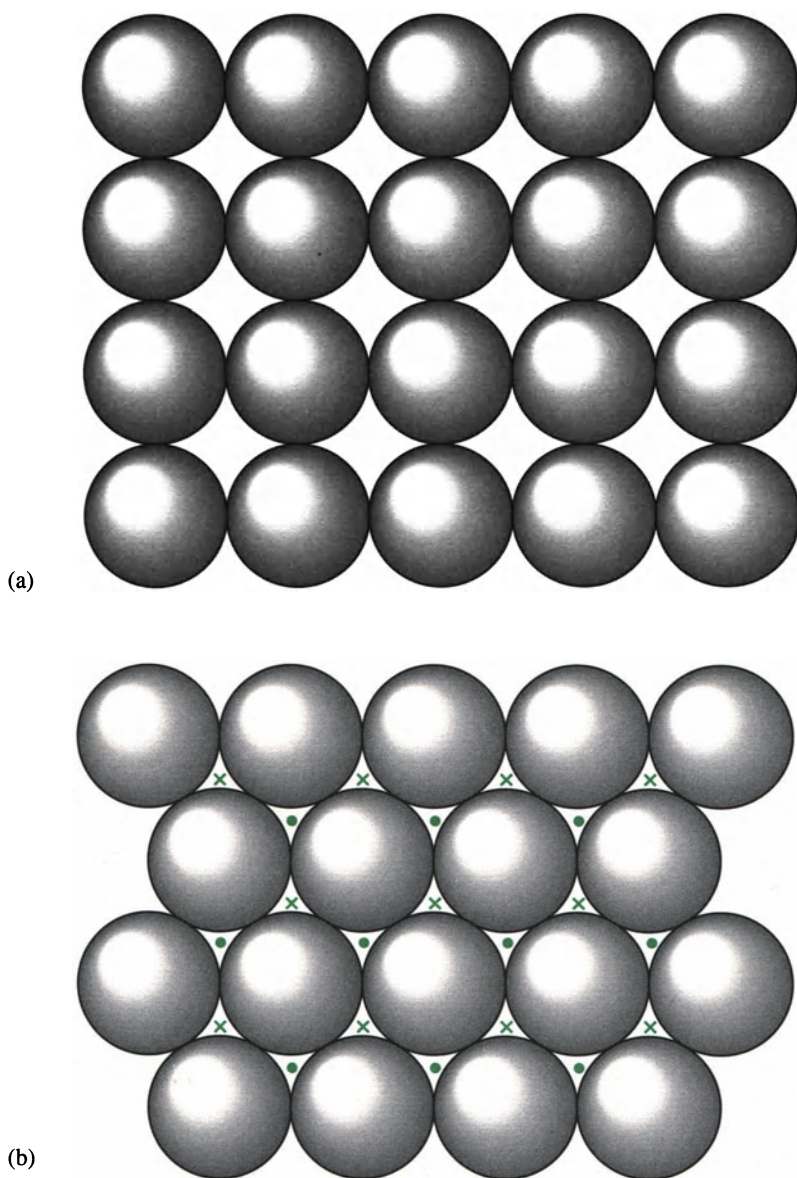


Figure 1.1 (a) A square array of spheres. (b) A close-packed layer of spheres.

To build up a close-packed structure in three dimensions we must now add a second layer (layer B). The spheres of the second layer sit in half of the hollows of the first layer: these have been marked with dots and crosses. The layer B (colour) in Figure 1.2 sits over the hollows marked

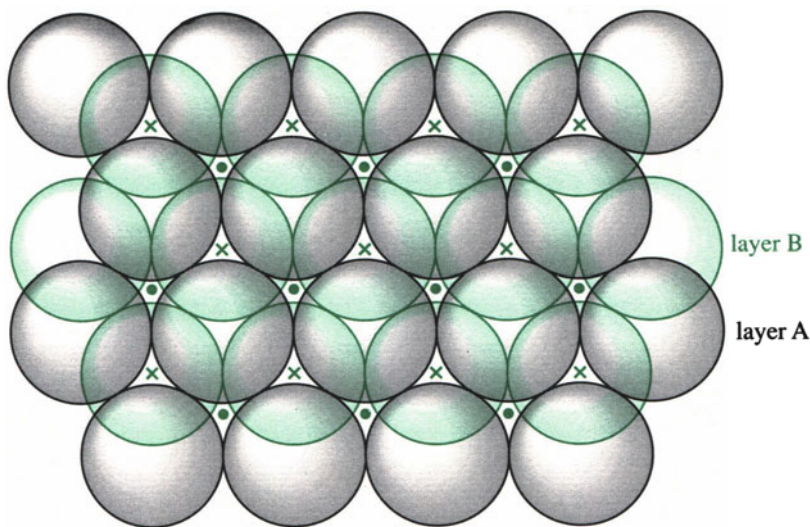


Figure 1.2 Two layers of close-packed spheres.

with a cross (although it makes no difference which type we choose). When we come to add a third layer there are two possible positions where it can go. First, it could go directly over layer A: if we then repeated this stacking sequence we would build up the layers ABABABA . . . and so on. This is known as **hexagonal close packing (hcp)**. Second, the third layer could be positioned over those spaces marked with a dot. This third layer, C, would not be directly over either A or B, and the stacking sequence when repeated would be ABCABCAB . . . and so on. This is known as **cubic close packing (ccp)**. (The names *hexagonal* and *cubic* for these structures arise from the resulting symmetry of the structure; this will be discussed more fully later on.)

Close packing represents the most efficient use of space when packing equal spheres; 74% of the volume is occupied by the spheres and the **packing efficiency** is said to be 74%. Each sphere in the structure is surrounded by 12 equidistant neighbours: six in the same layer, three in the layer above and three in the layer below. The **coordination number** of an atom in a close-packed structure is thus 12.

Another important feature of close-packed structures that we will use extensively later on, is the shape and number of the small amounts of space trapped in between the spheres. There are two different types of space within a close-packed structure: the first we will consider is called an **octahedral hole**. Figure 1.3 shows two close-packed layers again but now with the octahedral holes shaded (in colour). Each of these holes is surrounded by six spheres, three in one layer and three in the other. The

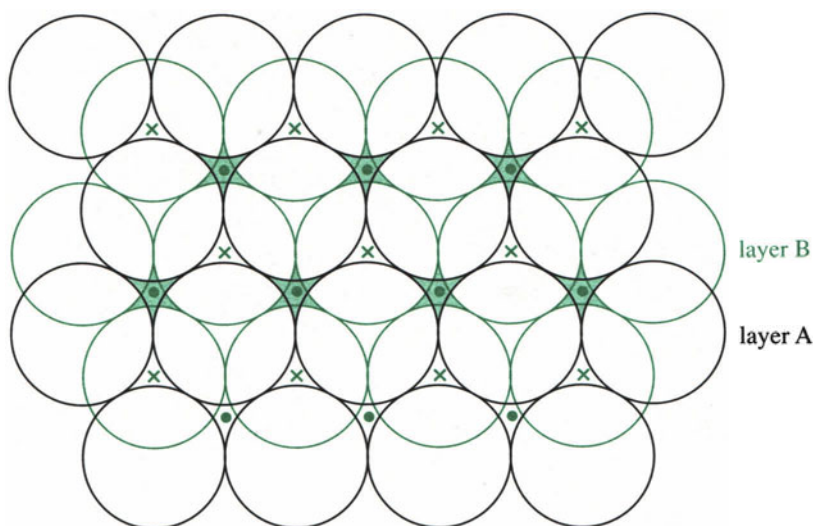


Figure 1.3 Two layers of close-packed spheres with the enclosed octahedral holes picked out in colour.

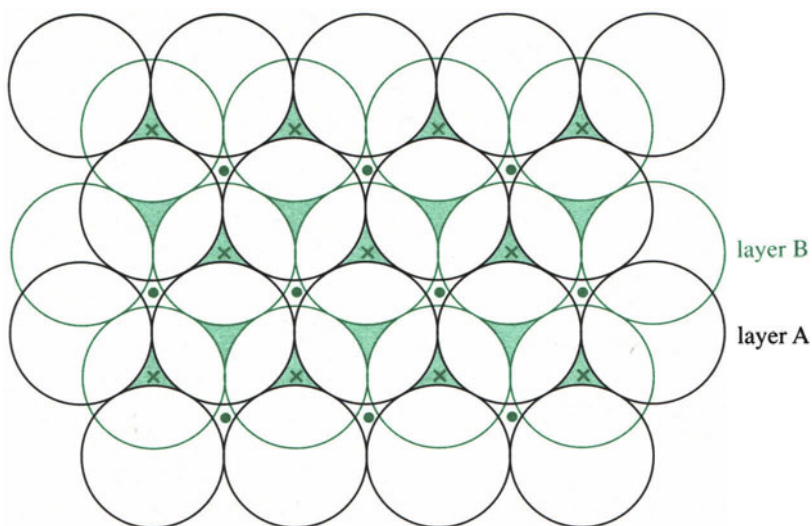


Figure 1.4 Two layers of close-packed spheres with the tetrahedral holes picked out in colour.

centres of the spheres lie at the corners of an octahedron, hence the name. If there are n spheres in the array, then there are also n octahedral holes. Similarly, Figure 1.4 shows two close-packed layers, now with the second type of space, **tetrahedral holes**, shaded in colour. Each of these

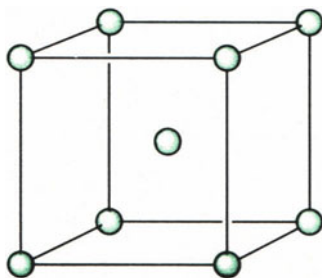


Figure 1.5 A body-centred cubic array.

holes is surrounded by four spheres with centres at the corners of a tetrahedron. If there are n spheres in the array, then there are $2n$ tetrahedral holes. The octahedral holes in a close-packed structure are much bigger than the tetrahedral holes; they are surrounded by six atoms rather than four. It is a matter of simple geometry to calculate that the radius of a sphere that will just fit in an octahedral hole in a close-packed array of spheres of radius r is $0.414r$. For a tetrahedral hole the radius is $0.225r$.

There are of course innumerable stacking sequences that are possible when repeating close-packed layers; however, the hexagonal close-packed and cubic close-packed are those of maximum simplicity and are those most commonly encountered in the crystal structures of the noble gases and of the metallic elements (only two other stacking sequences are found in perfect crystals of the elements: an ABAC repeat in La, Pr, Nd and Am, and a nine-layer repeat ABACACBCB in Sm).

1.3 BODY-CENTRED AND PRIMITIVE STRUCTURES

Some metals do not adopt a close-packed structure but have a slightly less efficient packing method: this is the **body-centred cubic structure (bcc)** shown in Figure 1.5. (Unlike the previous diagrams, the positions of the atoms are represented here, and in subsequent diagrams, by small circles which do not touch: this is merely a device to open up the structure and allow it to be seen more clearly. The whole question of atom and ion size is discussed in section 1.6.4). In this structure an atom in the middle of a cube is surrounded by eight equidistant atoms at the corners of the cube: the coordination number has dropped to eight and the packing efficiency is 68% (compared with 74% for close-packing).

The simplest of the cubic structures is the **primitive cubic structure**. This is built by placing square layers like the one shown in Figure 1.1a, directly on top of one another. Figure 1.6 illustrates this, and you can see

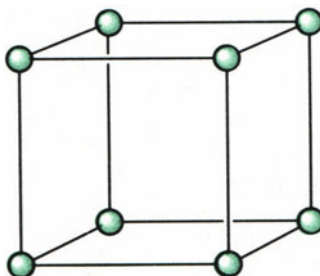


Figure 1.6 A primitive cubic array.

that each atom sits at the corner of a cube. The coordination number of an atom in this structure is six.

The majority of metals have one of the three basic structures: *hcp*, *ccp* or *bcc*. Polonium alone adopts the primitive structure. (The bonding in metals is discussed in Chapter 4). The distribution of the packing types among the most stable forms of the metals at 298 K is shown in Figure 1.7. As we noted earlier, very few metals have a mixed *hcp/ccp* structure of a more complex type. The structures of the actinides tend to be rather complex and are not included.

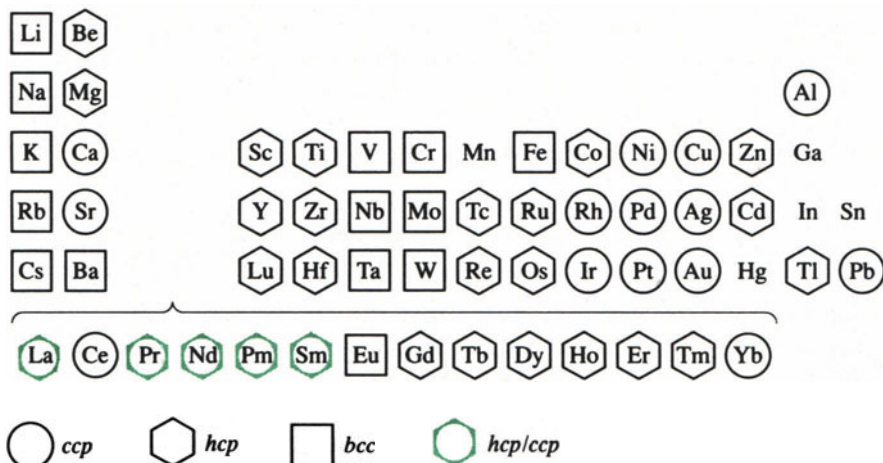


Figure 1.7 Occurrence of packing types among the metals.

1.4 SYMMETRY

Before we take the discussion of crystalline structures any further, we will look at the symmetry displayed by structures. The concept of symmetry is

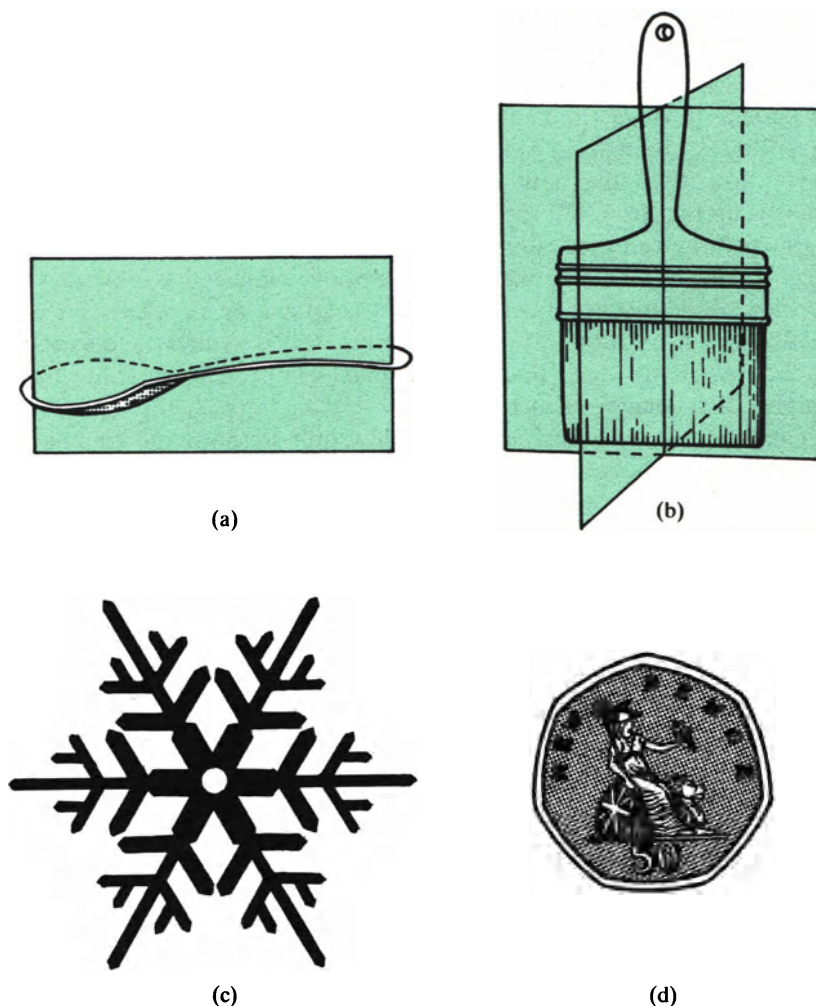


Figure 1.8 Common objects displaying symmetry: (a) a spoon, (b) a paintbrush, (c) a snowflake, (d) a 50p coin.

an extremely useful one when it comes to describing the shapes of both individual molecules and of regular repeating structures, as it provides a way of describing similar features in different structures so that they become unifying features. The symmetry of objects in everyday life is something that we tend to take for granted and recognize easily without having to think about it. Take some simple examples illustrated in Figure 1.8. If you imagine a mirror dividing the spoon in half along the plane indicated, then you can see that one half of the spoon is a mirror image or

reflection of the other. Similarly with the paintbrush, only now there are two mirror planes at right angles which divide it.

Objects can also possess rotational symmetry; in Figure 1.8c imagine an axle passing through the centre of the snowflake, in the same way as a wheel rotates about an axle; if the snowflake is rotated through $1/6$ of a revolution, then the new position is indistinguishable from the old. Similarly in Figure 1.8d, rotating the 50p coin by $1/7$ of a revolution brings us to the same position as we started (ignoring the pattern on the surface). The symmetry possessed by a single object that describes the repetition of identical parts of the object is known as its **point symmetry**.

Actions such as rotating a molecule are called **symmetry operations**, and the rotational axes and mirror planes possessed by objects are examples of **symmetry elements**.

There are two forms of symmetry notation in common use, and as chemists you will come across both. The **Schoenflies** notation is useful for describing the point symmetry of individual molecules and is used by spectroscopists. The **Hermann–Mauguin** notation can be used to describe the point symmetry of individual molecules but in addition can also describe the relationship of different molecules to one another in space – their so-called **space-symmetry**, and so is the form most commonly met in crystallography and the solid state. We give here the Schoenflies notation in parentheses after the Hermann-Mauguin notation.

1.4.1 Axes of rotation

In the same way that we saw above for the snowflake and the 50p coin, molecules and crystals can also possess rotational symmetry. Figure 1.9 illustrates this for several molecules. In Figure 1.9a the rotational axis is shown as a vertical line through the O atom in OF_2 ; rotation about this line by 180° in the direction of the arrow, produces an identical looking molecule. The line about which the molecule rotates is called an **axis of symmetry**, and in this case it is a twofold axis because we have to perform the operation twice to return the molecule to its starting position.

Axes of symmetry are denoted by the symbol n (C_n), where n is the order of the axis. So the rotational axis of the OF_2 molecule is 2 (C_2).

The BF_3 molecule in Figure 1.9b possesses a threefold axis of symmetry, 3 (C_3), because each $1/3$ of a revolution leaves the molecule looking the same, and three turns brings the molecule back to its starting position. In the same way, the XeF_4 molecule in Figure 1.9c has a fourfold axis, 4 (C_4), and four quarter turns are necessary to bring it back to the beginning. All linear molecules have an ∞ (C_∞) axis, which is illustrated for the BeF_2 molecule in Figure 1.9d; however small a fraction of a circle it is rotated through, it always looks identical. The smallest

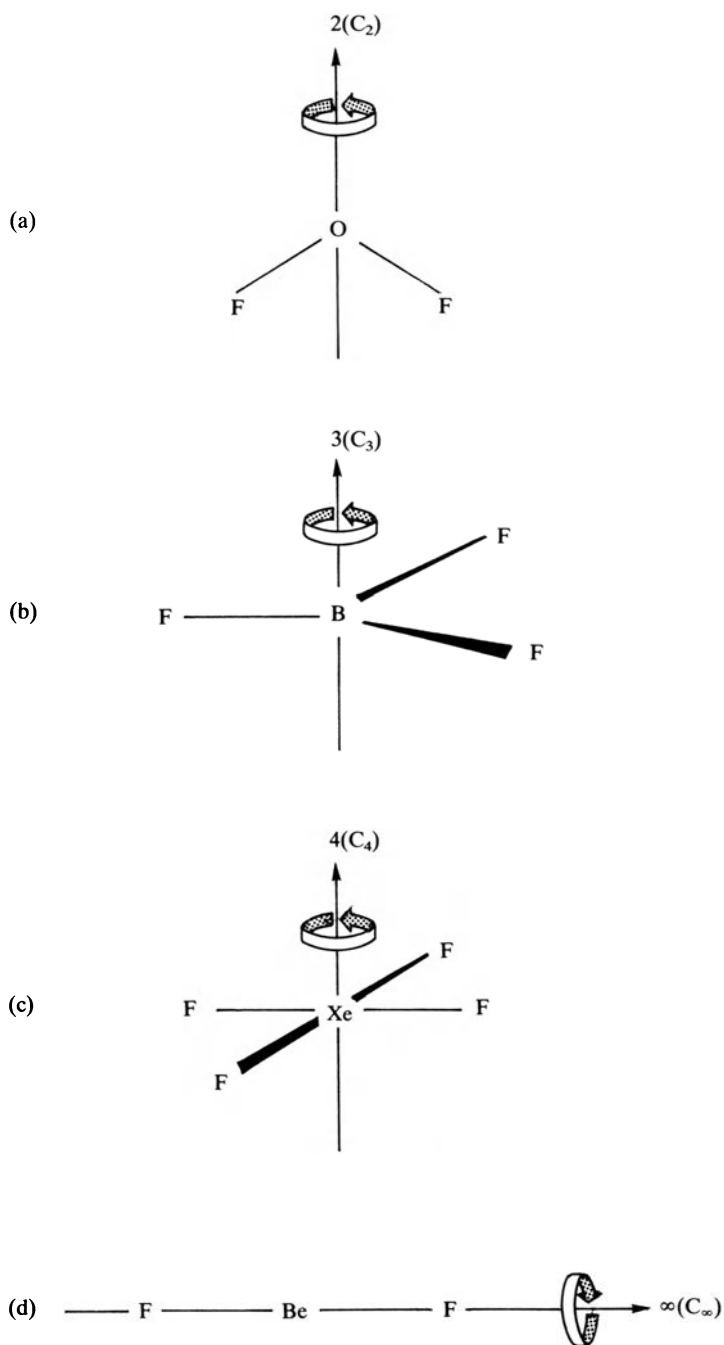


Figure 1.9 Axes of rotation in molecules: (a) twofold axis in OF_2 , (b) threefold axis in BF_3 , (c) fourfold axis in XeF_4 , (d) ∞ -fold axis in BeF_2 .

rotation possible is $1/\infty$, and so the axis is an infinite-order axis of symmetry.

1.4.2 Planes of symmetry

Mirror planes occur in isolated molecules and in crystals, such that everything on one side of the plane is a mirror image of the other. In a structure, such a mirror plane is known as a **plane of symmetry** and is given the symbol σ (σ). Molecules may possess one or more planes of symmetry, and the diagrams in Figure 1.10 illustrate some examples. The planar OF_2 molecule has two planes of symmetry (Figure 1.10a): one is the plane of the molecule, the other is at right angles to this. For all planar molecules, the plane of the molecule is a plane of symmetry. The diagrams for BF_3 and XeF_4 (also planar molecules) only show the planes of symmetry which are perpendicular to the plane of the molecule.

1.4.3 Inversion

The third symmetry operation that we show in this section is called **inversion** through a centre of symmetry and is given the symbol $\bar{1}$ (i). In this operation you have to imagine a line drawn from any atom in the molecule, through the centre of symmetry and then continued for the

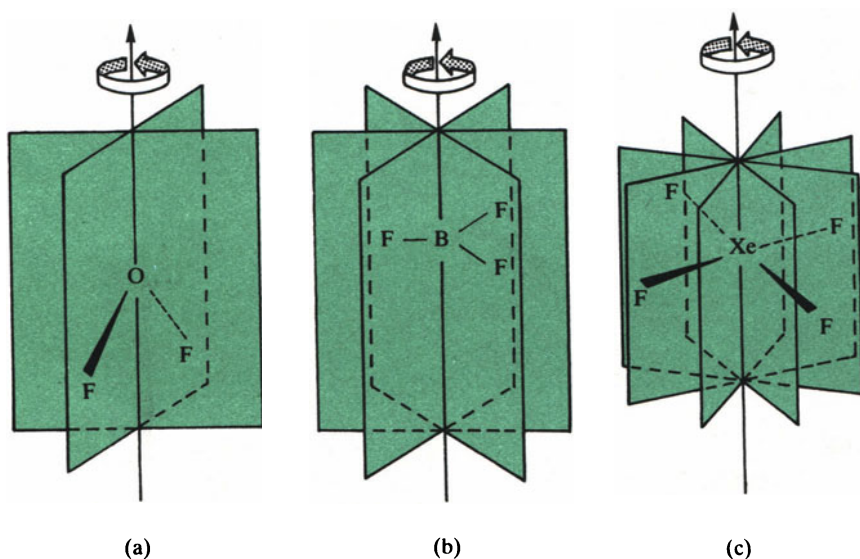


Figure 1.10 Planes of symmetry in molecules: (a) planes of symmetry in OF_2 , (b) planes of symmetry in BF_3 , (c) planes of symmetry in XeF_4 .

same distance the other side; if for every atom this meets with an identical atom on the other side, then the molecule has a centre of symmetry. Of the molecules in Figure 1.9, XeF_4 and BeF_2 both have a centre of symmetry, and BF_3 and OF_2 don't.

1.4.4 Inversion axes and improper rotation axes

The final symmetry element is described differently by the two systems, although both descriptions use a combination of the symmetry elements described above. The Hermann–Mauguin **inversion axis** is a combination of rotation and inversion and is given the symbol $\bar{n}$. The symmetry element consists of a rotation by $1/n$ of a revolution about the axis, followed by inversion through the centre of symmetry. An example of a $\bar{4}$ inversion axis is shown in Figure 1.11 for a tetrahedral molecule such as

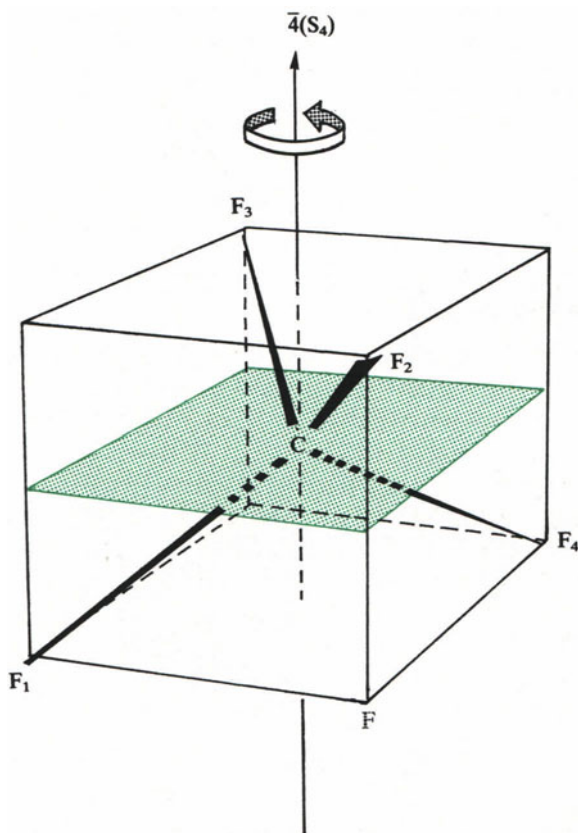


Figure 1.11 The $\bar{4}(\text{S}_4)$ inversion (improper) axis of rotation in the tetrahedral CF_4 molecule.

CF₄. The molecule is shown inside a cube as this makes it easier to see the symmetry elements. Rotation about the axis through 90° takes F₁ to the position shown dotted; inversion through the centre then takes this atom to the F₃ position.

The equivalent symmetry element in the Schoenflies notation is the **improper axis of rotation, S_n**, which is a combination of rotation and reflection. The symmetry element consists of a rotation by 1/*n* of a revolution about the axis, followed by reflection through a plane at right angles to the axis. Figure 1.11 thus shows an S₄ axis, where the F₁ rotates to the dotted position and then reflects to F₂. The equivalent inversion axes and improper rotation axes for the two systems are shown in Table 1.1.

Table 1.1 Equivalent symmetry elements in the Schoenflies and Hermann–Mauguin systems

<i>Schoenflies</i>	<i>Hermann–Mauguin</i>
S ₁	$\bar{2} \equiv m$
S ₂ $\equiv i$	$\frac{1}{2}$
S ₃	$\frac{1}{6}$
S ₄	$\frac{1}{4}$
S ₆	$\frac{1}{3}$

1.4.5 Symmetry in crystals

The discussion so far has only shown the symmetry elements that belong to individual molecules. However, in the solid state we are interested in regular arrays of atoms, ions and molecules, and they too are related by these same symmetry elements. Figure 1.12 shows examples (not real) of how molecules could be arranged in a crystal. In Figure 1.12a two OF₂ molecules are related to one another by a plane of symmetry; in Figure 1.12b three OF₂ molecules are related to one another by a threefold axis of symmetry; in Figure 1.12c two OF₂ molecules are related by a centre of inversion. Notice that in both Figures 1.12b and 1.12c the molecules are related in space by a symmetry element that they themselves do not possess; this is said to be their **site symmetry**.

1.5 LATTICES AND UNIT CELLS

Crystals are regular-shaped solid particles with flat shiny faces. It was first noted by Hooke in 1664 that the regularity of their external appearance is a reflection of a high degree of internal order. Crystals of the same

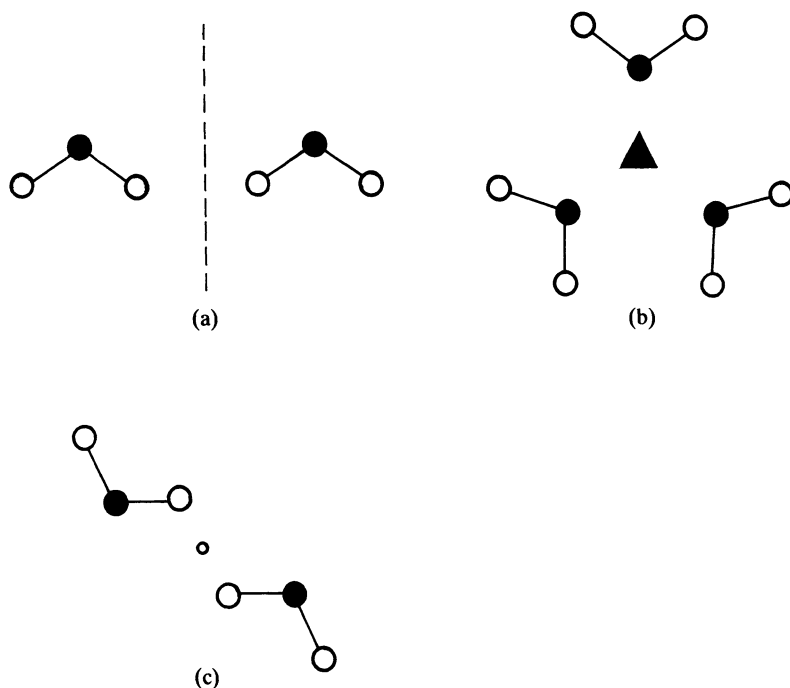


Figure 1.12 Symmetry in solids: (a) two OF_2 molecules related by a plane of symmetry, (b) three OF_2 molecules related by a threefold axis of symmetry, (c) two OF_2 molecules related by a centre of inversion.

substance, however, vary in shape considerably. Steno observed in 1671 that this is not because their internal structure varies but because some faces develop more than others. The angle between similar faces on different crystals of the same substance is always identical. The constancy of the interfacial angles reflects the internal order within the crystals. Each crystal is derived from a basic ‘building block’ that repeats over and over again, in all directions, in a perfectly regular way. This ‘building block’ is known as the **unit cell**.

In order to talk about and compare the many thousands of crystal structures that are known, there has to be a way of defining and categorizing the structures. This is achieved by defining the shape and symmetry of each unit cell, and also its size and the positions of the atoms within it.

1.5.1 Lattices

The simplest regular array is a line of evenly spaced objects such as is depicted by the commas in Figure 1.13a. There is a dot at the same place

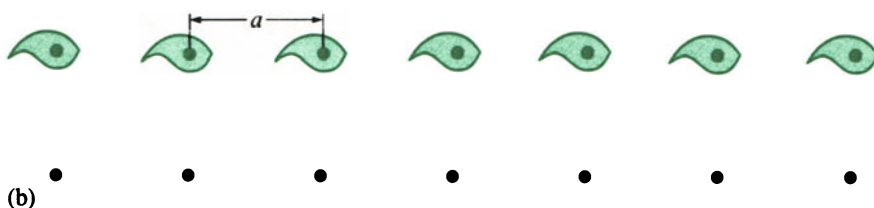


Figure 1.13 A one-dimensional lattice.

in each object: if we now remove the objects leaving the dots, we have a line of equally spaced dots, with spacing a (Figure 1.13b). The line of dots is called the **lattice**, and each **lattice point** (dot) must have identical surroundings. This is the only example of a one-dimensional lattice and it can vary only in the spacing a .

1.5.2 Two-dimensional lattices

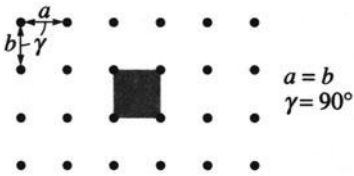
There are five possible two-dimensional lattices and these are shown in Figure 1.14, together with the restrictions on their repeat distances and angles. Everyday examples of these are to be seen in wallpapers and tiling.

These nets are important in low energy electron diffraction (LEED), which is used to study the structures of surfaces (which are of course two-dimensional) and the pattern of adsorption on a surface by a gas – important in catalysis. In these cases the lattice points are located on metal atoms, for instance, if studying a metal surface, or on small gaseous molecules such as ammonia, NH_3 , if investigating the adsorption of ammonia on a surface.

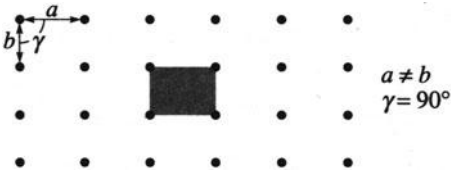
1.5.3 One and two-dimensional unit cells

The unit cell for the one-dimensional lattice in Figure 1.15a lies between the two vertical lines. If we took this unit cell and repeated it over and over again we would reproduce the original array. Notice that it does not matter where in the structure we place the lattice points as long as they each have identical surroundings. In Figure 1.15b we have moved the lattice points and the unit cell, but repeating this unit cell will still give the same array; we have simply moved the origin of the unit cell. There is never one unique unit cell that is ‘correct’; there are always many that could be chosen and the choice depends both on convenience and convention. This is equally true in two and three dimensions.

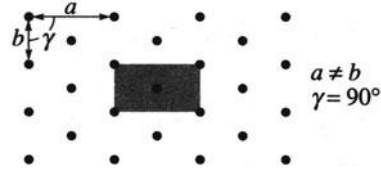
The conventional unit cells for the five types of two-dimensional lattice are shown in Figure 1.14: notice that they are all parallelograms with



1 square



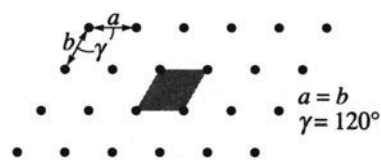
2 (a) rectangular



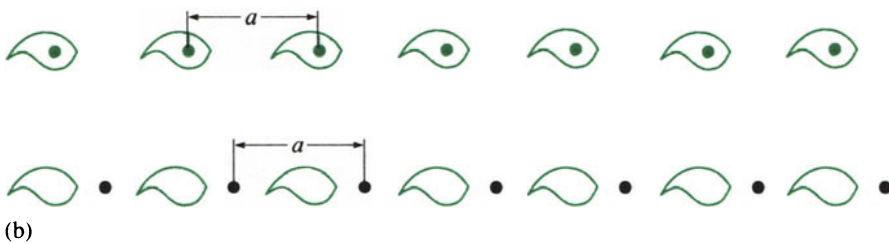
2 (b) centred rectangular



3 oblique



4 hexagonal

Figure 1.14 The five two-dimensional lattices.

(b)

Figure 1.15 Choice of unit cell in a one-dimensional lattice.

their corners at equivalent positions in the array, i.e. the corners of a unit cell are lattice points. The five different unit cell shapes fall into four classes because there are two different types of rectangular unit cell. In Figure 1.16 we show a square array with several different unit cells depicted. All of these, if repeated, would reproduce the array: it is conventional to choose the smallest cell that fully represents the symmetry of the structure. Both unit cells (1a) and (1b) are the same size but clearly (1a) shows that it is a square array, and this would be the conventional

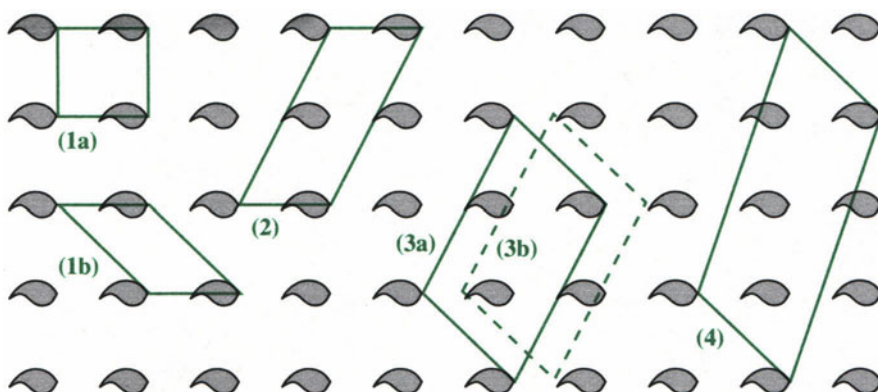


Figure 1.16 Choice of unit cells in a square two-dimensional lattice.



Figure 1.17 Choice of unit cell in a centred rectangular lattice.

choice. Figure 1.17 demonstrates the same principles but for a centred rectangular array, where (a) would be the conventional choice because it includes information on the centring; the smaller unit cell (b) loses this information. It is always possible to define a non-centred oblique unit cell, but information about the symmetry of the lattice may be lost by doing so.

Unit cells such as (1a) and (1b) in Figure 1.16 and (b) in Figure 1.17 have a lattice point at each corner. However, they each contain a total of one lattice point because each lattice point is shared by four adjacent unit cells. They are known as **primitive unit cells** and given the symbol P. The unit cell marked (a) in figure 1.17 contains a total of two lattice points – one from the shared four corners and one totally enclosed within the cell. This cell is said to be **centred** and is given the symbol C.

1.5.4 Translational symmetry elements

In section 1.4 we introduced you to the idea of symmetry, both in individual molecules and for extended arrays of molecules, such as are

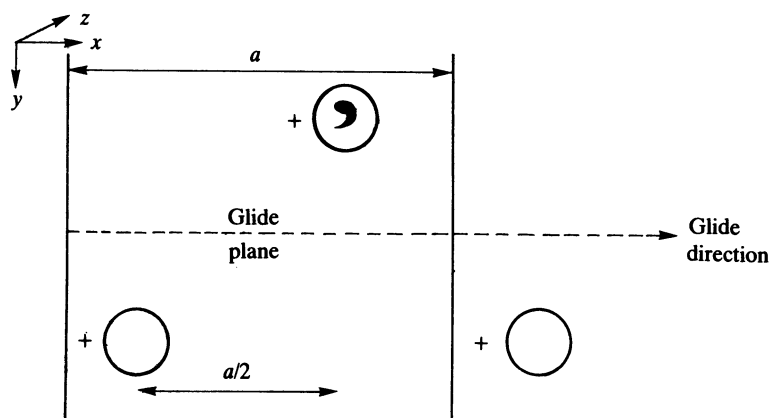


Figure 1.18 An a glide perpendicular to b .

found in crystals. Before going on to discuss three-dimensional lattices and unit cells, it is important to introduce two more symmetry elements: these elements involve translation and are only found in the solid state.

The **glide plane** combines translation with reflection. Figure 1.18 shows an example of this symmetry element. The diagram shows part of a repeating three-dimensional structure projected on to the plane of the page; the circle represents a molecule or ion in the structure and there is distance a between identical positions in the structure. The '+' sign next to the circle indicates that the molecule lies above the plane of the page. The plane of symmetry is in the xz plane perpendicular to the paper, and is indicated by the dashed line. The symmetry element consists of reflection through the plane of symmetry, followed by translation. The translation can be either in the x or in the z direction (or along a diagonal) and the translation distance is half of the repeat distance in that direction. In the example illustrated, the translation takes place in the x direction. The repeat distance between identical molecules is a , and so the translation is by $a/2$, and the symmetry element is called an a glide. You will notice two things about the molecule generated by this symmetry element: first, it still has a '+' sign against it, because the reflection in the plane leaves the z coordinate the same and second, it now has a comma on it. Some molecules, when they are reflected through a plane of symmetry are enantiomorph, which means that they are not superimposable on their mirror image: the presence of the comma indicates that this molecule could be an enantiomorph.

The **screw axis** combines translation with rotation. Screw axes have the general symbol n_i where n is the rotational order of the axis, i.e. twofold, threefold, etc., and the translation distance is given by the ratio i/n . Figure 1.19 illustrates a 2_1 screw axis. In this example, the screw axis lies

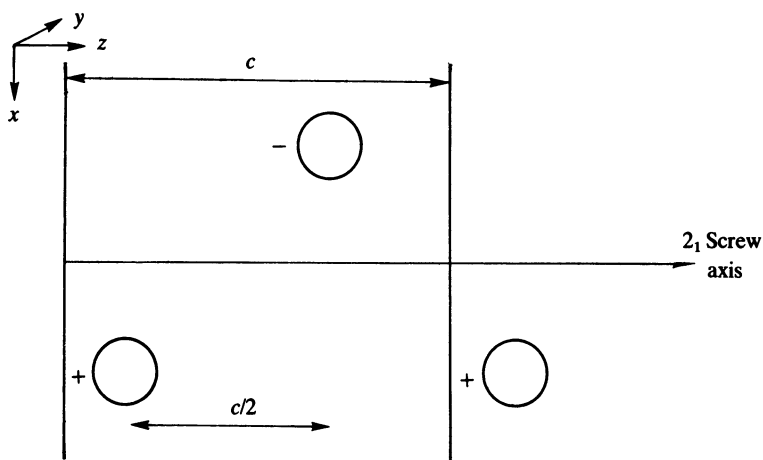


Figure 1.19 A 2_1 screw axis along c .

along z and so the translation must also be in the z direction by $c/2$, where c is the repeat distance in the z direction. Notice that in this case the molecule starts above the plane of the paper (indicated by the '+' sign) but the effect of a twofold rotation is to take it below the plane of the paper ('-' sign). Figure 1.20 shows the different effects that rotational and screw axes of the same order have on a repeating structure. Rotational and screw axes produce objects that are superimposable on the original. All other symmetry elements – glide plane, mirror plane, inversion centre and inversion axis – produce a mirror image of the original.

1.5.5 Three-dimensional unit cells

When moving into three dimensions matters are more complicated. The unit cell of a three-dimensional lattice is a parallelepiped defined by three distances, a , b and c , and three angles, α , β and γ (Figure 1.21). Of course, because the unit cells are the basic building blocks of the crystals, they must be space-filling, i.e. they must pack together to fill all space. All the possible unit cell shapes are illustrated in Figure 1.22 and their specifications are listed in Table 1.2. These are known as the **seven crystal systems**. The unit cell shapes are determined by minimum symmetry requirements (Table 1.2).

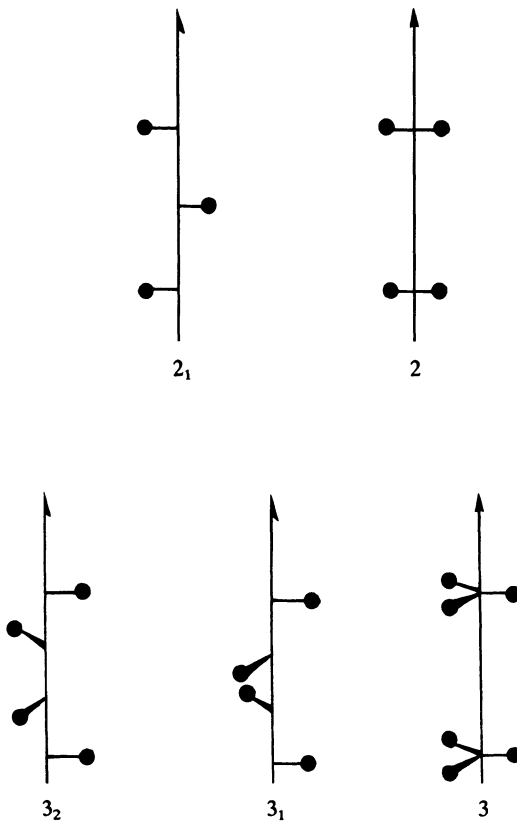


Figure 1.20 Comparison of the effects of twofold and threefold rotation axes and screw axes.

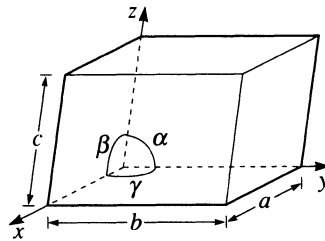


Figure 1.21 Definition of axes, unit cell dimensions and angles for a general unit cell.

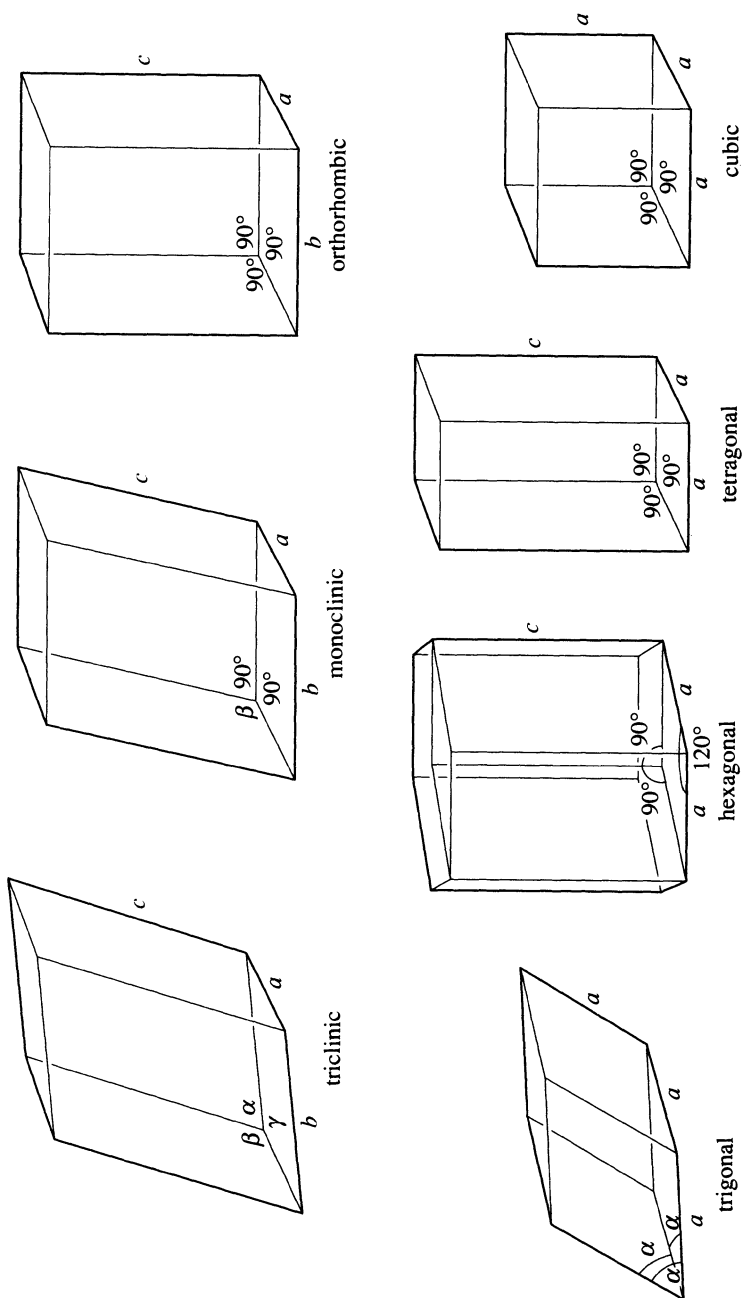


Figure 1.22 The unit cells of the seven crystal systems.

Table 1.2 The seven crystal systems

<i>System</i>	<i>Unit cell</i>	<i>Minimum symmetry requirements</i>
Triclinic	$\alpha \neq \beta \neq \gamma \neq 90^\circ$ $a \neq b \neq c$	None
Monoclinic	$\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$ $a \neq b \neq c$	One twofold axis or one symmetry plane
Orthorhombic	$\alpha = \beta = \gamma = 90^\circ$ $a \neq b \neq c$	Any combination of three mutually perpendicular twofold axes or planes of symmetry
Trigonal	$\alpha = \beta = \gamma \neq 90^\circ$ $a = b = c$	One threefold axis
Hexagonal	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$ $a = b \neq c$	One sixfold axis or one sixfold improper axis
Tetragonal	$\alpha = \beta = \gamma = 90^\circ$ $a = b \neq c$	One fourfold axis or one fourfold improper axis
Cubic	$\alpha = \beta = \gamma = 90^\circ$ $a = b = c$	Four threefold axes at $109^\circ 28'$ to each other

There are four different types of three-dimensional unit cell (Figure 1.23).

1. The **primitive** unit cell (symbol P) contains one lattice point.
2. The **body-centred** unit cell (symbol I) has a lattice point at each corner and also one at the centre of the cell.
3. The **face-centred** unit cell (symbol F) has a lattice point at each corner and one in the centre of each face.
4. The **face-centred** unit cell (symbol A, B or C) has a lattice point at each corner, and one in the centres of one pair of opposite faces, e.g. an A-centred cell has lattice points in the centres of the *bc* faces.

When these four types of lattice are combined with the seven possible unit cell shapes, 14 permissible **Bravais lattices** (Figure 1.24) are produced. (It is not possible to combine some of the shapes and lattice types *and* still retain the symmetry requirements listed in Table 1.2. For instance, it is not possible to have an A-centred, cubic, unit cell; if only two of the six faces are centred, the unit cell necessarily loses its cubic symmetry and cannot have the properties of a cube.)

The symmetry of a crystal is a point group taken from a point at the centre of a perfect crystal. Only certain point groups are possible because of the constraint made by the fact that unit cells must be able to stack exactly with no spaces – so only 1, 2, 3, 4 and 6-fold axes are

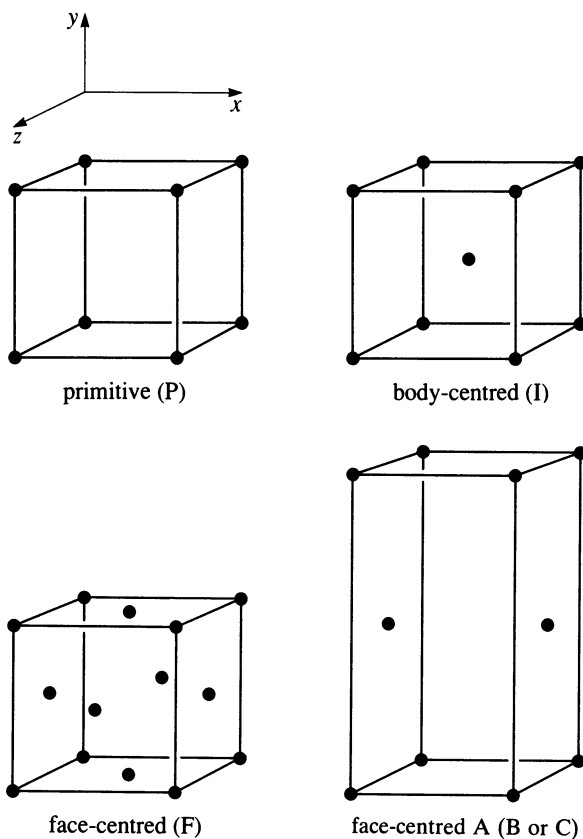


Figure 1.23 Primitive (P), body-centred (I), face-centred (F) and face-centred A, B or C (A shown) unit cells.

possible. Combining this with mirrors and centre of symmetry, we find there are 32 point groups which can describe the shapes of perfect crystals.

As a final comment, if we combine the 32 crystal point groups with the 14 Bravais lattices we find that there are 230 three-dimensional **space groups** that crystal structures can adopt, i.e. 230 different space-filling patterns! These are all documented in detail in International Tables (see Further Reading section).

It is important not to lose sight of the fact that the lattice points represent equivalent positions in a crystal structure and not atoms. In a real crystal a lattice point could be occupied by an atom, a complex ion, a molecule or even a group of molecules. The lattice points are used to simplify the repeating patterns within a structure, but they tell us nothing of the chemistry or bonding within the crystal; for that we have to include the atomic positions. This we will do later in the chapter when we look at some real structures.

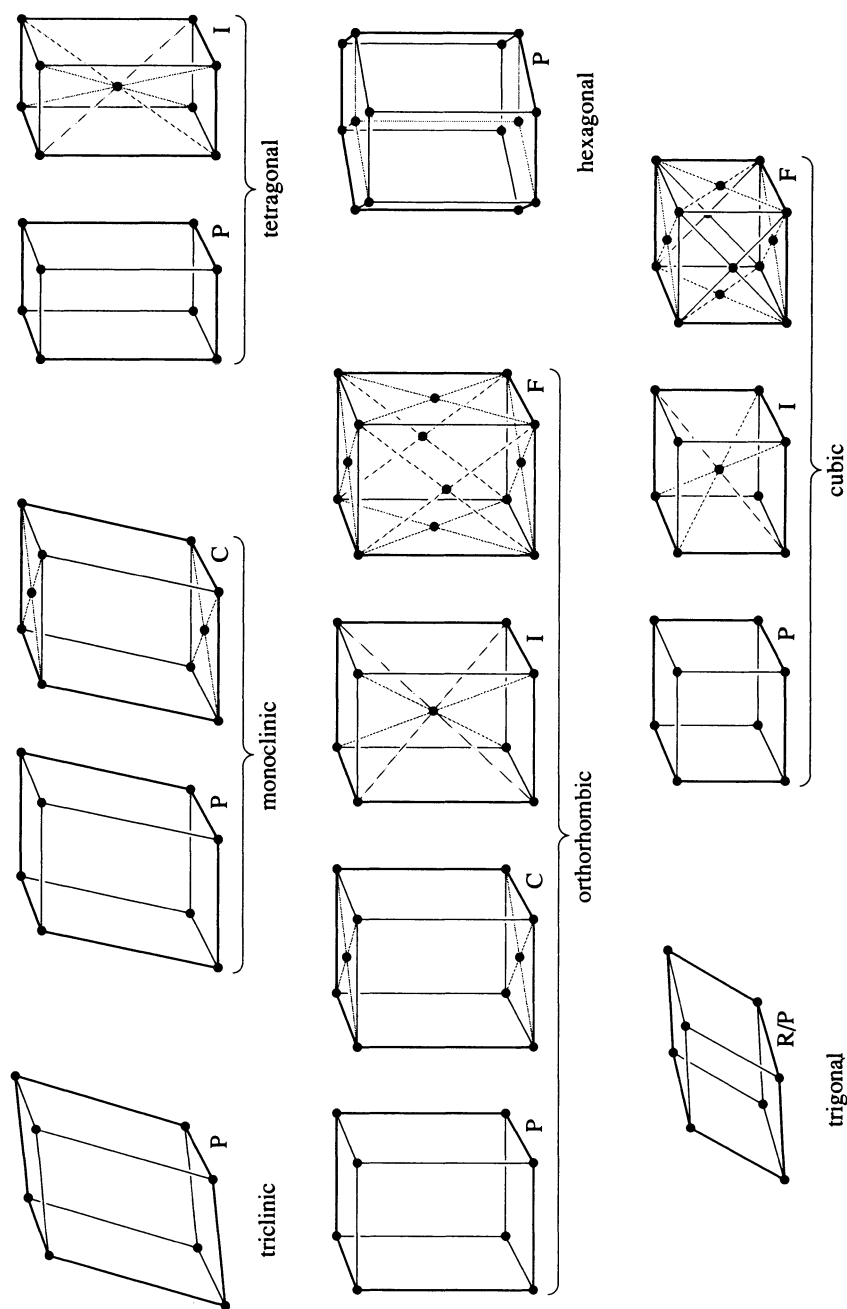


Figure 1.24 The 14 Bravais lattices.

Table 1.3 Number of molecules in four types of cell

<i>Name</i>	<i>Symbol</i>	<i>Number of molecules in unit cell</i>
Primitive	P	1
Body-centred	I	2
Face-centred	A or B or C	2
All face-centred	F	4

It is instructive to note how much of a structure these various types of unit cell represent. We noted a difference between the centred and primitive two-dimensional unit cell, where the centred cell contains two lattice points whereas the primitive cell contains only one. We can work out similar occupancies for the three-dimensional case. Look back to Figure 1.23 and in each case imagine that the lattice points have been replaced by a single identical molecule. The number of unit cells sharing a particular molecule depends on its site. A corner site is shared by eight unit cells, an edge site by four, a face site by two and a molecule at the body centre is not shared by any other unit cell. Using these figures we can work out the number of molecules in each of the four types of cell in Figure 1.23, assuming that one molecule is occupying each lattice point. The results are listed in Table 1.3.

1.5.6 Miller indices

The faces of crystals, both when they grow and when they are formed by cleavage, tend to be parallel either to the sides of the unit cell or to planes in the crystal that contain a high density of atoms. It is useful to be able to refer to both crystal faces and to the planes in the crystal in some way – to give them a name – and this is usually done by using **Miller indices**.

First, we'll describe how Miller indices are derived for lines in two-dimensional nets, and then move on to look at planes in three-dimensional lattices. Figure 1.25 shows a rectangular net with several sets of lines, and a unit cell is marked on each set with the origin of each in the bottom lefthand corner corresponding to the directions of the x and y axes. A set of parallel lines is defined by two indices, h and k , where h and k are the number of parts into which a and b , the unit cell edges, are divided by the lines. Thus the indices of a line hk are defined so that the line intercepts a at a/h and b at b/k . Start by finding a line next to the one passing through the origin. In the set of lines marked A, the line next to the one passing through the origin leaves a undivided but divides b into two; both intercepts lie on the positive side of the origin, so in this case the indices of the set of lines hk are 12 , spoken of as the 'one-two' set. If the set of lines lies

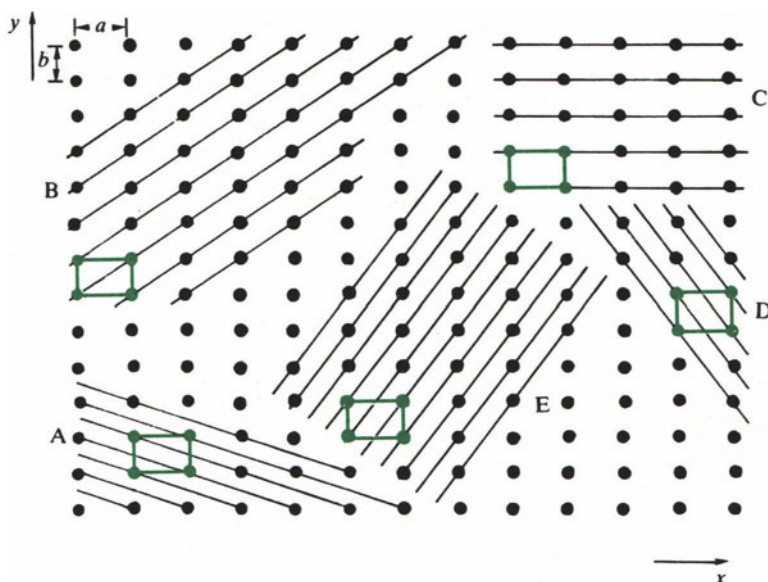


Figure 1.25 A rectangular net showing five sets of lines, A–E, with unit cells marked.

parallel to one of the axes, there is no intercept and the index becomes zero. If the intercepted cell edge lies on the negative side of the origin then the index is written with a bar on the top e.g. $\bar{2}$ – called ‘bartwo’. Notice that if we had selected the line on the other side of the origin in A we would have indexed the lines as the $\bar{1}\bar{2}$; there is no difference between the two pairs of indices, and the hk and $\bar{h}\bar{k}$ lines are always the same set of lines. Try Question 8 for more examples. Notice also in Figure 1.25, that the lines with the lower indices are more widely spaced.

The Miller indices for planes in three-dimensional lattices are given by hkl , where l is now the index for the z axis. The principles are exactly the same. Thus a plane is indexed hkl when it makes intercepts a/h , b/k , and c/l with the unit cell edges a , b , and c . Figure 1.26 shows some cubic lattices with various planes shaded. The positive directions of the axes are marked and these are orientated to conform with the conventional right-hand rule as illustrated in Figure 1.27. In Figure 1.26a the shaded planes lie parallel to y and z , but leave the unit cell edge a undivided; the Miller indices of these planes are thus 100 . Now try the other examples in Question 9. Again take note that the hkl and $\bar{h}\bar{k}\bar{l}$ planes are the same.

1.5.7 Interplanar spacings

It is sometimes useful to be able to calculate the perpendicular distance d_{hkl} between parallel planes (Miller indices hkl). When the axes are at

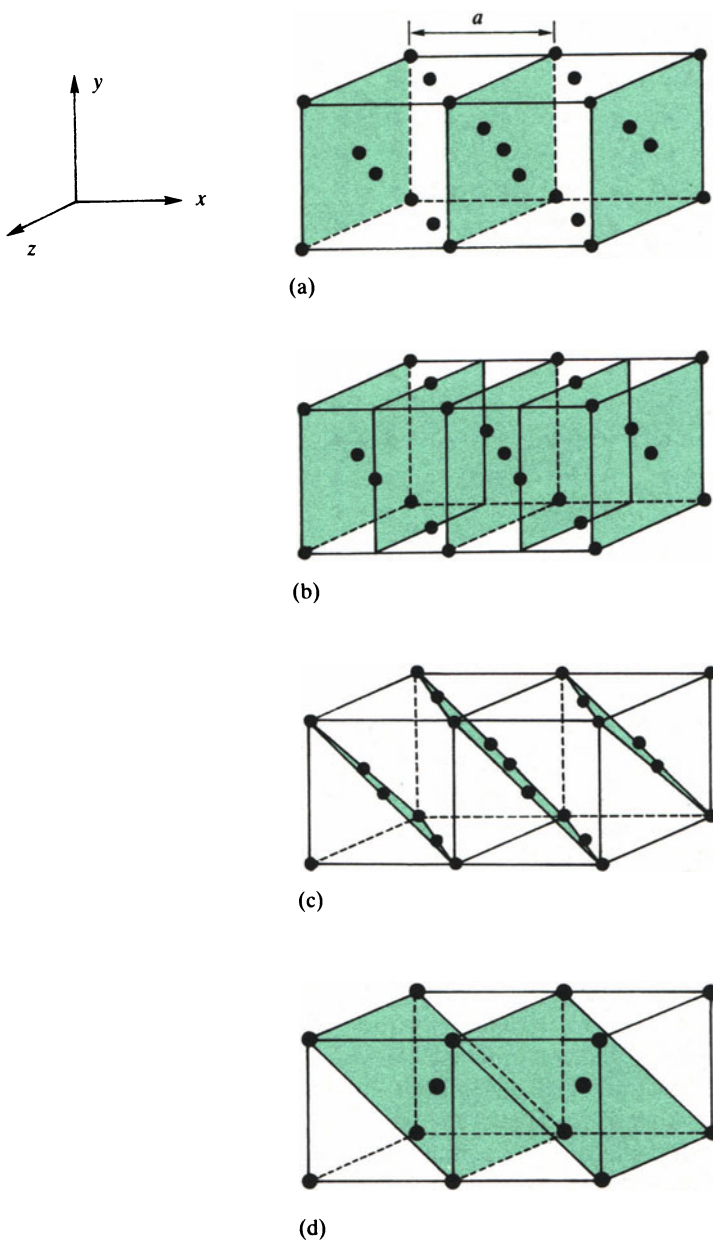


Figure 1.26 (a)–(c) Planes in a face-centred cubic lattice. (d) Planes in a body-centred cubic lattice (two unit cells are shown).

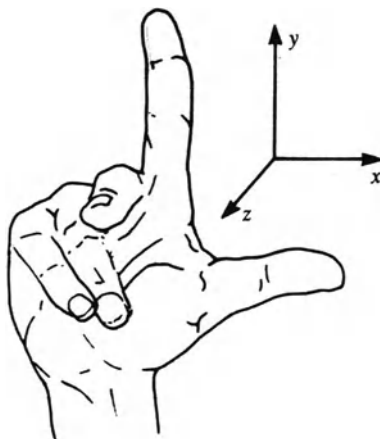


Figure 1.27 The right-handed rule for labelling axes.

right angles to one another (orthogonal) the geometry is simple, and for an orthorhombic system where $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$ this gives

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

and for a cubic system where $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$ this reduces to

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

1.5.8 Packing diagrams

Drawing structures in three dimensions is not easy and so crystal structures are often represented by two-dimensional plans or projections of the unit cell contents, in much the same way as an architect makes building plans. These projections are called packing diagrams as they are particularly useful in molecular structures for showing how the molecules pack together in the crystal.

The position of an atom or ion in a unit cell is described by its **fractional coordinates**; these are simply the coordinates based on the unit cell axes (known as the **crystallographic axes**), but expressed as fractions of the unit cell lengths. It has the simplicity of a universal system which enables unit cell positions to be compared from structure to structure regardless of variation in unit cell size.

To take a simple example, in a cubic unit cell with $a = 1000\text{ pm}$, an atom with an x coordinate of 500 pm has a fractional coordinate in the x

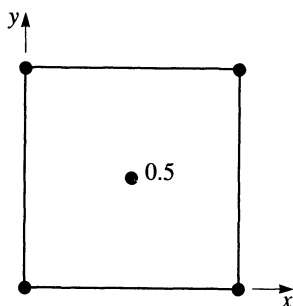


Figure 1.28 Packing diagram for a body-centred unit cell.

direction of $x/a = 500/1000 = 0.5$. Similarly, in the y and z directions, the fractional coordinates are given by y/b and z/c , respectively.

A packing diagram is shown in Figure 1.28 for the body-centred unit cell of Figure 1.5. The projection is shown on the yx plane, i.e., we are looking at the unit cell straight down the z -axis. The z -fractional coordinate of any atoms/ions lying in the top or bottom face of the unit cell will be 0 or 1 (depending on where you take the origin) and it is conventional for this not to be marked on the diagram. Any z -coordinate that is not 0 or 1 is marked on the diagram in a convenient place. There is an opportunity to practice constructing these types of diagram in the questions at the end of the chapter.

Many crystallographic papers in the literature contain packing diagrams. You will notice that often the projection of the unit cell is not taken down an axis on to a unit cell face (for the triclinic system this is not possible anyway as none of the axes are at right-angles). Usually this is because the crystallographer has decided that a better view of the unit cell contents is achieved by rotating the cell somewhat.

1.6 CRYSTALLINE SOLIDS

We start this section by looking at the structures of some simple **ionic solids**. Ions tend to be formed by the elements in the Groups at the far left and far right of the Periodic Table. Thus we expect the metals in Groups I and II to form cations and the non-metals of Groups VI and VII and nitrogen to form anions, because by doing so they are able to achieve a stable noble gas configuration. Cations can also be formed by some of the Group III elements, such as aluminium (Al^{3+}), by some of the low oxidation state transition metals and even occasionally by the high atomic number elements in Group IV, such as tin and lead, giving Sn^{4+} and Pb^{4+} . Each successive ionization becomes more difficult because the

remaining electrons are more strongly bound due to the greater effective nuclear charge, and so highly charged ions are rather rare.

An **ionic bond** is formed between two oppositely charged ions because of the electrostatic attraction between them. Ionic bonds are strong but are also non-directional. Ionic crystals are therefore composed of infinite arrays of ions, which have packed together in such a way as to maximize the coulombic attraction between oppositely charged ions and to minimize the repulsions between ions of the same charge. We expect to find ionic compounds in the halides and oxides of the Group I and II metals and it is with these crystal structures that this section begins.

However, just because it is possible to form a particular ion does not mean that this ion will always exist whatever the circumstances. In many structures we find that the bonding is not purely ionic but possesses some degree of **covalency**: the electrons are shared between the two bonding atoms and not merely transferred from one to the other. This is particularly true for the elements in the centre of the Periodic Table. This point is taken up in section 1.6.4 where we discuss the size of ions and the limitations of the concept of ions as hard spheres.

Two later sections (1.6.5 and 1.6.6) look at the crystalline structures of covalently bonded species. First, extended covalent arrays are investigated, such as the structure of **diamond** (one of the forms of elemental carbon) where each atom forms strong covalent bonds to the surrounding atoms, forming an infinite three-dimensional network of localized bonds throughout the crystal. Second, we look at molecular crystals which are formed from small, individual, covalently bonded molecules. These molecules are held together in the crystal by weak forces known as **van der Waals forces** (or **London dispersion forces**). These forces arise because instantaneous dipoles form in atoms which are in turn capable of inducing other dipoles. The net result is a very weak attractive force that falls off very quickly with distance.

Finally in this section we take a very brief look at the structures of some silicates, the compounds which largely form the earth's crust.

1.6.1 Ionic solids with formula MX

The caesium chloride structure

A unit cell of the caesium chloride (CsCl) structure is shown in Figure 1.29. It shows a caesium ion, Cs^+ , at the centre of the cubic unit cell, surrounded by eight chloride ions, Cl^- , at the corners. It could equally well have been drawn the other way round, with chloride at the centre and caesium at the corners, because the structure consists of two interpenetrating primitive cubic arrays. Note the similarity of this unit cell to the body-centred cubic structure adopted by some of the elemental metals

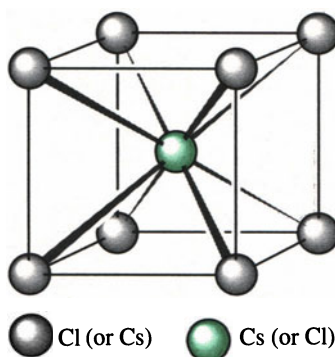


Figure 1.29 The crystal structure of caesium chloride (CsCl). This type of diagram is termed a **clinographic projection**, in which the diagram is viewed in a convenient direction from a point at infinity: all parallel lines are still parallel in projection. Important interatomic interactions are represented by heavier lines than the outline of the unit cell. The wedge-shaped bonds are designed to give some feeling of depth to the diagram: the widest part of the wedge is nearest.

such as the Group 1 (alkali) metals. However, the CsCl structure is *not* body-centred cubic because the environment of the caesium at the centre of the cell is not the same as the environment of the chlorides at the corners: a body-centred cell would have chlorides at the corners, i.e. at $(0, 0, 0)$ etc., *and* at the body centre $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Each caesium is surrounded by eight chlorines at the corners of a cube and vice versa, so the coordination number of each type of atom is eight. The unit cell contains one formula unit of CsCl, with the eight corner chlorines each being shared by eight unit cells. With ionic structures like this individual molecules are not distinguishable because individual ions are surrounded by ions of the opposite charge.

Caesium is a large ion (ionic radii are discussed in detail in section 1.6.4) and so is able to coordinate eight chloride ions around it. Other compounds with large cations that can also accommodate eight anions and crystallize with this structure include CsBr, CsI, TlCl, TlBr, TlI and NH_4Cl .

The sodium chloride (or rock salt) structure

A unit cell of the sodium chloride (NaCl) or rock-salt structure is illustrated in Figure 1.30. The unit cell is cubic and the structure consists of two interpenetrating face-centred (F) arrays, one of Na^+ and the other of Cl^- ions. Each sodium ion is surrounded by six equidistant chloride ions situated at the corners of an octahedron and in the same way each chloride ion is surrounded by six sodium ions: we say that the coordination is 6:6.

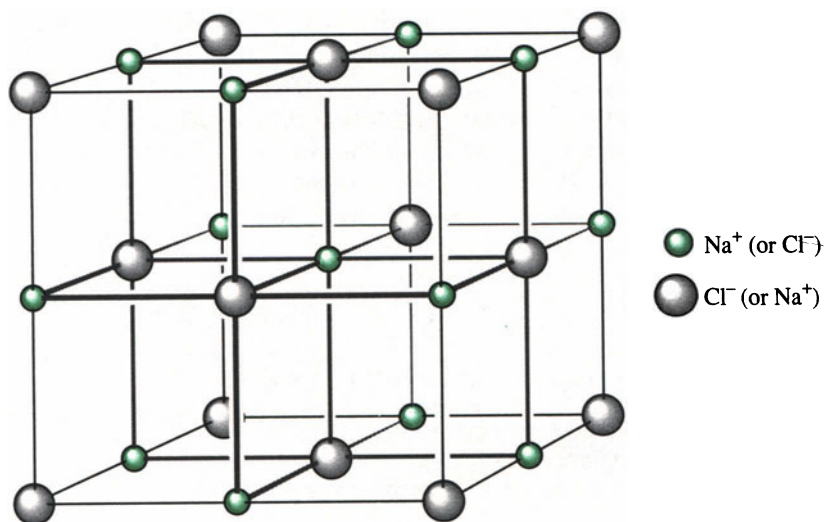


Figure 1.30 The crystal structure of sodium chloride (NaCl).

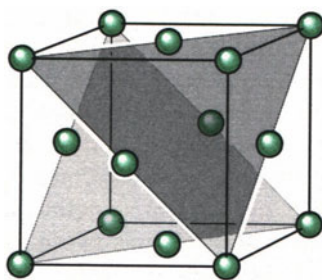


Figure 1.31 A unit cell of sodium chloride showing the position of the close-packed layers.

An alternative way of viewing this structure is to think of it as a cubic close-packed array of chloride ions with sodium ions filling all the octahedral holes. The conventional unit cell of a *ccp* array is an F face-centred cube (hence the cubic in *ccp*); the close-packed layers lie at right-angles to a cube diagonal (Figure 1.31). Filling all the octahedral holes gives a $\text{Na}:\text{Cl}$ ratio of 1:1 with the structure as illustrated in Figure 1.30. Interpreting simple ionic structures in terms of the close packing of one of the ions with the other ion filling some or all of either the octahedral or tetrahedral holes, is extremely useful: it makes it particularly easy to see both the coordination geometry around a specific ion and also the available spaces within a structure.

As you might expect from their relative positions in Group I, a sodium ion is smaller than a caesium ion and so it is now only possible to pack six chlorides around it and not eight as in CsCl. The NaCl unit cell contains four formula units of NaCl. If you find this difficult to see, work it out for yourself by counting up the numbers of ions in the different sites using the information given on p. 24. Table 1.4 lists some of the compounds that adopt the NaCl structure; there are more than 200 known.

Table 1.4 Compounds that have the NaCl (rock-salt) type of crystal structure

Most alkali halides, MX, and AgF, AgCl, AgBr
 All the alkali hydrides, MH
 Monoxides, MO, of Mg, Ca, Sr, Ba
 Monosulphides, MS, of Mg, Ca, Sr, Ba

Many of the structures described in this book can be viewed as linked octahedra, where each octahedron consists of a metal atom surrounded by six other atoms situated at the corners of an octahedron (Figure 1.32a, b). These are often depicted, viewed from above with contours marked, as in Figure 1.32c. Octahedra can link together via corners, edges and faces, as seen in Figure 1.33. If you find this difficult to visualize, it is quite easy to make small octahedra from paper and see how they join together; Figure 1.34 gives you a template to copy and cut out and glue. (The four shaded triangles provide a template for making tetrahedra.) The linking of octahedra by different methods effectively eliminates atoms because some of the atoms are now shared between them: two $[\text{MO}_6]$ octahedra linked through a vertex has the formula M_2O_{11} ; two

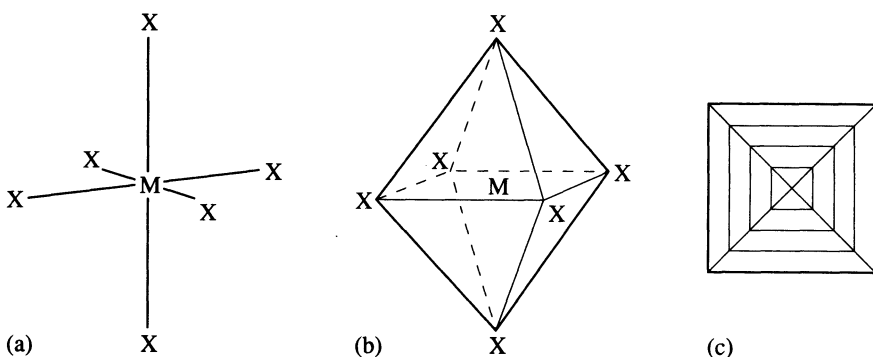


Figure 1.32 (a) An $[\text{MX}_6]$ octahedron. (b) The solid octahedron. (c) Plan of an octahedron with contours.

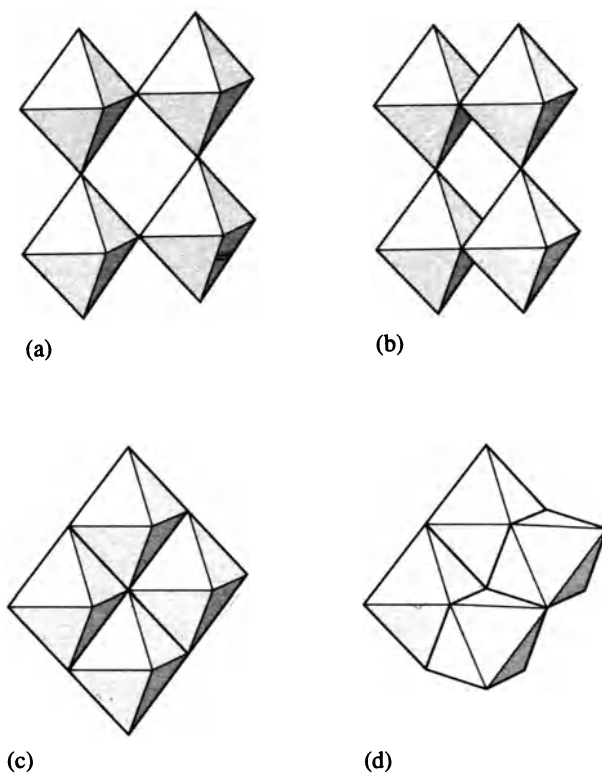


Figure 1.33 The conversion of (a) corner-shared MX_6 octahedra to (b) edge-shared octahedra, and (c) edge-shared octahedra to (d) face-shared octahedra.

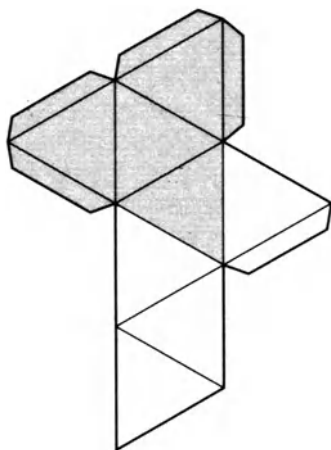


Figure 1.34 Template for making octahedra and tetrahedra.

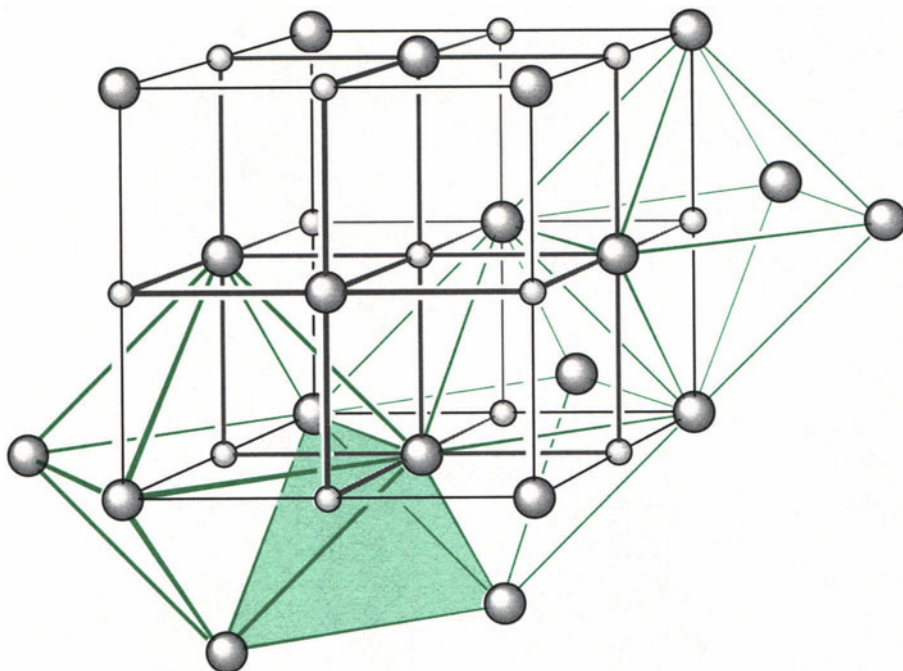


Figure 1.35 NaCl structure showing edge sharing of octahedra. (A tetrahedral space is also shown shaded in colour.)

$[\text{MO}_6]$ octahedra linked through an edge has the formula M_2O_{10} ; two $[\text{MO}_6]$ octahedra linked through a face has the formula M_2O_9 .

The NaCl structure can be described in terms of $[\text{NaCl}_6]$ octahedra sharing edges. An octahedron has 12 edges, and each one is shared by two octahedra in the NaCl structure. This is illustrated in Figure 1.35, which shows a NaCl unit cell with three $[\text{NaCl}_6]$ octahedra picked out in colour: the common edges are picked out by a thick broken line. A maximum of only six octahedra can meet at a point, and one of the resulting tetrahedral spaces is depicted by shading.

The nickel arsenide structure

The nickel arsenide (NiAs) structure is the equivalent of the NaCl structure in hexagonal close packing. It can be thought of as an *hcp* array of arsenic atoms with nickel atoms occupying the octahedral holes (Figure 1.36). The geometry about the nickel atoms is thus octahedral. This is not the case for arsenic: each arsenic atom sits in the centre of a **trigonal prism** of six nickel atoms (Figure 1.37).

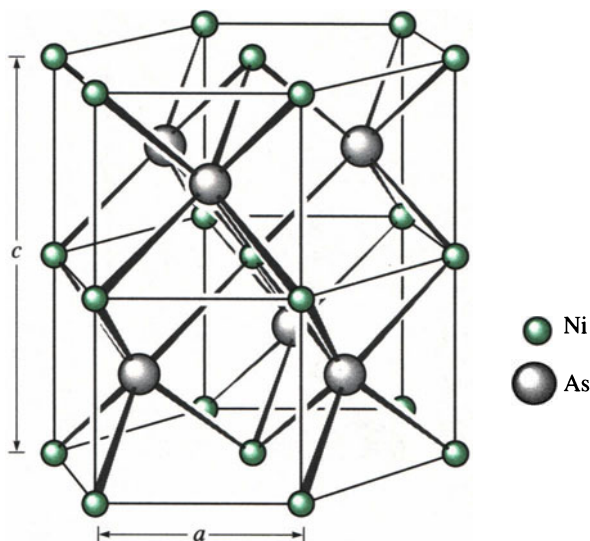


Figure 1.36 The crystal structure of nickel arsenide (NiAs). (For undistorted *hcp* the ratio $c/a = 1.633$. In reality this ratio varies considerably for the compounds adopting this structure. For example, iron(II) sulphide (FeS) adopts this structure with $c/a = 1.68$.)

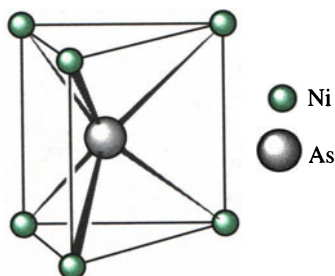


Figure 1.37 The trigonal prismatic coordination of arsenic in NiAs.

The zinc blende and wurtzite structures

Unit cells of these two structures are shown in Figure 1.38 and 1.39, respectively. They are named after two different naturally occurring mineral forms of zinc sulphide (ZnS). Structures of the same compound which differ only in their atomic arrangements are termed **polymorphs**.

The zinc blende structure can be thought of as a *ccp* array of sulphide ions with zinc ions occupying every other tetrahedral hole. Each zinc ion

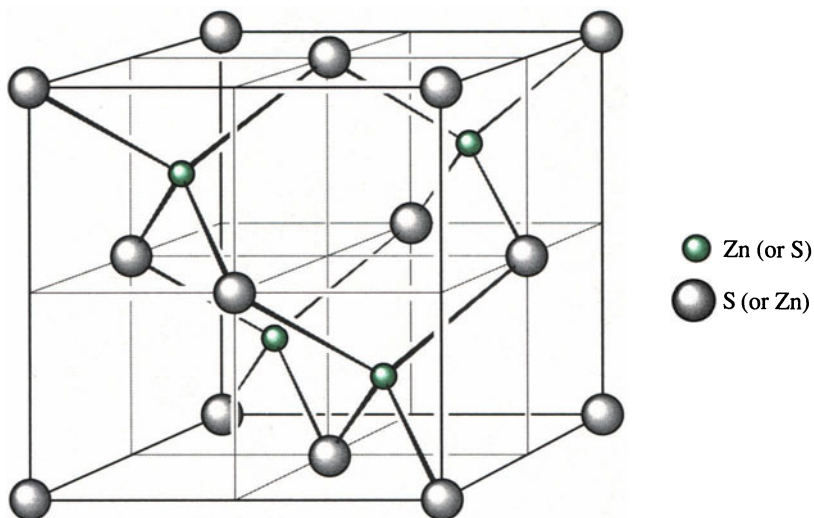


Figure 1.38 The crystal structure of zinc blende (ZnS).

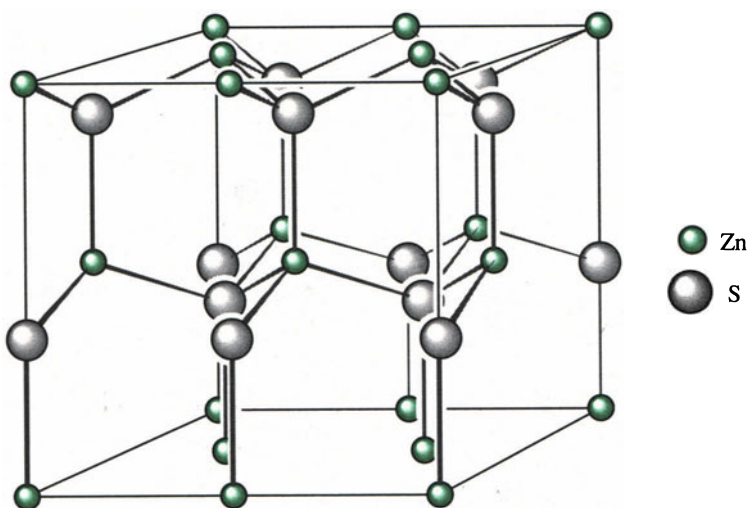


Figure 1.39 The crystal structure of wurtzite (ZnS).

is thus tetrahedrally coordinated by four sulphides and vice versa. Compounds adopting this structure include the copper halides and Zn, Cd and Hg sulphides. Notice that if all the atoms were identical, the structure would be exactly the same as that of diamond (see section 1.6.5).

The wurtzite structure is composed of an *hcp* array of sulphide ions with alternate tetrahedral holes occupied by zinc ions. Each zinc ion is tetrahedrally coordinated by four sulphide ions and vice versa. Compounds adopting the structure include BeO, ZnO, and NH_4F .

Notice how the coordination numbers of these structures have changed. The coordination number for close packing, where all the atoms are the same size, is 12. In the CsCl structure it is eight, in NaCl, six, and in both of the ZnS structures it is four. As a general rule, the larger a cation is, the more anions it can pack around itself (section 1.6.4).

1.6.2 Solids with general formula MX_2

The fluorite and antfluorite structures

The fluorite structure is named after the mineral form of calcium fluoride (CaF_2) and is illustrated in Figure 1.40. It can be thought of as related to a *ccp* array of calcium ions with fluorides occupying all the tetrahedral holes. There is a problem with this as a description because calcium ions are rather smaller than fluoride ions, and so physically fluoride ions would not be able to fit into the tetrahedral holes of a calcium ion array. Nevertheless it gives an exact description of the *relative* positions of the ions. The diagram in Figure 1.40a shows the fourfold tetrahedral coordination of the fluoride ions very clearly. Notice also that the larger octahedral holes are vacant in this structure; one of them can be seen at the body centre of the unit cell in Figure 1.40a. This becomes a very important feature when we come to look at the movement of ions through defect structures in Chapter 5.

By extending the structure a little and drawing cubes with fluoride ions at each corner, as has been done in Figure 1.40b, you can see that there is eightfold cubic coordination of each calcium cation. Indeed, it is possible to move the origin and redraw the unit cell so that this feature can be seen more clearly, as has been done in Figure 1.40c. The unit cell is now divided into eight smaller cubes called **octants**, with each alternate octant occupied by a calcium cation.

In the antfluorite structure the positions of the cations and anions are merely reversed, and the description of the structure as cations occupying all the tetrahedral holes in a *ccp* array of anions becomes more realistic. In the example with the biggest anion and smallest cation, Li_2Te , the telluriums are approximately close-packed (even though there is a considerable amount of covalent bonding). For the other compounds adopting this structure, such as the oxides and sulphides of the alkali metals, M_2O and M_2S , the description accurately shows the relative positions of the atoms but the anions could not be described as close-packed because they are not touching: the cations are too big to fit in the

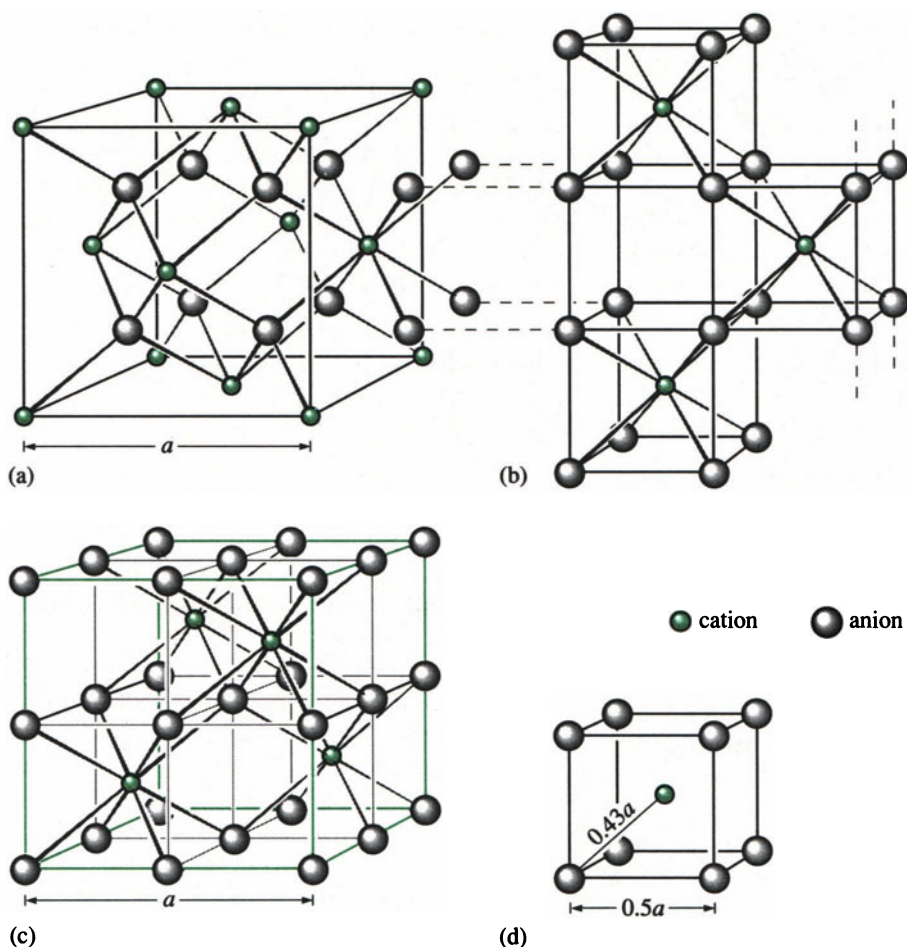


Figure 1.40 The crystal structure of fluorite (CaF_2). (a) Unit cell as a *ccp* array of cations. (b) and (c) The same structure redrawn as a primitive cubic array of anions: the unit cell is marked by a coloured outline in (c). (d) Relationship of unit cell dimensions to the primitive anion cube (the octant).

tetrahedral holes and so the anion–anion distance is greater than for close packing. These are the only structures where 8:4 coordination is found.

The cadmium chloride and cadmium iodide structures

Both of these structures are based on the close-packing of the appropriate anion with half of the octahedral holes occupied by cations. In both structures the cations occupy all the octahedral holes in every other anion layer, giving an overall layer structure with 6:3 coordination. The cadmium

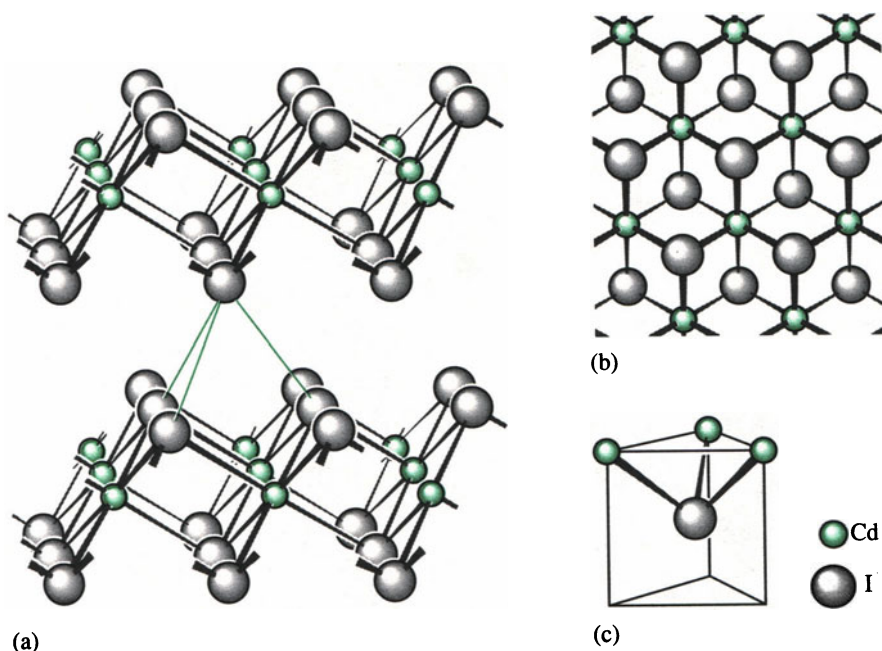


Figure 1.41 (a) The crystal structure of cadmium iodide (CdI_2). (b) The structure of the layers in CdI_2 and CdCl_2 ; the halogen atoms lie in planes above and below that of the metal atoms. (c) The coordination around one iodine atom in CdI_2 .

chloride (CdCl_2) structure is based on a *ccp* array of chloride ions whereas the cadmium iodide (CdI_2) structure is based on an *hcp* array of iodide ions. The CdI_2 structure is shown in Figure 1.41. Figure 1.41a shows clearly that an iodide anion in this structure is surrounded by three cadmium cations on one side but by three iodides on the other, i.e. it is not completely surrounded by ions of the opposite charge as we would expect for an ionic structure. In fact, this is evidence that the bonding in some of these structures is not entirely ionic as we have tended to imply so far. This is a point that is taken up again in more detail in section 1.6.4.

The rutile structure

The rutile structure is named after one mineral form of titanium dioxide (TiO_2). A unit cell is illustrated in Figure 1.42. The unit cell is tetragonal and the structure again demonstrates 6:3 coordination but is not based on close packing: each titanium atom is coordinated by six oxygens at the corners of a (slightly distorted) octahedron and each oxygen atom is surrounded by three planar titaniums which lie at the corners of an

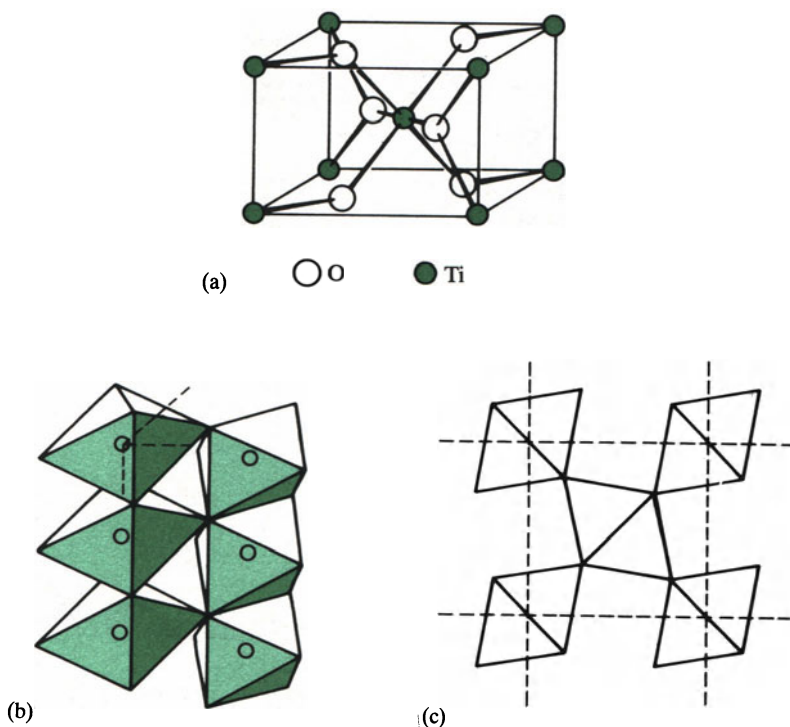


Figure 1.42 The crystal structure of rutile (TiO_2). (a) Unit cell; (b) parts of two columns of $[\text{TiO}_6]$ octahedra; (c) projection of structure on base of unit cell.

(almost) equilateral triangle. It is not geometrically possible for the coordination around titanium to be a perfect octahedron *and* for the coordination around oxygen to be a perfect equilateral triangle.

The structure can be viewed as chains of linked $[\text{TiO}_6]$ octahedra, where each octahedron shares a pair of opposite edges, and the chains are linked by sharing vertices (Figure 1.42b). Figure 1.42c shows a plan of the unit cell looking down the chains of octahedra so that they are seen in projection.

Occasionally, the **antirutile** structure is encountered where the metal and non-metals have swapped places, such as in Ti_2N .

The β -cristobalite structure

The β -cristobalite structure is named after one mineral form of silicon dioxide (SiO_2). The silicon atoms are in the same positions as both the zinc and sulphurs in zinc blende (or the carbons in diamond, which we look at later in section 1.6.5): each pair of silicon atoms is joined by an oxygen midway between. This structure is characterized by 4:2 coordination and the only metal halide adopting it is beryllium fluoride (BeF_2).

1.6.3 Other important crystal structures

As the valency of the metal increases, the bonding in these simple binary compounds becomes more covalent and the highly symmetrical structures characteristic of the simple ionic compounds occur far less frequently, with molecular and layer structures being common. There are many thousands of inorganic crystal structures; here we describe just a few of those which are commonly encountered and which occur in later chapters.

The bismuth triiodide structure, BiI_3

This structure is based on an *hcp* array of iodides with the bismuths occupying one-third of the octahedral holes. Alternate pairs of layers have two-thirds of the octahedral sites occupied.

Corundum, $\alpha\text{-Al}_2\text{O}_3$

This structure may be described as an *hcp* array of oxygen atoms with two-thirds of the octahedral holes occupied by aluminium atoms. Geometrical constraints dictate that octahedral coordination of the aluminiums precludes tetrahedral coordination of the oxygens. However, it is suggested that this structure is adopted in preference to other possible ones because the four aluminiums surrounding an oxygen approximate most closely to a regular tetrahedron. The structure is also adopted by Ti_2O_3 , V_2O_3 , Cr_2O_3 , $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Ga}_2\text{O}_3$ and Rh_2O_3 .

The rhenium trioxide structure, ReO_3

This structure (also called the aluminium fluoride structure) is adopted by the fluorides of Al, Sc, Fe, Co, Rh and Pd; also by the oxides WO_3 (at high temperature) and ReO_3 (section 5.8.1). The structure consists of $[\text{ReO}_6]$ octahedra linked together through each corner to give a highly symmetrical three-dimensional network with cubic symmetry. Part of a layer through the structure is shown in Figure 1.43, and part of two layers is illustrated in Figure 1.45b.

Mixed oxide structures

There are three important mixed oxide structures: **spinel**, **perovskite** and **ilmenite**.

The spinel and inverse-spinel structures

The spinels have the general formula AB_2O_4 , taking their name from the mineral spinel, MgAl_2O_4 : generally, A is a divalent ion, A^{2+} , and B is trivalent, B^{3+} . The structure can be thought of as being based on a cubic close-packed array of oxide ions, with A^{2+} ions occupying tetrahedral holes and B^{3+} ions occupying octahedral holes. A spinel crystal containing $n\text{AB}_2\text{O}_4$ formula units has $8n$ tetrahedral holes and $4n$ octahedral

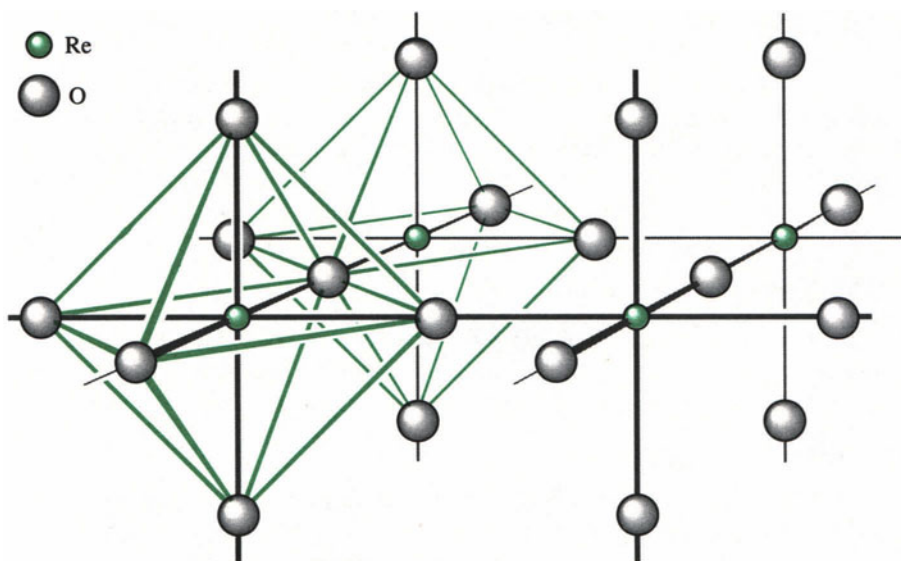


Figure 1.43 Part of the ReO_3 structure showing the linking of octahedra through the corners. Part of a single layer.

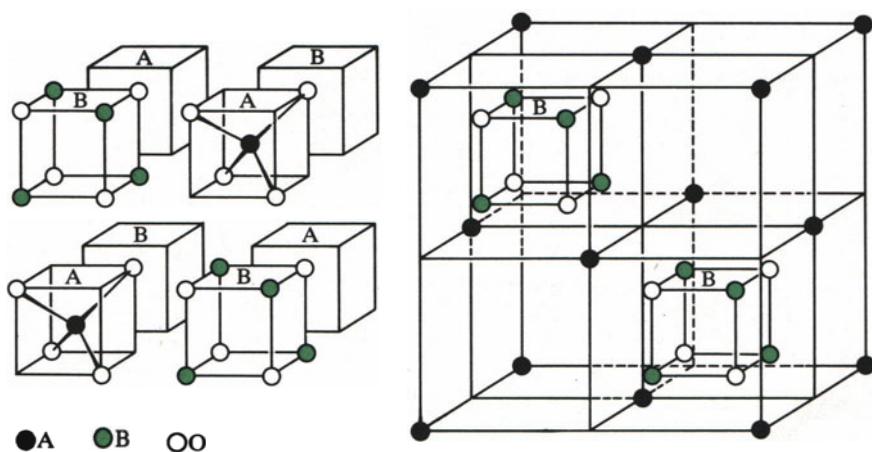


Figure 1.44 The spinel structure, AB_2O_4 .

holes; accordingly one-eighth of the tetrahedral holes are occupied by A^{2+} ions and one-half of the octahedral holes by the B^{3+} ions. A unit cell is illustrated in Figure 1.44; it has been broken down into eight octants, of which there are only two kinds, shown on the left. The A ions occupy tetrahedral positions in the A-type octants together with the corners and

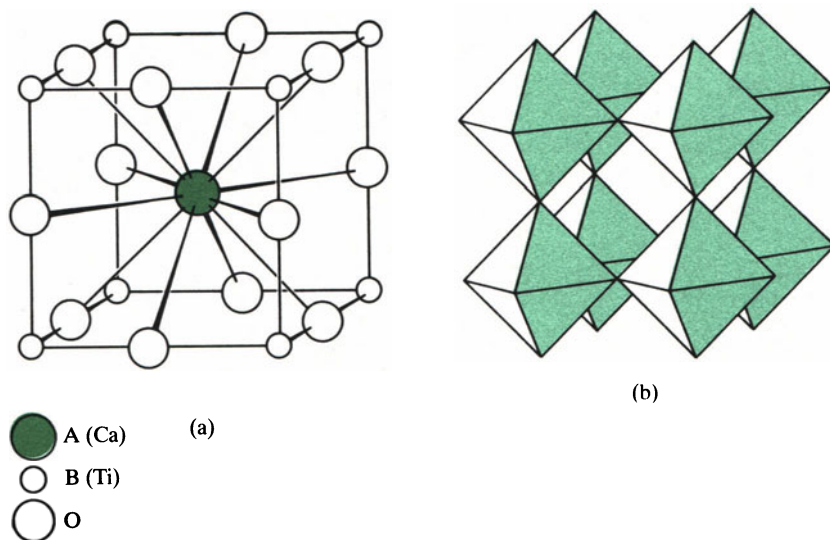


Figure 1.45 (a) The perovskite structure for compounds ABX_3 , such as $CaTiO_3$.
 (b) Part of two layers in the ReO_3 structure.

face-centres of the unit cell. The B ions occupy octahedral sites, which take up half the corners of the B-type octants. Spinel with this structure include compounds of formula MAI_2O_4 , where M is Mg, Fe, Co, Ni, Mn or Zn.

When compounds of general formula AB_2O_4 adopt the inverse-spinel structure, the formula is better written as $B(AB)O_4$, because this indicates that half of the B^{3+} ions now occupy tetrahedral sites, and the remaining half, together with the A^{2+} ions, occupy the octahedral sites. Examples of inverse spinels include Fe_3O_4 , $Fe(MgFe)O_4$ and $Fe(ZnFe)O_4$.

The perovskite structure

This structure is named after the mineral $CaTiO_3$. A unit cell is shown in Figure 1.45a: this unit cell is termed the A-type, because if we take the general formula ABX_3 for the perovskites, then in this cell the A atom is in the centre. The central Ca (A) atom is coordinated to eight Ti atoms (B) at the corners and to 12 oxygens (X) at the midpoints of the cell edges. The structure can be usefully described in other ways. First, it can be thought of as a *ccp* array of A and X atoms with the B atoms occupying the octahedral holes (compare with the unit cell of NaCl in Figure 1.30 if you want to check this). Second, perovskite has the same octahedral framework as ReO_3 based on $[BX_6]$ octahedra with an A atom added in at the centre of the cell (Figure 1.45b). Compounds adopting this structure include $SrTiO_3$, $SrZrO_3$, $SrHfO_3$, $SrSnO_3$ and $BaSnO_3$.

The ilmenite structure

The ilmenite structure is adopted by oxides of formula ABO_3 when A and B are similar in size and their total charge adds up to +6. The structure is named after the mineral of $Fe^{II}Ti^{IV}O_3$, and the structure is very similar to the corundum structure described above, an *hcp* array of oxygens but now there are two different cations present occupying two-

Table 1.5 Structures related to close-packed arrangements of anions

Formula	Cation:anion coordination	Type and number of holes occupied	Examples	
			Cubic close packing	Hexagonal close packing
MX	6:6	All octahedral	Sodium chloride: NaCl, FeO, MnS, TiC	Nickel arsenide: NiAs, FeS, NiS
	4:4	Half tetrahedral; every alternate site occupied	Zinc blende: ZnS, CuCl, γ -AgI	Wurtzite: ZnS, β -AgI
MX ₂	8:4	All tetrahedral	Fluorite: CaF ₂ , ThO ₂ , ZrO ₂ , CeO ₂	None
	6:3	Half octahedral; alternate layers have fully occupied sites	Cadmium chloride: CdCl ₂	Cadmium iodide: CdI ₂ , TiS ₂
MX ₃	6:2	One-third octahedral; alternate pairs of layers have two-thirds of the octahedral sites occupied		Bismuth iodide: BiI ₃ , FeCl ₃ , TiCl ₃ , VCl ₃
M ₂ X ₃	6:4	Two-thirds octahedral		Corundum: Al ₂ O ₃ , Fe ₂ O ₃ , V ₂ O ₃ , Ti ₂ O ₃ , Cr ₂ O ₃
ABO ₃		Two-thirds octahedral		Ilmenite: FeTiO ₃
AB ₂ O ₄		One-eighth tetrahedral and one-half octahedral	Spinel: MgAl ₂ O ₄ Inverse spinel: MgFe ₂ O ₄	Olivine: Mg ₂ SiO ₄

thirds of the octahedral holes. The Fe and Ti atoms occur in alternate layers.

The structures related to close packing are summarized in Table 1.5.

1.6.4 Ionic radii

We know from quantum mechanics that atoms and ions do not have precisely defined radii. However, from the foregoing discussion of ionic crystal structures we have seen that ions pack together in an extremely regular fashion in crystals and that their atomic positions, and thus their interatomic distances, can be measured very accurately. It is a very useful concept, therefore, particularly for those structures based on close-packing, to think of ions as hard spheres, each with a particular radius.

If we take a series of alkali metal halides, all with the rock salt structure, as we replace one metal ion with another, say sodium with potassium, we would expect the metal–halide internuclear distance to change by the same amount each time, if the concept of an ion as a hard sphere with a particular radius holds true. Table 1.6 shows the results of this procedure for a range of alkali halides: the change in internuclear distance on swapping one ion for another is shown in Table 1.6. From this table, we can see that the change in internuclear distance on changing ion is not constant, but also that the variation is not great: this provides us with some experimental evidence that it is not unreasonable to think of the ions as having a fixed radius. We can see, however, that the picture is not precisely true, neither would we expect it to be, because atoms and ions are squashable entities and their size is going to be affected by their environment. Nevertheless, it is a useful concept to develop further as it enables us to describe some of the ionic crystal structures in a simple pictorial way.

There have been many suggestions as to how individual ionic radii can be assigned, and the literature contains several different sets of values: each set is named after the person(s) who originated the method of

Table 1.6 Interatomic distances of some alkali halides, r_{M-X} (pm)

	F^-		Cl^-		Br^-		I^-
Li^+	201	56	257	18	275	27	302
	30		24		23		21
Na^+	231	50	281	17	298	25	323
	35		33		31		30
K^+	266	48	314	15	329	24	353
	16		14		14		13
Rb^+	282	46	328	15	343	23	366

determining the radii. We will describe some of these methods briefly before listing the values most commonly used at present. It is most important to remember that radii from more than one set of values must not be mixed. Even though the values vary considerably from set to set, each set is internally consistent, i.e. if you add together two radii from one set of values you will obtain an approximately correct internuclear distance as determined from the crystal structure.

The internuclear distances can be determined by X-ray crystallography: in order to obtain values for individual ionic radii from these, the value of one radius needs to be fixed by some method. Originally in 1920, Landé suggested that in the alkali halide with the largest anion and smallest cation, LiI, the iodide ions must be in contact with each other with the tiny Li^+ ion inside the octahedral hole: as the I–I distance is known, it is then a matter of simple geometry to determine the iodide radius. Once the iodide radius is known, the radii of the metal cations can be found from the structures of the metal iodides, and so on. Bragg and Goldschmidt later extended the list of ionic radii using similar methods. It is very difficult to come up with a consistent set of values for the ionic radii, because of course the ions are not hard spheres, they are somewhat elastic, and the radii are affected by their environment, such as the nature of the oppositely charged ligand and the coordination number. Pauling proposed a theoretical method of calculating the radii from the internuclear distances; he produced a set of values that is both internally consistent and also shows the expected trends in the Periodic Table. Pauling's method was to take a series of alkali halides with isoelectronic cations and anions and assume that they are in contact: by assuming that each radius is inversely proportional to the effective nuclear charge felt by the outer electrons of the ion, a radius for each ion can be calculated from the internuclear distance. Divalent ions undergo additional compression in a lattice and compensation has to be made for this effect in calculating their radii. With some refinements this method gave a consistent set of values that has been widely used for many years; they are usually known as **effective ionic radii**.

More recently, it has been possible to determine accurate electron density maps for the ionic crystal structures using X-ray crystallography. Such a map is shown for NaCl and for LiF in Figure 1.46. The electron density contours fall to a minimum, although not to zero, in between the nuclei and it is suggested that this minimum position should be taken as the radius position for each ion. These experimentally determined ionic radii are often called **crystal radii**: the values are somewhat different from the older sets and tend to make the anions smaller and the cations bigger than previously; various values for Li^+ and F^- are shown in Figure 1.47. The most comprehensive set of radii has been compiled by Shannon and Prewitt using data from almost 1000 crystal structure determinations.

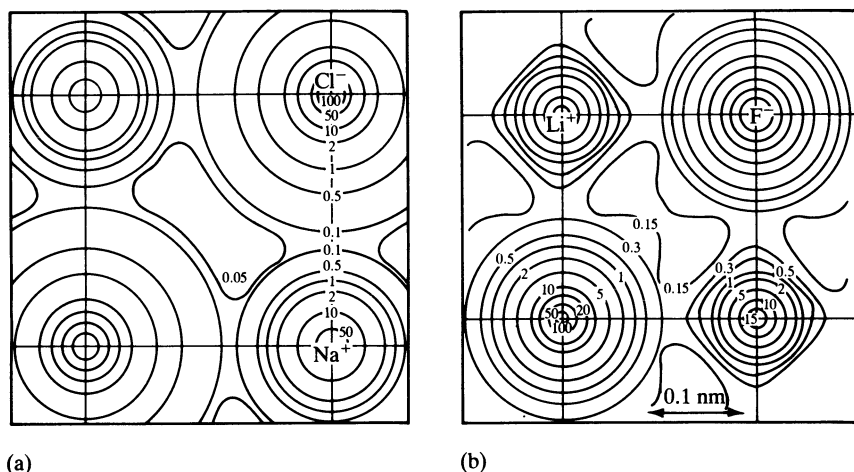


Figure 1.46 Electron density maps for (a) NaCl and (b) LiF.

Their crystal radii are based on conventional values of 126 pm and 119 pm for the radii of the O^{2-} and F^- ions, respectively. These values differ by a constant amount of 14 pm from traditional values but it is generally accepted that they correspond more closely to the actual physical size of ions in a crystal. A selection of this data is shown in Table 1.7. Several important trends in the sizes of ions can be noted from the data in Table 1.7.

1. The radii of ions within a Group of the Periodic Table, such as the alkali metals, increase with atomic number, Z . The number of electrons increases as we go down a group, and the outer ones are further from the nucleus.
2. In a series of isoelectronic cations, such as Na^+ , Mg^{2+} , Al^{3+} , the radius decreases rapidly with increasing positive charge. The number of electrons is constant but the nuclear charge increases and so pulls the electrons in and the radii decrease.
3. For pairs of isoelectronic anions, the radius increases with increasing charge because the more highly charged ion has a smaller nuclear charge.
4. For elements with more than one oxidation state, e.g. Ti^{2+} and Ti^{3+} , the radii decrease as the oxidation state increases; in this case the nuclear charge stays the same but the number of electrons that it acts on decreases.
5. On moving across the Periodic Table for a series of similar ions, such as the first row transition metal divalent ions, M^{2+} , there is an overall decrease in radius. This is due to an increase in nuclear charge across

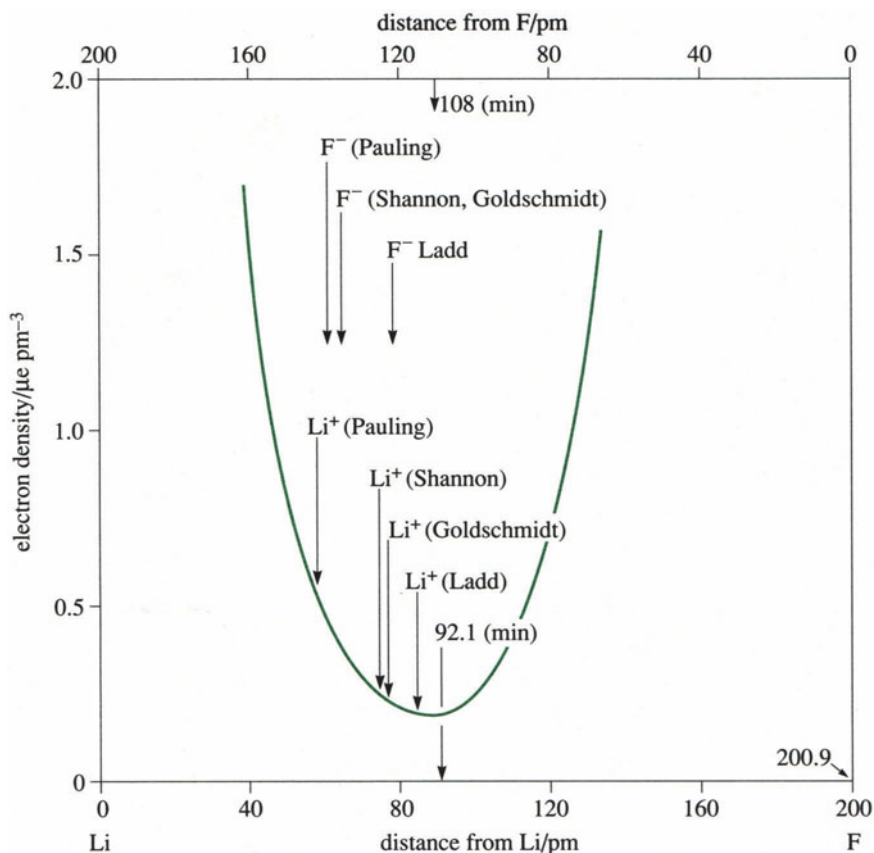


Figure 1.47 Plot showing the variation of electron density along the Li–F direction near the minimum with markers showing the various values of r_+ for Li^+ and r_- for F^- assigned by different methods.

the table because electrons in the same shell do not screen the nucleus from each other very well. A similar effect is seen for the M^{3+} ions of the lanthanides and this is known as the **lanthanide contraction**.

6. For transition metals the spin state affects the ionic radius.
7. The crystal radii increase with an increase in coordination number (see examples Cu^+ and Zn^{2+} in Table 1.7). One can think of fewer ligands around the central ion as allowing the counterions to compress the central ion.

The picture of ions as hard spheres works best for fluorides and oxides, both of which are small, fairly incompressible ions. As the ions get larger, they are more easily compressed, i.e. the electron cloud is more easily distorted, and they are said to be more **polarizable**.

Table 1.7 Crystal radii of some selected ions (pm)*

Ion	Radius	Ion	Radius	Ion	Radius	Ion	Radius	Ion	Radius	Ion	Radius	Ion	Radius
Li ⁺	90	Be ²⁺	59	B ³⁺	41	C ⁴⁺	30	Ti ²⁺	100	Ti ³⁺	81	OH ⁻	123
Na ⁺	116	Mg ²⁺	86	Al ³⁺	68	Si ⁴⁺	54	V ²⁺	93	V ³⁺	78	F ⁻	119
K ⁺	152	Ca ²⁺	114	Ga ³⁺	76	Ge ⁴⁺	67	Cr ²⁺	87/94 [†]	Cr ³⁺	76	Cl ⁻	167
Rb ⁺	166	Sr ²⁺	132	In ³⁺	94	Sn ⁴⁺	83	Mn ²⁺	81/97 [†]	Mn ³⁺	72/79 [†]	Br ⁻	182
Cs ⁺	181	Ba ²⁺	149	Tl ³⁺	103	Pb ⁴⁺	92	Fe ²⁺	75/92 [†]	Fe ³⁺	69/79 [†]	I ⁻	206
Cu ⁺	74/91 [‡]	Zn ²⁺	74/88 [‡]	Sc ³⁺	89	Ti ⁴⁺	75	Co ²⁺	79/89 [†]	Co ³⁺	69/75 [†]	O ²⁻	126
Ag ⁺	129	Cd ²⁺	109	Y ³⁺	104	Zr ⁴⁺	86	Ni ²⁺	69/63 [§]	Ni ³⁺	70/74 [†]	S ²⁻	170
Au ⁺	151	Hg ²⁺	116	Lu ³⁺	100	Hf ⁴⁺	85	Cu ²⁺	87	Cu ³⁺	68/- [†]	Se ²⁻	184
La ³⁺	117	Ce ³⁺	115	Pr ³⁺	113	Nd ³⁺	112	Pm ³⁺	111	Sm ³⁺	110	N ³⁻	132
Gd ³⁺	108	Tb ³⁺	106	Dy ³⁺	105	Ho ³⁺	104	Er ³⁺	103	Tm ³⁺	102	Eu ³⁺	109
												Yb ³⁺	101

* Values are taken from R.D. Shannon (1976) *Acta Crystallographica*, **A32**, 751, and are for octahedral coordination, unless noted otherwise.

[†] Low spin/high spin.

[‡] Tetrahedral/octahedral.

[§] Tetrahedral/square planar.

|| Tetrahedral.

When discussing particular crystal structures in the previous section it was noted that a larger cation such as Cs^+ was able to pack eight chloride ions around itself whereas the smaller Na^+ only accommodated six. If we continue to think of ions as hard spheres for the present, for a particular structure, as the ratio of the cation and anion radii changes there will come a point when the cation is so small that it will no longer be in touch with the anions. The lattice would not be stable in this state because the negative charges would be too close together for comfort and we would predict that the structure would change to one of lower coordination, allowing the anions to move further apart. If the ions are hard spheres, using simple geometry, it is possible to quantify the radius ratio (i.e. $r_{\text{cation}}/r_{\text{anion}} = r_+/r_-$) at which this happens, and this is illustrated for the octahedral case in Figure 1.48.

Taking a plane through the centre of an octahedrally coordinated metal cation, the stable situation is shown in Figure 1.48a and the limiting case for stability, when the anions are touching, in Figure 1.48b. The anion radius, r_- , in Figure 1.48b is OC, and the cation radius, r_+ , is (OA – OC). From the geometry of the right-angled triangle we can see that $\cos 45^\circ = \text{OC}/\text{OA} = 0.707$. The radius ratio, r_+/r_- , is given by $(\text{OA} - \text{OC})/\text{OC} = (\text{OA}/\text{OC} - 1) = (1.414 - 1) = 0.414$. Using similar calculations it is possible to calculate limiting ratios for the other geometries: these are summarized in Table 1.8.

On this basis we would expect to be able to use the ratio of ionic radii to predict possible crystal structures for a given substance. Indeed for many substances this can be done quite successfully: take for example

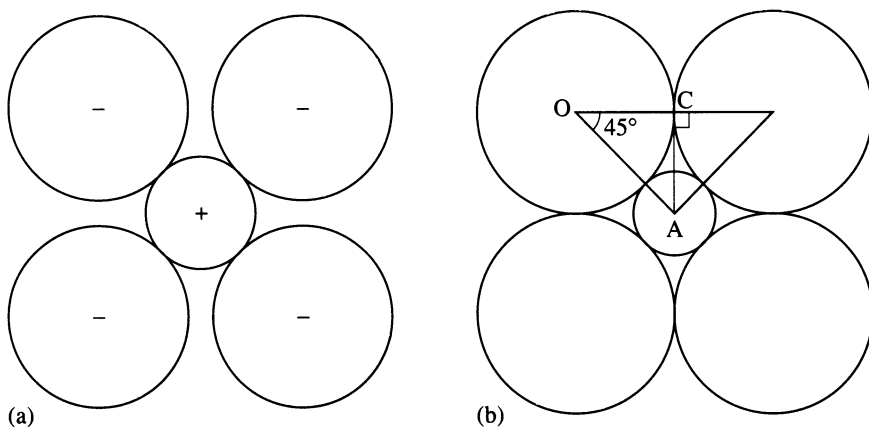


Figure 1.48 (a) Anions packed around a cation on a horizontal plane. (b) Anion–anion contact on a horizontal plane through an octahedron.

Table 1.8 Limiting radius ratios for different coordination numbers

<i>Coordination number</i>	<i>Geometry</i>	<i>Limiting radius ratio</i>	<i>Possible structures</i>
4	Tetrahedral	0.225	Wurtzite, zinc blende
6	Octahedral	0.414	Rock salt, rutile
8	Cubic	0.732	Caesium chloride, fluorite
		1.00	

MgO – Mg^{2+} (86 pm), O^{2-} (126 pm) gives $r_+/r_- = 0.68$, correctly predicting six-coordination (MgO has the rock-salt structure). Unfortunately, however, things are not this simple, and taking the radius ratio quite often predicts the wrong structure. In Figure 1.49, where we have plotted the radius ratios of each alkali halide and also indicated what the actual structure is, only about 50% of the structures are correctly predicted. This plot uses the Shannon and Prewitt crystal radii derived from experimental measurements; however, even if one uses the traditional radii based on the hard-sphere model there is very little improvement in the number of correct predictions.

What is the reason for this? As stated earlier, the model is too simplistic; ions are not hard spheres, but rather are polarized under the influence of cations. This means that the bonding involved is rarely truly ionic but frequently involves at least some degree of covalency. The higher the formal charge on a metal ion the greater will be the proportion of covalent bonding between the metal and its ligands. The higher the degree of covalency, the less likely is the concept of ionic radii and of their ratios to work. It also seems that there is little energy difference between the six-coordinate and eight-coordinate structures and the six-coordinate structure is usually preferred; eight-coordinate structures are rarely found, there are no eight-coordinate oxides for instance. The preference for the six-coordinate rock-salt structure is thought to be due to a small amount of covalent-bond contribution: in this structure the three orthogonal p orbitals lie in the same direction as the vectors joining the cation to the surrounding six anions, they are thus well placed for good overlap of the orbitals necessary for σ bonding to take place. The potential overlap of the p orbitals in the caesium chloride structure is less favourable.

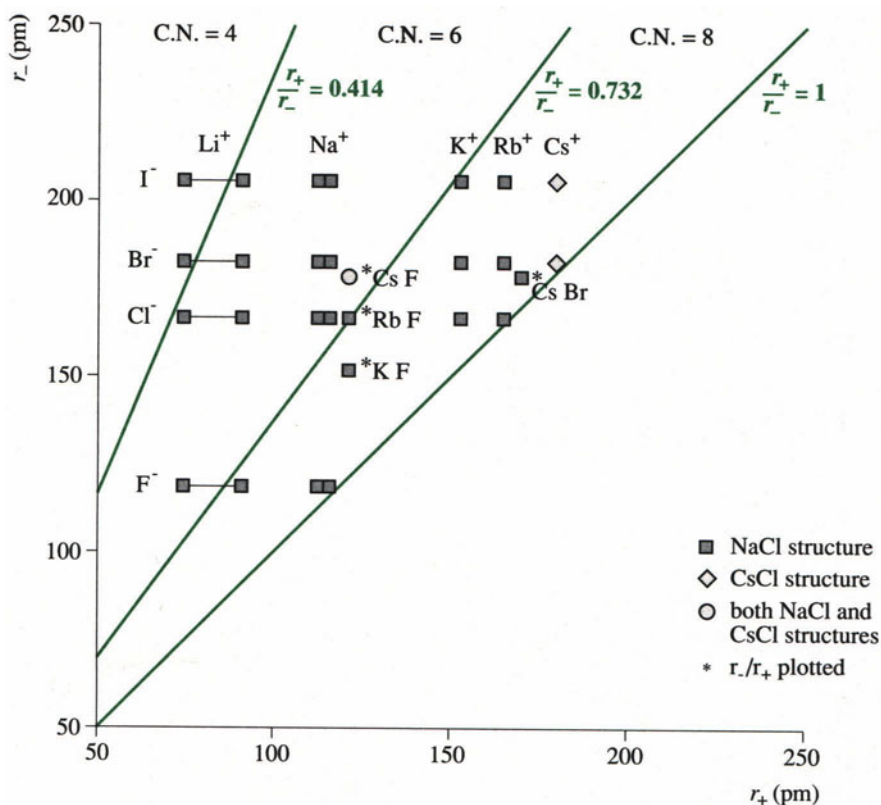


Figure 1.49 Actual crystal structures of the alkali halides compared with the structures predicted by the radius ratio rule. (Because the radii of Li^+ and Na^+ vary significantly with coordination, two values for these ions are given using values of the radii for CN = 4 and CN = 6.)

1.6.5 Extended covalent arrays

In the last section we noted that many ‘ionic’ compounds in fact possess some degree of covalency in their bonding. As the formal charge on an ion becomes greater we expect the degree of covalency to increase, so we would generally expect compounds of elements in the centre of the Periodic Table to be covalently bonded. Indeed, some of these elements themselves are covalently bonded solids at room temperature. Examples include elements from Group III: boron; Group IV: carbon, silicon, germanium; Group V: phosphorus, arsenic; and Group VI: selenium, tellurium; they form **extended covalent arrays** in their crystal structures.

Take for instance one of the forms of carbon – **diamond**. Diamond has a cubic crystal structure with an F-centred lattice (Figure 1.50); the

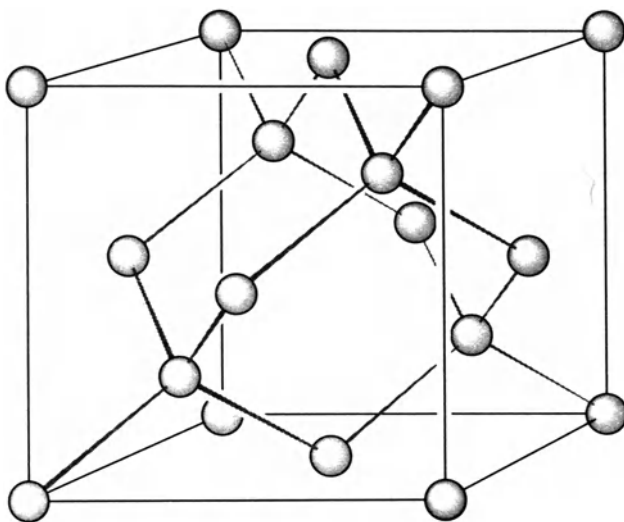


Figure 1.50 A unit cell of the diamond structure.

positions of the atomic centres are the same as in the zinc blende structure, with carbon now occupying both the zinc and the sulphur positions. Each carbon is equivalent and is tetrahedrally linked to four others, forming a **giant molecule** (covalently bonded) throughout the crystal: the carbon–carbon distances are all identical (154 pm). It is interesting to note that the carbons are all identical atoms of the same size, the same situation as for close-packed metals, but the coordination number is now restricted to four because this is the maximum number of covalent bonds that carbon can form. In the case of a metallic element such as magnesium forming a close-packed structure, each atom is 12-coordinated (bonding in metals is discussed in Chapter 4). The covalent bonds in diamond are strong and the rigid three-dimensional network of atoms makes diamond the hardest substance known; it also has a high melting temperature (3773 K). Silicon carbide (SiC), known as carborundum, also has this structure, with silicons and carbons alternating throughout as in zinc blende; it, too, is very hard and is used for polishing and grinding.

Silica (SiO_2) gives us other examples of giant molecular structures. There are two crystalline forms of silica at atmospheric pressure: **quartz** and **cristobalite**. Each of these also exist in low- and high-temperature forms, α - and β - respectively. (We have already discussed the structure of β -cristobalite in terms of close-packing in section 1.6.2.) Quartz is commonly encountered in nature; the structure of β -quartz is illustrated in Figure 1.51, and consists of $[\text{SiO}_4]$ tetrahedra linked so that each oxygen atom is shared by two tetrahedra, thus giving the overall stoichiometry of

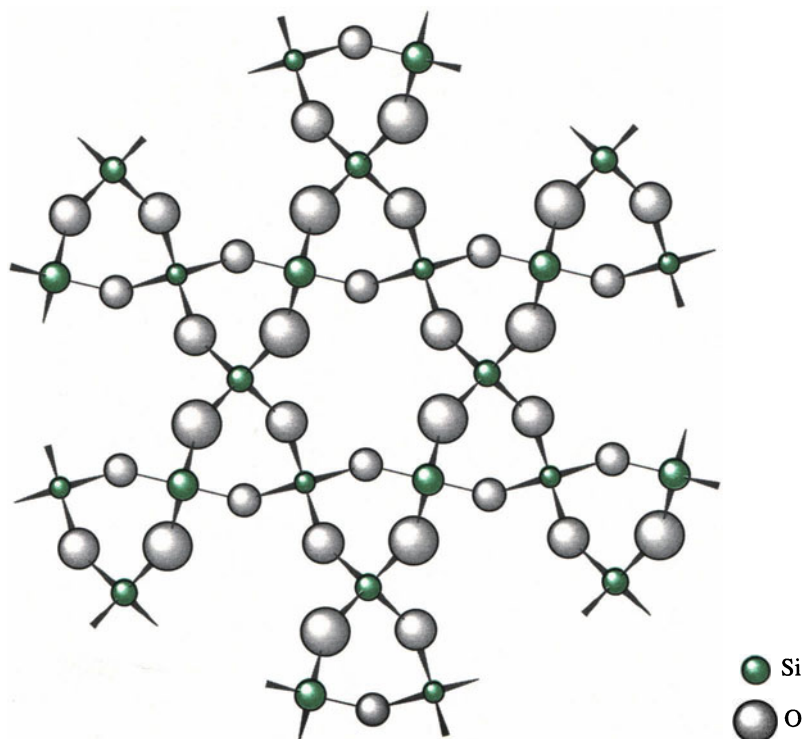


Figure 1.51 View down the helical axis of β -quartz.

SiO_2 . Notice how once again the covalency of each atom dictates the coordination around itself, silicon having four bonds and oxygen two, rather than the larger coordination numbers that are found for metallic and some ionic structures. The silicon–oxygen bonds in SiO_2 have considerable ionic character. Quartz is unusual in that the linked tetrahedra form **helices** or spirals throughout the crystal, which are all either left- or right-handed, producing laevo- or dextrorotatory crystals, respectively.

For our final examples in this section we will look at the structures of two other polymorphs of carbon. First, normal **graphite**, shown in Figure 1.52a (there are other graphite structures which are more complex). The structure of normal graphite consists of two-dimensional layers of carbon atoms joined together in a hexagonal array. Within the layers each carbon atom is strongly bonded to three others at a distance of 142 pm: this carbon–carbon distance is rather shorter than the one observed in diamond, due to the presence of some double-bonding (the planar hexagonal configuration of the carbon atoms puts some of the $2p$ orbitals in a suitable position for π -overlap in a similar fashion to the π -bonding in benzene, where the carbon–carbon distance is 139.7 pm.). The distance

between the graphite layers is much greater, 335 pm; this is indicative of weak bonding between the layers due to van der Waals forces. Graphite is a soft grey solid with a high melting temperature and low density. The weak bonding and large distance between the layers explains the low density of graphite. It is also found that graphite crystals shear easily parallel to the layers. It is a popular myth, however, that it is this ease of shearing that makes graphite a useful lubricant. In fact, its lubricant properties are dependent on adsorbed layers of oxygen or water vapour and when these are lost under extreme conditions, such as low pressure or high temperature, the lubricant properties are also lost. When graphite is used as a lubricant under high vacuum conditions, such as pertain in outer space, surface additives have to be incorporated to maintain the low-friction properties. The electrons in the delocalized π orbital are

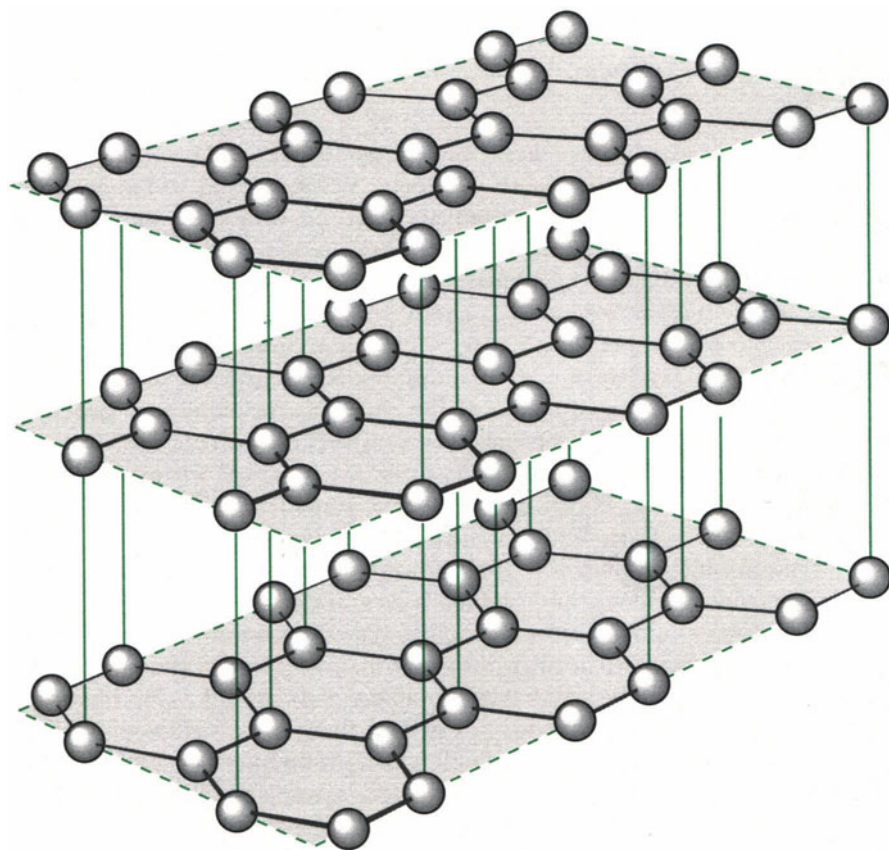


Figure 1.52a The crystal structure of graphite.

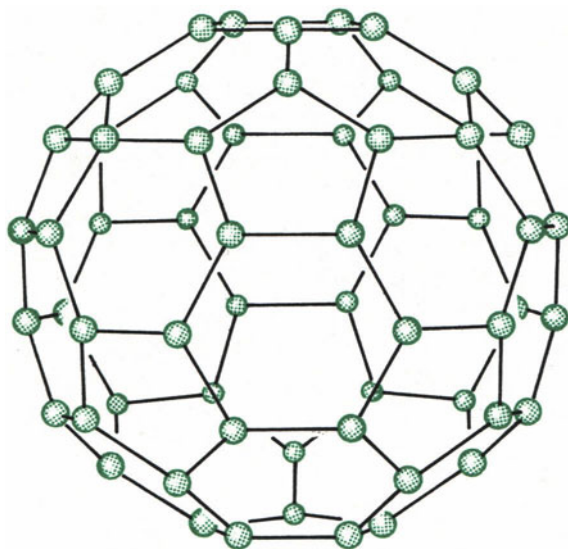


Figure 1.52b The structure of buckminsterfullerene, C_{60} .

mobile, and so graphite is electrically conducting in the layers like a two-dimensional metal, but is a poor conductor perpendicular to the layers.

Second, the polymorph **buckminsterfullerene**, which is illustrated in Figure 1.52b, was only discovered in 1985, and is made by passing an electric arc between two carbon rods in a partial atmosphere of helium. The molecule has the formula C_{60} and has the same shape as a soccer ball – a truncated icosahedron; it takes its name from the engineer and philosopher Buckminster Fuller who discovered the architectural principle of the hollow geodesic dome that the molecule resembles (a geodesic dome was built for EXPO 67 in Montreal). The molecule is extremely symmetrical with every carbon atom in an identical environment; it consists of 12 pentagons of carbon atoms joined to 20 hexagons. The carbon–carbon distance between adjacent hexagons is 139 pm, and where a hexagon joins a pentagon the carbon–carbon distance is 143 pm – similar to that found in the graphite layers. Indeed we can think of this structure as a carbon sheet with graphite-type delocalized bonding, which bends back on itself to form a polyhedron. (There are other fullerenes known, such as C_{70} ; they all have 12 pentagons of carbon atoms linked to different numbers of hexagons.) The C_{60} molecules, commonly called ‘buckyballs’, pack together in a cubic close-packed array in the crystals. Fullerene chemistry is currently a very active research area, and one of the interesting features is the formation of salts with the alkali metals, known as buckides. For instance potassium buckide, K_3C_{60} , has a *ccp* array of buckyballs with all the octahedral holes and tetrahedral holes

filled by potassiums: this is a metallic substance which becomes superconducting¹ below 18 K. Other alkali metal buckides become superconducting at even higher temperatures.

1.6.6 Molecular structures

Finally, we will consider structures that do not contain any extended arrays of atoms. The example of graphite in the previous section in a way forms a bridge between these structures and the structures with infinite three-dimensional arrays. Many crystals contain small, discrete, covalently bonded molecules that are held together only by weak forces, usually either van der Waals forces or **hydrogen bonding**. A hydrogen bond exists when a hydrogen atom is bonded to two or more other atoms. Usually, the hydrogen is attached to two very electronegative atoms such as oxygen or fluorine, with one short covalent bond and one longer, weaker hydrogen bond which can be thought of as a dipole–dipole interaction. Examples of molecular crystals are found throughout organic, organometallic and inorganic chemistry. The crystals are characterized by low melting and boiling temperatures. We will look at just two examples, carbon dioxide and water (ice), both familiar, small, covalently bonded molecules.

Gaseous carbon dioxide (CO_2) when cooled sufficiently forms a molecular crystalline solid (Figure 1.53). Notice that the unit cell contains

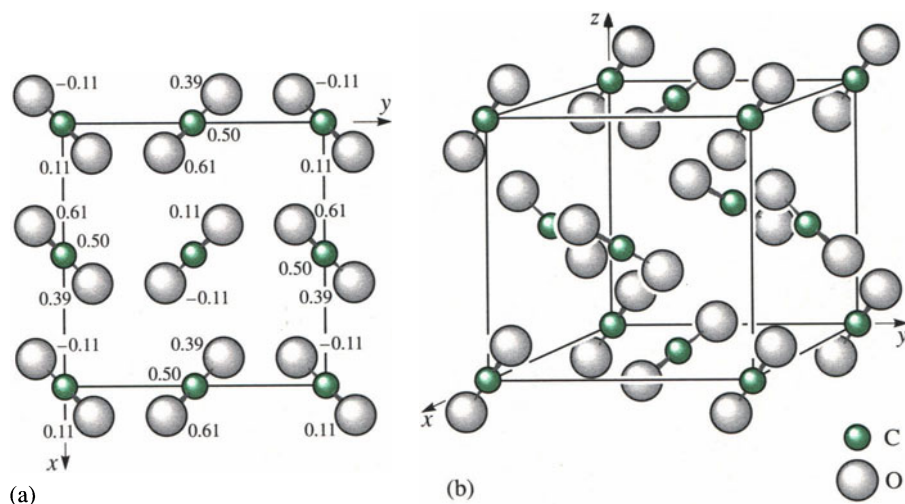


Figure 1.53 (a) Packing diagram of the unit cell of the cubic structure of carbon dioxide (CO_2) projected perpendicular to the z -axis. The heights of the atoms are expressed as fractional coordinates of c . (b) The crystal structure of CO_2 .

¹ See Chapter 10 for a discussion of superconductivity.

clearly discernible CO_2 molecules; these are held together in the crystal by weak van der Waals forces. From structures such as this, atoms can be assigned a **van der Waals radius**, which is defined as a non-bonded distance of closest approach. Data are compiled from the smallest interatomic distances in crystal structures which are not considered to be bonded to one another. If the sum of the van der Waals radii of two adjacent atoms is greater than the measured distance between them, then it is reasonable to suppose that there is a degree of bonding between them.

The structure of one form of ice (crystalline water) is shown in Figure 1.54 (there are many polymorphs of ice but the one illustrated is the hexagonal form I_h that forms at atmospheric pressure). Each H_2O molecule is tetrahedrally surrounded by four others. The crystal structure is held together by the hydrogen bonds formed between a hydrogen atom on one water molecule and the oxygen of the next, forming a three-dimensional arrangement throughout the crystal.

A summary of the various types of crystalline solids is given in Table 1.9, relating the type of structure to its physical properties. It is important to realize, however, that this only gives a broad overview, intended as a guide only. Not every crystal will fall exactly into one of these categories.

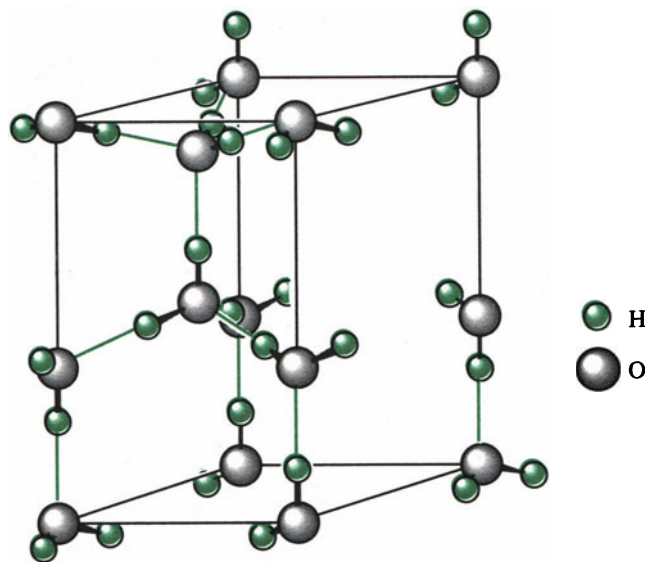


Figure 1.54 The crystal structure of hexagonal ice (I_h).

Table 1.9 Classification of crystal structures

<i>Type</i>	<i>Structural unit</i>	<i>Bonding</i>	<i>Characteristics</i>	<i>Examples</i>
Ionic	Cations and anions	Electrostatic, non-directional	Hard, brittle, crystals of high m.t.; moderate insulators; melts are conducting	Alkali metal halides
Extended covalent array	Atoms	Mainly covalent	Strong hard crystals of high m.t.; insulators	Diamond, silica
Molecular	Molecules	Mainly covalent between atoms in molecule, van der Waals or hydrogen bonding between molecules	Soft crystals of low m.t. and large coefficient of expansion; insulators	Ice, organic compounds
Metallic	Metal atoms	Band model (see Chapter 4)	Single crystals are soft; strength depends on structural defects and grain; good conductors; m.t.s vary but tend to be high	Iron, aluminium, sodium

m.t. = Melting temperature.

1.6.7 Silicates

The **silicates** form a large group of crystalline compounds with rather complex but interesting structures. A great part of the earth's crust is formed from these complex oxides of silicon.

Silicon itself crystallizes with the same structure as diamond. Its normal oxide, silica (SiO_2), is polymorphic and in previous sections we have discussed the crystal structure of two of its polymorphs: β -cristobalite (section 1.6.2) and β -quartz (section 1.6.5). Quartz is one of the commonest minerals on the earth, occurring as sand on the seashore, as a constituent in granite and flint and, in less pure form, as agate and opal. The silicon atom in all these structures is tetrahedrally coordinated.

The silicate structures are most conveniently discussed in terms of the $[\text{SiO}_4]^{4-}$ unit. The $[\text{SiO}_4]^{4-}$ unit has tetrahedral coordination of silicon by oxygen and is represented in these structures by a small tetrahedron as shown in Figure 1.55a. The silicon–oxygen bonds possess considerable covalent character.

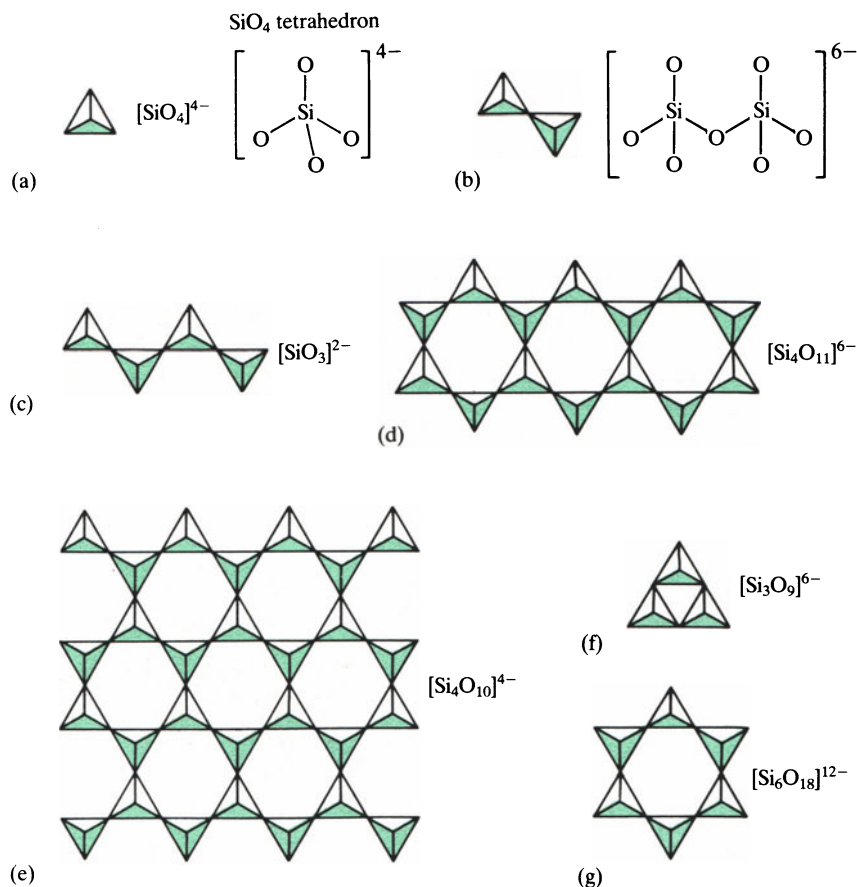


Figure 1.55 A structural classification of mineral silicates.

There are some minerals, **olivines** for instance, which contain discrete [SiO₄]⁴⁻ tetrahedra: these compounds do not contain Si—O—Si—O—Si—... chains but there is considerable covalent character in the metal–silicate bonds. These are often described as **orthosilicates**, salts of orthosilicic acid, Si(OH)₄ or H₄SiO₄, which is a very weak acid. The structure of olivine itself, (Mg,Fe)₂SiO₄, which can be described as an assembly of [SiO₄]⁴⁻ ions and Mg²⁺ (or Fe²⁺) ions, appears earlier in Table 1.5 because an alternative description is of an *hcp* array of oxygens with silicons occupying one-eighth of the tetrahedral holes and magnesium ions occupying one-half of the octahedral holes.

In most silicates, however, the [SiO₄]⁴⁻ tetrahedra are linked by oxygen sharing through a vertex, such as is illustrated in Figure 1.55b for two linked tetrahedra to give [Si₂O₇]⁶⁻. Notice that each terminal oxygen

confers a negative charge on the anion and the shared oxygen is neutral. The diagrams of silicate structures showing the silicate frameworks (Figure 1.55) omit these charges as they can be readily calculated. By the sharing of one or more oxygen atoms through the vertices, the tetrahedra are able to link up to form chains, rings, layers, etc. The negative charges on the silicate framework are balanced by metal cations in the lattice. Some examples are discussed below.

Discrete $[\text{SiO}_4]^{4-}$ units

Examples are found in **olivine** (see above), an important constituent of basalt; **garnets**, $\text{M}_3^{\text{II}}\text{M}_2^{\text{III}}(\text{SiO}_4)_3$ (where M^{II} can be Ca^{2+} , Mg^{2+} , or Fe^{2+} and M^{III} can be Al^{3+} , Cr^{3+} or Fe^{3+}), the framework of which is composed of $[\text{M}^{\text{III}}\text{O}_6]$ octahedra which are joined to six others via vertex-sharing $[\text{SiO}_4]$ tetrahedra, the M^{II} ions are coordinated by eight oxygens in dodecahedral interstices; **Ca_2SiO_4** , found in mortars and Portland cement; and **zircon** (ZrSiO_4) which has eight-coordinate Zr.

Disilicate units, $[\text{Si}_2\text{O}_7]^{6-}$

Structures containing this unit (Figure 1.55b) are not common but occur in **thortveitite** ($\text{Sc}_2\text{Si}_2\text{O}_7$) and **hemimorphite** ($\text{Zn}_4(\text{OH})_2\text{Si}_2\text{O}_7$).

Chains

$[\text{SiO}_4]^{4-}$ units share two corners to form infinite chains (Figure 1.55c). The repeat unit is $[\text{SiO}_3]^{2-}$. Minerals with this structure are called **pyroxenes**, e.g. **diopside** ($\text{CaMg}(\text{SiO}_3)_2$) and **enstatite** (MgSiO_3). The silicate chains lie parallel to one another and are linked together by the cations which lie between them.

Double chains

Here alternate tetrahedra share two and three oxygen atoms, respectively (Figure 1.55d). This class of minerals is known as the **amphiboles**, an example of which is **tremolite** ($\text{Ca}_2\text{Mg}_5(\text{OH})_2(\text{Si}_4\text{O}_{11})_2$). Most of the asbestos minerals fall in this class. The repeat unit is $[\text{Si}_4\text{O}_{11}]^{6-}$.

Infinite layers

The tetrahedra all share three oxygen atoms (Figure 1.55e). The repeat unit is $[\text{Si}_4\text{O}_{10}]^{4-}$. Examples are **talc** ($\text{Mg}_3(\text{OH})_2\text{Si}_4\text{O}_{10}$) which contains a sandwich of two layers with octahedrally coordinated Mg^{2+} between the layers; **micas**, e.g. $\text{KMg}_3(\text{OH})_2\text{Si}_3\text{AlO}_{10}$; and clay minerals such as **kaolin** ($\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5$).

Rings

Each $[\text{SiO}_4]^{4-}$ unit shares two corners as in the chains. Figures 1.55f and 1.55g show three and six tetrahedra linked together; these have the

general formula $[\text{SiO}_3]_n^{2n-}$; rings also may be made from four tetrahedra. An example of a six-tetrahedra ring is **beryl** (emerald; $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$); here the rings lie parallel with metal ions between them. Other examples include **diopase** ($\text{Cu}_6\text{Si}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$) and **benitoite** ($\text{BaTiSi}_3\text{O}_9$).

Three-dimensional structures

If $[\text{SiO}_4]^{4-}$ tetrahedra share all four oxygens, then the structure of silica (SiO_2) is produced. However, if some of the silicon atoms are replaced by the similarly sized atoms of the Group III element aluminium (i.e. if $[\text{SiO}_4]^{4-}$ is replaced by $[\text{AlO}_4]^{5-}$), then other cations must be introduced to balance the charges. Such minerals include the **feldspars** (general formula, $\text{M}(\text{Al},\text{Si})_4\text{O}_8$) the most abundant of the rock-forming minerals; the **zeolites**, which are used as ion exchangers, molecular sieves and catalysts (these are discussed in detail in Chapter 7); the **ultramarines**, which are coloured silicates manufactured for use as pigments, **lapis lazuli** being a naturally occurring mineral of this type.

As one might expect there is an approximate correlation between the solid state structure and the physical properties of a particular silicate. For instance, cement contains discrete $[\text{SiO}_4]^{4-}$ units and is soft and crumbly; asbestos minerals contain double chains of $[\text{SiO}_4]^{4-}$ units and are characteristically fibrous; mica contains infinite layers of $[\text{SiO}_4]^{4-}$ units and the weak bonding between the layers is easily broken and micas show cleavage parallel to the layers; granite contains feldspars which are based on three-dimensional $[\text{SiO}_4]^{4-}$ frameworks and are very hard.

1.7 LATTICE ENERGY

The **lattice energy** (L_0) of a crystal is defined as the internal energy change when one mole of the solid is formed from the gaseous ions at infinite separation, at atmospheric pressure and 0 K. For example, in sodium chloride we can approximate this to be the enthalpy change for the reaction in equation (1.1) under these conditions.



As it is not possible to measure lattice energies directly, they are usually determined either from a **Born–Haber cycle** or by calculation.

1.7.1 The Born–Haber cycle

A Born-Haber cycle is the application of **Hess's law** to the enthalpy of formation of an ionic solid at 298 K. Hess's law states that the enthalpy of a reaction is the same whether the reaction takes place in one step or in several. A Born–Haber cycle for a metal chloride, MCl , is shown in

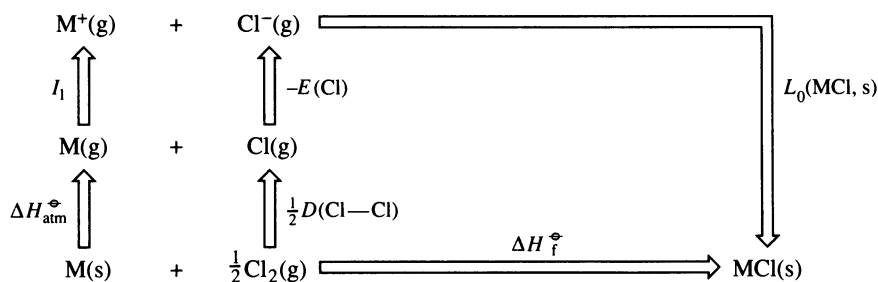


Figure 1.56 The Born-Haber cycle for a metal chloride, MCl .

Figure 1.56; the metal chloride is formed from the constituent elements in their standard state in the equation at the bottom, and by the clockwise series of steps above. From Hess's law, the sum of the enthalpy changes for each step around the cycle can be equated with the standard enthalpy of formation, giving

$$\Delta H_f^\circ(\text{MCl, s}) = \Delta H_{\text{atm}}^\circ(\text{M, s}) + I_1(\text{M}) + \frac{1}{2}D(\text{Cl}-\text{Cl}) - E(\text{Cl}) + L_0(\text{MCl, s}) \quad (1.2)$$

By rearranging this equation, we can write an expression for the lattice energy in terms of the other quantities, which can then be calculated if the values for these are known. The terms in the Born-Haber cycle are defined in Table 1.10 together with some sample data. Notice that the way in which we have defined lattice energy gives **negative** values; equation (1.1) may be written the other way round in some texts, in which case positive lattice energies will be quoted. It is not important which convention is chosen, providing you stick to it! The energy changes for each step are standard enthalpies, and although the symbol L_0 is conventionally used in the cycle for lattice energy, strictly we should have used L_{298} because this is the temperature at which standard enthalpies are determined. The error introduced into the determination of L_0 by this approximation is only of the order of 10 kJ mol^{-1} .

Cycles such as this can clearly be constructed for other compounds such as oxides, MO , sulphides, MS , higher valent metal halides, MX_n , etc. The difficulty in these cycles sometimes comes in the determination of values for the electron affinity, E . (We can think of E as being the heat evolved when an electron is added to an atom: as an enthalpy change refers to the heat absorbed, the two must have opposite signs.) In the case of an oxide, it is necessary to know the double electron affinity for oxygen (minus the enthalpy change of the following reaction):



Table 1.10 Terms in the Born–Haber cycle

<i>Term</i>	<i>Definition of the reaction to which the term applies</i>	<i>NaCl (kJ mol⁻¹)</i>	<i>AgCl (kJ mol⁻¹)</i>
$\Delta H_{\text{atm}}^{\circ}(\text{M})$	$\text{M}(\text{s}) = \text{M}(\text{g})$ standard enthalpy of atomization of metal M	107.8	284.6
$I_1(\text{M})^*$	$\text{M}(\text{g}) = \text{M}^+(\text{g}) + \text{e}^-(\text{g})$ first ionization energy of metal M	494	732
$\frac{1}{2}D(\text{Cl}-\text{Cl})^*$	$\frac{1}{2}\text{Cl}_2(\text{g}) = \text{Cl}(\text{g})$ half the dissociation energy of Cl_2	122	122
$-E(\text{Cl})^*$	$\text{Cl}(\text{g}) + \text{e}^-(\text{g}) = \text{Cl}^-(\text{g})$ the energy change of this reaction is defined as minus the electron affinity of chlorine	-349	-349
$L_0(\text{MCl}, \text{s})^*$	$\text{M}^+(\text{g}) + \text{Cl}^-(\text{g}) = \text{MCl}(\text{s})$ lattice energy of $\text{MCl}(\text{s})$		
$\Delta H_{\text{f}}^{\circ}(\text{MCl}, \text{s})$	$\text{M}(\text{s}) + \frac{1}{2}\text{Cl}_2(\text{g}) = \text{MCl}(\text{s})$ standard enthalpy of formation of $\text{MCl}(\text{s})$	-411.1	-127.1

*These quantities are defined as internal energy changes at 0 K. In practice this is approximated by using the enthalpy change for the reaction shown.

This can be broken down into two stages:



and



It is impossible to determine the enthalpy of reaction for equation (1.5) experimentally, and so this value can only be found if the lattice energy is known – a Catch 22 situation! To overcome problems such as this, methods of calculating (rather than measuring) the lattice energy have been devised and they are described in the next section.

1.7.2 Calculating lattice energies

For an ionic crystal of known structure, it should be a simple matter to calculate the energy released on bringing the ions from an infinite separation to form the crystal, using the equations of simple electrostatics. The energy of an ion pair, $\text{M}^+ \text{X}^-$ (assuming they are point charges), separated by distance, r , is given by **Coulomb's law**:

$$E = -\frac{e^2}{4\pi\epsilon_0 r} \quad (1.6)$$

and where the *magnitudes* of the charges on the ions are Z_+ and Z_- , for the cation and anion respectively, by

$$E = -\frac{Z_+ Z_- e^2}{4\pi\epsilon_0 r} \quad (1.7)$$

(e is the electronic charge, 1.6×10^{-19} C, and ϵ_0 is the permittivity of a vacuum, 8.854×10^{-12} F m $^{-1}$).

The energy due to coulombic interactions in a crystal is calculated for a particular structure by summing all the ion pair interactions, thus producing an infinite series. The series will include terms due to the attraction of the opposite charges on cations and anions and also repulsion terms due to cation–cation and anion–anion interactions. Some of these interactions are shown in Figure 1.57 for the NaCl structure: the Na^+ ion in the centre is immediately surrounded by six Cl^- ions at a distance of r , then by 12 cations at a distance of $\sqrt{2}r$, then by eight anions at $\sqrt{3}r$, followed by a further six cations at $2r$, and so on. The coulombic energy of interaction E_C is given by the summation of all these interactions:

$$E_C = -\frac{e^2}{4\pi\epsilon_0 r} \left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \frac{24}{\sqrt{5}} \dots \right) \quad (1.8)$$

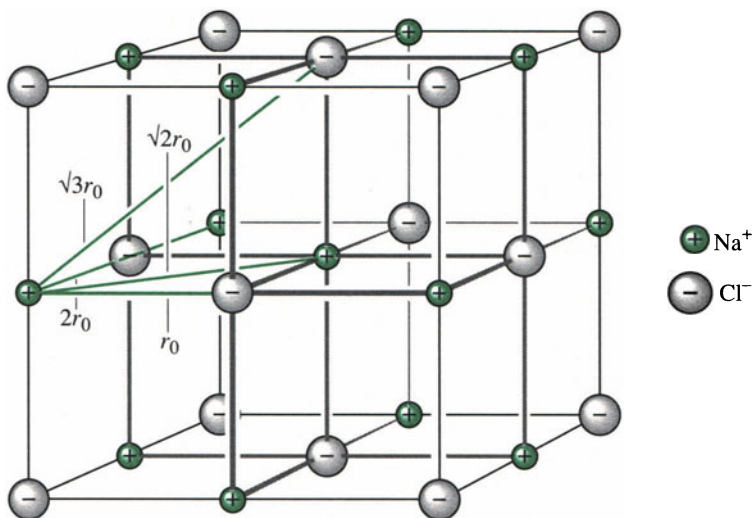


Figure 1.57 Sodium chloride structure showing internuclear distances.

The term inside the parentheses is known as the **Madelung constant** (A), in this case for the NaCl structure. The series is slow to converge but nevertheless values of the Madelung constant have been computed, not only for NaCl, but for most of the simple ionic structures. For one mole of NaCl we can write

$$E_C = -\frac{N_A A e^2}{4\pi\epsilon_0 r} \quad (1.9)$$

where N_A is the **Avogadro number**, $6.022 \times 10^{23} \text{ mol}^{-1}$. (Note that the expression is multiplied by N_A and not by $2N_A$, even though there are N_A cations and N_A anions present; this avoids counting every interaction twice!) The value of the Madelung constant is dependent only on the geometry of the lattice, and not on its dimensions; values for various structures are given in Table 1.11.

Ions, of course, are *not* point charges, but consist of positively charged nuclei surrounded by electron clouds. At small distances these electron clouds repel each other, and this too needs to be taken into account when calculating the lattice energy of the crystal. At large distances the repulsion energy is negligible but as the ions approach one another closely it increases very rapidly. Born suggested that the form of this repulsive interaction could be expressed by

$$E_R = \frac{B}{r^n} \quad (1.10)$$

where B is a constant and n (known as the **Born exponent**) is large and also a constant.

We can now write an expression for the lattice energy in terms of the energies of the interactions that we have considered:

$$L_0 = E_C + E_R = -\frac{N_A A Z_+ Z_- e^2}{4\pi\epsilon_0 r} + \frac{B}{r^n} \quad (1.11)$$

Table 1.11 Madelung constants for some common ionic lattices

Structure	Madelung constant (A)	$\frac{A}{v}$	Coordination
Caesium chloride	1.763	0.88	8:8
Sodium chloride	1.748	0.87	6:6
Fluorite	2.519	0.84	8:4
Zinc blende	1.638	0.82	4:4
Wurtzite	1.641	0.82	4:4
Corundum	4.172	0.83	6:4
Rutile	2.408	0.80	6:3

The lattice energy will be a minimum when the crystal is at equilibrium, i.e. when the internuclear distance is at the equilibrium value of r_0 . We can minimize the lattice energy function by differentiating with respect to r and equating to zero:

$$\frac{dL_0}{dr} = \frac{N_A A Z_+ Z_- e^2}{4\pi\epsilon_0 r^2} - \frac{nB}{r^{n+1}}$$

but

$$\begin{aligned} \frac{dL_0}{dr} &= 0, \quad \text{when } r = r_0 \\ \frac{nB}{r_0^{n+1}} &= \frac{N_A A Z_+ Z_- e^2}{4\pi\epsilon_0 r_0^2} \\ B &= \frac{N_A A Z_+ Z_- e^2 r_0^{n+1}}{n4\pi\epsilon_0 r_0^2} = \frac{N_A A Z_+ Z_- e^2 r_0^{n-1}}{n4\pi\epsilon_0} \\ L_0 &= -\frac{N_A A Z_+ Z_- e^2}{4\pi\epsilon_0 r_0} + \frac{N_A A Z_+ Z_- e^2 r_0^{n-1}}{n4\pi\epsilon_0 r_0^n} \\ L_0 &= -\frac{N_A A Z_+ Z_- e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right) \end{aligned} \quad (1.12)$$

This is known as the **Born–Landé equation**: the values of r_0 and n can be obtained from X-ray crystallography and from compressibility measurements, respectively. The other terms in the equation are well-known constants, and when values for these are substituted we get

$$L_0 = -\frac{1.389 \times 10^5 A Z_+ Z_-}{r_0} \left(1 - \frac{1}{n}\right) \quad (1.13)$$

If the units of r_0 are pm, then the units of L_0 will be kJ mol^{-1} .

Pauling showed that the values of n can be approximated with reasonable accuracy for compounds of ions with noble gas configurations, by averaging empirical constants for each ion. The values of these constants are given in Table 1.12. For example, n for rubidium chloride (RbCl) is 9.5 (average of 9 and 10) and for strontium chloride (SrCl_2) is 9.33 (average of 9, 9 and 10).

It has been suggested that the repulsion term in the lattice energy expression is better represented by

$$E_R = b e^{-(r/\rho)}, \quad (1.14)$$

where b and ρ are constants also determined from compressibility measurements. This gives an expression for the lattice energy of:

Table 1.12 Constants used to calculate n

<i>Ion type</i>	<i>Constant</i>
[He]	5
[Ne]	7
[Ar]	9
[Kr]	10
[Xe]	12

$$L_0 = -\frac{N_A A Z_+ Z_- e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{\rho}{r_0}\right) \quad (1.15)$$

This is known as the **Born–Mayer equation**.

Notice what a dramatic effect the charge on the ions can have on the value of the lattice energy. A structure containing one doubly charged ion has a factor of two in the equation ($Z_+ Z_- = 2$), whereas one containing two doubly charged ions is multiplied by a factor of four ($Z_+ Z_- = 4$). Structures containing multiply charged ions tend to have much larger (numerically) lattice energies.

Some lattice energy values that have been calculated by various methods are shown in Table 1.13 for comparison with experimental values that have been computed using a Born–Haber cycle. Remarkably good agreement is achieved, considering all the approximations involved. The largest discrepancies are for the large polarizable ions, where, of course, the ionic model is not expected to be perfect. The equations can be improved to help with these discrepancies by including the effect of van der Waals forces, zero point energy (the energy due to the vibration of the ions at 0 K) and heat capacity. The net effect of these corrections is only of the order of 10 kJ mol^{-1} and the values thus obtained for the lattice energy are known as **extended-calculation values**.

It is important to note that the good agreement achieved between the Born–Haber and calculated values for lattice energy do not in any way prove that the ionic model is valid. This is because the equations possess a self-compensating feature in that they use *formal charges* on the ions, but take *experimental internuclear distances*. The values of r_0 are the result of all the various types of bonding in the crystal, not just of the ionic bonding, and so are rather shorter than one would expect for purely ionic bonding.

Kapustinskii noted that if the Madelung constants, A , for a number of structures are divided by the number of ions in one formula unit of the structure, v , the resulting values are almost constant (Table 1.11), and this led to the idea that it would be possible to set up a general lattice

Table 1.13 Lattice energies of some alkali and alkaline earth metal halides at 0 K

Compound	Structure	$L_0(\text{kJ mol}^{-1})$			
		Born–Haber cycle*	Born–Landé equation (1.12) [†]	Extended calculation [‡]	Kapustinskii equation (1.17)
LiF	NaCl	–1025		–1033	–970
LiI	NaCl	–756		–738	–725
NaF	NaCl	–910	–904	–906	–882
NaCl	NaCl	–772	–757	–770	–753
NaBr	NaCl	–736	–720	–735	–720
NaI	NaCl	–701	–674	–687	–673
KCl	NaCl	–704	–690	–702	–679
KI	NaCl	–646	–623	–636	–613
CsF	NaCl	–741	–724	–734	–716
CsCl	CsCl	–652	–623	–636	–629
CsI	CsCl	–611	–569	–592	–572
MgF ₂	Rutile	–2922	–2883	–2914	
CaF ₂	Fluorite	–2597	–2594	–2610	
CaCl ₂	Deformed rutile	–2226		–2223	

* D.A. Johnson (1982) *Some Thermodynamic Aspects of Inorganic Chemistry*, Cambridge.

[†] D.F.C. Morris (1957) *J. Inorg. Nucl. Chem.*, **4**, 8.

[‡] D. Cubicciotti (1961) *J. Chem. Phys.*, **34**, 2189; T.E. Brackett and E.B. Brackett (1965) *J. Phys. Chem.*, **69**, 3611; H.D.B. Jenkins and K.F. Pratt (1977) *Proc. R. Soc. Series A*, **356**, 115.

energy equation that could be applied to any crystal regardless of its structure. For the six-coordinate NaCl structure, the value of A/v is 0.874, and this can be plugged into either the Born–Landé or the Born–Mayer equation and used to calculate the lattice energy of an unknown structure. In these equations r_0 can then be replaced by $(r_+ + r_-)$, where r_+ and r_- are the cation and anion radii for six-coordination; n can be assigned an average value of 9. With these substitutions in equation (1.12) we get

$$L_0 = - \frac{1.079 \times 10^5 v Z_+ Z_-}{r_+ + r_-} \quad (1.16)$$

ρ in equation (1.15) is approximately 34.5 pm for the alkali halides, and so substituting in equation (1.15) gives us:

$$L_0 = - \frac{1.214 \times 10^5 v Z_+ Z_-}{r_+ + r_-} \left(1 - \frac{34.5}{r_+ + r_-} \right) \quad (1.17)$$

Table 1.14 Thermochemical radii of polyatomic ions*

<i>Ion</i>	<i>pm</i>	<i>Ion</i>	<i>pm</i>	<i>Ion</i>	<i>pm</i>
NH ₄ ⁺	151	ClO ₄ ⁻	226	MnO ₄ ²⁻	215
Me ₄ N ⁺	215	CN ⁻	177	O ₂ ²⁻	144
PH ₄ ⁺	171	CNS ⁻	199	OH ⁻	119
AlCl ₄ ⁻	281	CO ₃ ²⁻	164	PtF ₆ ²⁻	282
BF ₄ ⁻	218	IO ₃ ⁻	108	PtCl ₆ ²⁻	299
BH ₄ ⁻	179	N ₃ ⁻	181	PtBr ₆ ²⁻	328
BrO ₃ ⁻	140	NCO ⁻	189	PtI ₆ ²⁻	328
CH ₃ COO ⁻	148	NO ₂ ⁻	178	SO ₄ ²⁻	244
ClO ₃ ⁻	157	NO ₃ ⁻	165	SeO ₄ ²⁻	235

* J.E. Huheey (1983) *Inorganic Chemistry*, 3rd edn, Harper and Row, London, based on data from H.D.B Jenkins and K.P. Thakur (1979) *Journal of Chemical Education*, **56**, 576.

These are known as the **Kapustinskii equations**. Values computed using equation (1.17) are also contained in Table 1.13 for comparison with the other equations.

As we end this section let us reconsider ionic radii briefly. Many ionic compounds contain complex or polyatomic ions. Clearly, it is going to be extremely difficult to measure the radii of ions such as ammonium (NH₄⁺) or carbonate (CO₃²⁻), for instance. However, Yatsimirskii has devised a method which determines a value of the radius of a polyatomic ion by applying the Kapustinskii equation to lattice energies determined from thermochemical cycles. Such values are called **thermochemical radii** and Table 1.14 lists some of these values.

1.7.3 Calculations using thermochemical cycles and lattice energies

It is not yet possible to measure a lattice energy directly, which is why the best experimental values for the alkali halides (Table 1.13) are derived from a thermochemical cycle. This in itself is not always easy for compounds other than the alkali halides, because as noted before, not all of the data are necessarily available. Electron affinity values are known from experimental measurements for most of the elements, but when calculating a lattice energy for a sulphide (say) we need to know the enthalpy change for the reaction in equation (1.18)



which is minus a **double electron affinity** and is not so readily available. This is where lattice energy calculations come into their own, because we can use one of the methods discussed above to calculate a value of L_0 for the appropriate sulphide and then plug it into the thermochemical cycle to calculate the enthalpy change of equation (1.18).

Proton affinities can be accessed in a similar way: a proton affinity is defined as the enthalpy change of the reaction shown in equation (1.19), where a proton is lost by the species A.



This value can be obtained from a suitable thermochemical cycle providing the lattice energy is known. Take as an example the formation of the ammonium ion, $\text{NH}_4^+(\text{g})$:



The enthalpy change of the reaction in equation (1.20) is minus the proton affinity of ammonia, $-P(\text{NH}_3(\text{g}))$. This could be calculated from the thermochemical cycle shown in Figure 1.58, provided the lattice energy of ammonium chloride is known.

Thermochemical cycles can also be used to provide us with information on the thermodynamic properties of compounds with metals in unusual oxidation states which have not yet been prepared. For instance, we can use arguments to determine whether it is possible to prepare a compound of sodium in a higher oxidation state than normal, NaCl_2 . In order to calculate a value for the enthalpy of formation and thence ΔG_f° ($\text{NaCl}_2(\text{s})$), we need to set up a Born–Haber cycle for $\text{NaCl}_2(\text{s})$ of the type shown in Figure 1.59. The only term in this cycle that is not known is the lattice energy of NaCl_2 , and for this we make the approximation that it will be the same as that of MgCl_2 which *is* known. The summation becomes

$$\begin{aligned} \Delta H_f^\circ(\text{NaCl}_2(\text{s})) &= \Delta H_{\text{atm}}^\circ(\text{Na}(\text{s})) + I_1(\text{Na}) + I_2(\text{Na}) + D_{\text{m}}(\text{Cl}-\text{Cl}) \\ &\quad - 2E(\text{Cl}) + L_0(\text{NaCl}_2(\text{s})) \end{aligned} \quad (1.21)$$

The values listed in Table 1.15 show that the enthalpy of formation of $\text{MgCl}_2(\text{s})$ is negative, but that of $\text{NaCl}_2(\text{s})$ is positive. Why? A glance at

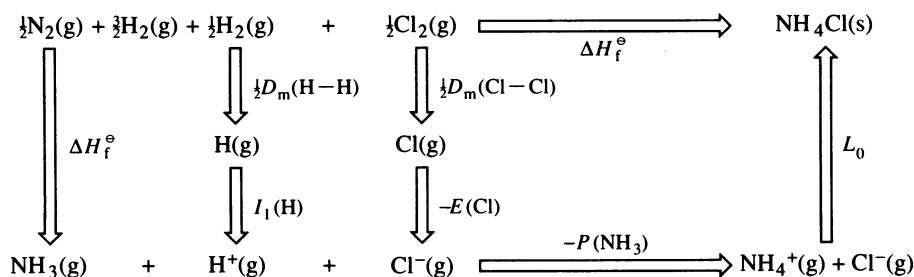


Figure 1.58 Thermochemical cycle for the calculation of the proton affinity of ammonia.

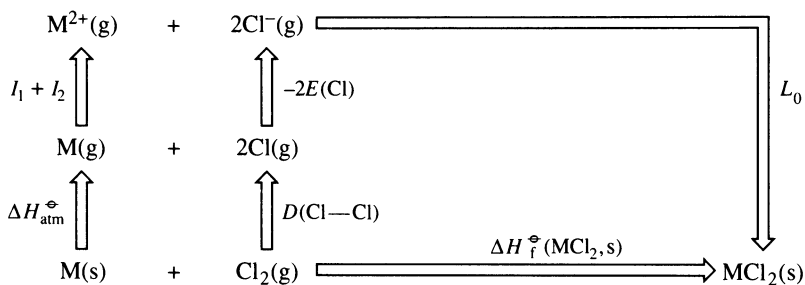


Figure 1.59 Born–Haber cycle for a metal dichloride, MCl_2 .

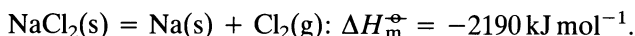
Table 1.15 Values of the Born–Haber cycle terms for NaCl_2 and MgCl_2 (kJ mol^{-1})

	<i>Na</i>	<i>Mg</i>
$\Delta H_{\text{atm}}^{\ominus}$	108	148
I_1	494	736
I_2^*	4565	1452
$D(\text{Cl}-\text{Cl})$	244	244
$-2E(\text{Cl})$	−698	−698
$L_0(\text{MCl}_2(\text{s}))$	−2523	−2523
$\Delta H_{\text{f}}^{\ominus}(\text{MCl}_2(\text{s}))$	2190	−641

* The second ionization energy, I_2 , refers to the energy change of the reaction: $\text{M}^+(\text{g}) - \text{e}^-(\text{g}) = \text{M}^{2+}(\text{g})$.

the figures in Table 1.15 reveals the answer: the second ionization energy for sodium is huge (because this relates to the removal of an inner shell electron) and this far outweighs the large negative lattice energy. So, NaCl_2 does not exist because the extra stabilization of the lattice due to a doubly charged ion is not enough to compensate for the large second ionization energy.

The calculation we have just performed shows that for the reaction



To be sure of the stability of the compound we need a value for $\Delta G_{\text{m}}^{\ominus}$. For the analogous reaction of $\text{MgCl}_2(\text{s})$, $\Delta S_{\text{m}}^{\ominus} = 166.1 \text{ J K}^{-1} \text{ mol}^{-1}$, and so

$$\begin{aligned}
 \Delta G_{\text{m}}^{\ominus} &= \Delta H_{\text{m}}^{\ominus} - T\Delta S_{\text{m}}^{\ominus} = -2190 - (298.15 \times 0.166) \\
 &= -2239 \text{ kJ mol}^{-1},
 \end{aligned}$$

suggesting that NaCl_2 would be unstable with respect to the elements sodium and chlorine.

Interestingly it was arguments and calculations of this sort that led Neil Bartlett to the discovery of the first noble gas compound, XePtF_6 . Bartlett had prepared a new complex, O_2PtF_6 , which by analogy with the diffraction pattern of KPtF_6 , he formulated as containing the dioxygenyl cation, $[\text{O}_2^+][\text{PtF}_6^-]$. He realized that the ionization energies of oxygen and xenon are very similar and that although the radius of the Xe^+ ion is slightly different, because the PtF_6^- anion is very large the lattice energy of $[\text{Xe}^+][\text{PtF}_6^-]$ should be very similar to that of the dioxygenyl complex and therefore should exist! Accordingly he mixed xenon and PtF_6 and obtained the orange-yellow solid of xenon hexafluoroplatinate – the first noble gas compound. (At room temperature the XePtF_6 reacts with another molecule of PtF_6 to give a product containing $[\text{XeF}]^+[\text{PtF}_6]^-$ and $[\text{PtF}_5]^-$.)

Several examples of problems involving these types of calculation are included in the questions at the end of the chapter.

1.8 CONCLUSION

In this opening chapter we have introduced many of the principles and ideas that lie behind a discussion of the crystalline solid state. We have discussed in detail the structure of a number of important ionic crystal structures and shown how they can be linked to a simple view of ions as hard spheres that pack together as closely as possible, but can also be viewed as the linking of octahedra or tetrahedra in various ways. Taking these ideas further, we have investigated the size of these ions in terms of their radii and thence the energy involved in forming a lattice with ionic bonding. We also noted that covalent bonding is present in many structures and that when covalent bonding only is present we tend to see a rather different type of crystal structure.

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QUESTIONS

1. How many tetrahedral and octahedral holes are there in a *ccp* array of n spheres?
2. What is the coordination number of any atom in an infinite *ccp* array?
3. What is the coordination number of an atom in an infinite primitive array?
4. Figure 1.60 shows several molecules. Find and draw all the symmetry elements possessed by each molecule.

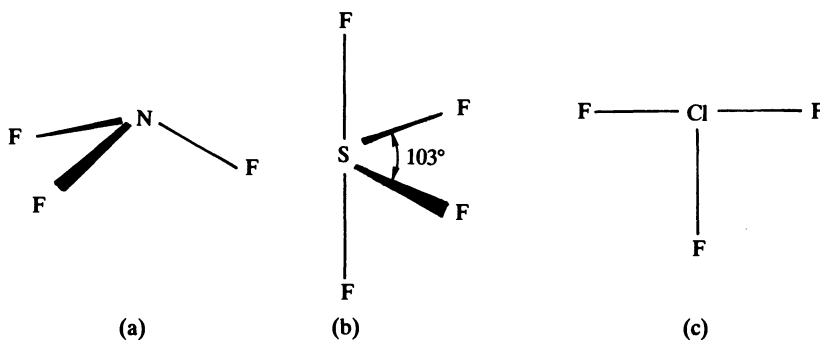


Figure 1.60 (a) NF_3 . (b) SF_4 . (c) ClF_3 .

5. Does the CF_4 molecule in Figure 1.11 possess a centre of inversion? What other rotation axis is coincident with the $\bar{4}$ (S_4)?
6. Assuming an asymmetric object, e.g. a molecule, to be placed on each lattice point, evaluate the number of molecules in a unit cell, for each type of unit cell, i.e. P, I, F and A, and see if they agree with the results in Table 1.3.
7. How many centred cells are drawn in Figure 1.16?

8. Index the sets of lines in Figure 1.25 marked B, C, D and E.
9. Index the sets of planes in Figure 1.26b, c and d.
10. Figure 1.23 shows a unit cell of a face-centred cubic structure (F). If a single atom is placed at each lattice point then this becomes the unit cell of the *ccp* (cubic close-packed) structure. Find the *100*, *110* and the *111* planes and calculate the density of atoms per unit area for each type of plane. (Hint: calculate the area of each plane assuming a cell length *a*. Decide the fractional contribution made by each atom to the plane.)
11. What are the coordination numbers of Cs^+ and Cl^- in the caesium chloride structure?
12. What is the Bravais lattice of the caesium chloride structure and how many formula units of CsCl are there in the unit cell?
13. What are the coordination numbers of Na^+ and Cl^- in the rock-salt structure?
14. Calculate the number of formula units of NaCl in the unit cell illustrated in Figure 1.30.
15. Describe and draw the geometry around Ni and As in the NiAs structure. What is the coordination number of each type of atom?
16. What are the coordination numbers of Zn and S in the zinc blende structure?
17. Using Figures 1.29, 1.30 and 1.38 together with models if necessary, draw unit cell projections for (a) CsCl ; (b) NaCl ; (c) ZnS (zinc blende).
18. How many formula units, ZnS , are there in the zinc blende unit cell?
19. Draw a projection of a unit cell for both the *hcp* and *ccp* structures, seen perpendicular to the close-packed layers (i.e. assume that the close-packed layer is the *ab* plane, draw in the *x*- and *y*-coordinates of the atoms in their correct positions and mark the third coordinate, *z*, as a fraction of the corresponding repeat distance, *c*).
20. Estimate a value for the radius of the iodide ion. The distance between the lithium and iodine nuclei in lithium iodide is 300 pm.
21. Calculate a radius for F^- from the data in Table 1.6 for NaI and NaF . Repeat the calculation using RbI and RbF .
22. The diamond structure is shown in Figure 1.50. Find the *100*, *110* and *111* planes and determine the relative atomic densities per unit area. (See Question 10.)

23. Use the Born–Haber cycle in Figure 1.59 and the data in Table 1.16 to calculate the lattice energy of solid calcium chloride (CaCl_2).

Table 1.16 Values of the Born–Haber cycle terms for CaCl_2 (kJ mol^{-1})

<i>Term</i>	<i>Value</i>
$\Delta H_{\text{atm}}^{\oplus}(\text{Ca(s)})$	178
$I_1(\text{Ca})$	590
$I_2(\text{Ca})$	1146
$D(\text{Cl–Cl})$	244
$-2E(\text{Cl})$	–698
$\Delta H_{\text{f}}^{\oplus}(\text{CaCl}_2(\text{s}))$	–795.8

24. Calculate the value of the Madelung constant for the structure in Figure 1.61. All bond lengths are equal and all bond angles are 90° . Assume that there are no ions other than those shown in the figure and that the charges on the cations and anions are $+1$ and -1 , respectively.

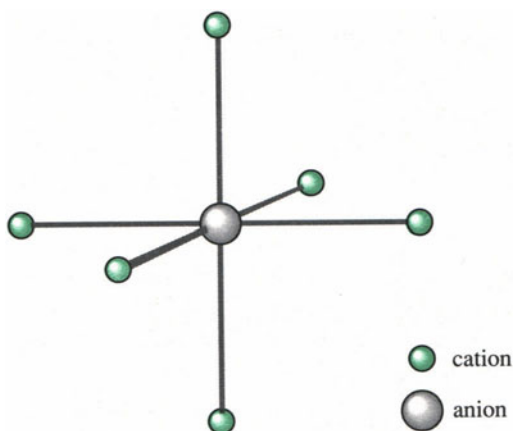


Figure 1.61 Structure for use with question 24. All bond lengths are equal and bond angles are 90° .

25. Calculate a value for the lattice energy of potassium chloride using equation (1.17). Compare this with the value you calculate from the thermodynamic data in Table 1.17.

Table 1.17 Values of the Born–Haber cycle terms for KCl (kJ mol⁻¹)

<i>Term</i>	<i>Value</i>
$\Delta H_{\text{atm}}^{\ominus}(\text{K(s)})$	89.1
$I_1(\text{K})$	418
$\frac{1}{2}D(\text{Cl–Cl})$	122
$-E(\text{Cl})$	-349
$\Delta H_{\text{f}}^{\ominus}(\text{KCl(s)})$	-436.7

26. Calculate a value for the electron affinity of sulphur for two electrons. Take iron(II) sulphide (FeS) as a model and devise a suitable cycle. Use the data given in Table 1.18.

Table 1.18 Values of the Born–Haber cycle terms for FeS (kJ mol⁻¹)

<i>Term</i>	<i>Value</i>
$\Delta H_{\text{atm}}^{\ominus}(\text{Fe(s)})$	416.3
$I_1(\text{Fe})$	761
$I_2(\text{Fe})$	1561
$\Delta H_{\text{atm}}^{\ominus}(\text{S(s)})$	278.8
$\Delta H_{\text{f}}^{\ominus}(\text{FeS(s)})$	-100.0
$E(\text{S})$	200

27. Calculate a value for the electron affinity of oxygen for two electrons. Take magnesium oxide (MgO) as a model and devise a suitable cycle. Use the data given in Table 1.19.

Table 1.19 Values of the Born–Haber cycle terms for MgO (kJ mol⁻¹)

<i>Term</i>	<i>Value</i>
$\Delta H_{\text{atm}}^{\ominus}(\text{Mg(s)})$	147.7
$I_1(\text{Mg})$	736
$I_2(\text{Mg})$	1452
$\frac{1}{2}D_{\text{m}}(\text{O–O})$	249
$\Delta H_{\text{f}}^{\ominus}(\text{MgO(s)})$	-601.7
$E(\text{O})$	141

28. Calculate a value for the proton affinity of ammonia using the cycle in Figure 1.58 and data in Table 1.20.

Table 1.20 Values of the Born–Haber cycle terms for NH_4Cl (kJ mol^{-1})

<i>Term</i>	<i>Value</i>
$\Delta H_f^\circ(\text{NH}_3)$	–46.0
$\Delta H_f^\circ(\text{NH}_4\text{Cl(s)})$	–314.4
$\frac{1}{2}D_m(\text{H–H})$	218
$\frac{1}{2}D_m(\text{Cl–Cl})$	122
$I(\text{H})$	1314
$E(\text{Cl})$	349
$r_+(\text{NH}_4^+)$	151 pm

29. Compounds of aluminium and magnesium in the lower oxidation states, Al(I) and Mg(I) , do not exist under normal conditions. If we make an assumption that the radius of Al^+ or Mg^+ is the same as that of Na^+ (same row of the Periodic Table) then we can also equate the lattice energies, $M\text{Cl}$. Use this information in a Born–Haber cycle to calculate a value of the enthalpy of formation, ΔH_f° , for AlCl(s) and MgCl(s) , using the data in Table 1.21.

Table 1.21 Values of the Born–Haber cycle terms for NaCl , MgCl and AlCl (kJ mol^{-1})

<i>Term</i>	<i>Na</i>	<i>Mg</i>	<i>Al</i>
$\Delta H_{\text{atm}}^\circ$	108	148	326
I_1	494	736	577
$\frac{1}{2}D(\text{Cl–Cl})$	122	122	122
$-E(\text{Cl})$	–349	–349	–349
$\Delta H_f^\circ(\text{NaCl(s)})$	–411		
$L_0(\text{MCl(s)})$			

2.1 INTRODUCTION

There is a vast array of physical methods for investigating the structures of solids, each technique with its own strengths and weaknesses – far too many for us to describe in a book of this sort. Some techniques are able to investigate the local coordination around a particular atom, whereas others are suited to elucidating the long range order of the structure. We have chosen to describe just one technique in some detail here which is used to determine the structures of crystalline solids. It has been used to solve more crystalline structures than all the other techniques put together. This technique is X-ray diffraction, and it is able to determine the precise atomic positions and therefore the bond lengths and angles of molecules within a single crystal. It too, of course, has its limitations and only gives an overall, average picture of a structure; it cannot usually identify localized defects or define the positions of small quantities of dopants and for this we need to turn to other techniques. However, when it is possible to use it, it is extremely powerful; the results are very accurate, giving bond lengths to a few tens of picometres.¹

2.2 GENERATION OF X-RAYS

The discovery of X-rays was made by a German physicist, Röntgen, in 1895. An electrically heated filament, usually tungsten, emits electrons, which are accelerated by a high potential difference (20–50 kV) and allowed to impinge on a metal target or anode which is water cooled (Figure 2.1a). The anode emits a continuous spectrum of ‘white’ X-radiation but superimposed on this are sharp, intense X-ray peaks (K_{α} , K_{β}) as shown in Figure 2.1b. The frequencies of the K_{α} and K_{β} lines are characteristic of the anode metal; the target metals most commonly used

¹ Many crystallographers still work in Ångströms, Å, – just multiply by 100 – 1 Å = 100 pm.

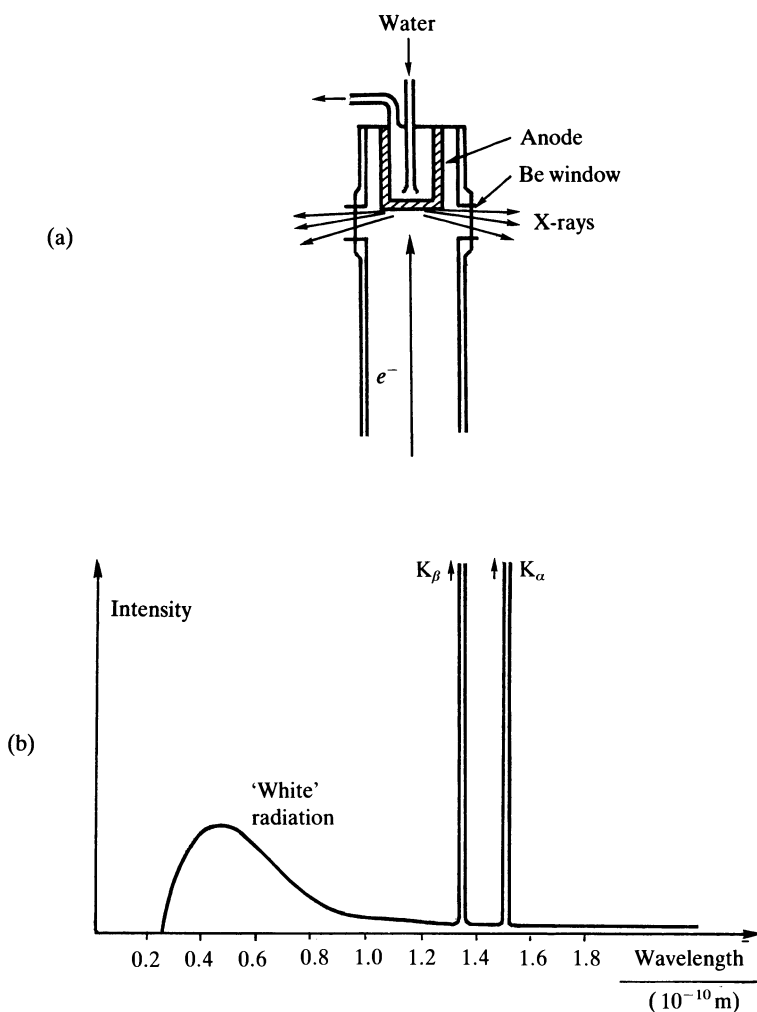


Figure 2.1 (a) Section through an X-ray tube. (b) An X-ray emission spectrum.

in X-ray crystallographic studies are copper and molybdenum, which have K_α lines at 154.18 pm and 71.07 pm respectively. These lines occur because the energy of the bombarding electrons is sufficient to knock out electrons from the innermost K shell ($n = 1$); this in turn creates vacancies which are filled by electrons descending from the shells above. The decrease in energy appears as radiation; electrons from the L shell ($n = 2$) give the K_α lines and electrons from the M shell ($n = 3$) give the K_β lines. (These lines are actually very closely spaced doublets – $K_{\alpha 1}$, $K_{\alpha 2}$ and $K_{\beta 1}$, $K_{\beta 2}$ – which are usually not resolved.) As the atomic number, Z , of the target increases, the lines shift to shorter wavelengths.

Normally in X-ray diffraction, monochromatic radiation (single wavelength or a very narrow range of wavelengths) is required. Usually the K_{α} line is selected and the K_{β} line is filtered out by using a filter made of a thin metal foil of the element adjacent ($Z - 1$) in the Periodic Table; thus nickel effectively filters out the K_{β} line of copper, and niobium is used for molybdenum. A monochromatic beam of X-rays can also be selected by reflecting the beam from a plane of a single crystal, normally graphite (the reasons why this works will become obvious after you have read the next section).

2.3 DIFFRACTION OF X-RAYS

By 1912 the nature of X-rays – whether they were particles or waves – was still unresolved; a demonstration of X-ray diffraction effects was needed to demonstrate their wave nature. This was eventually achieved by von Laue using a crystal of copper sulphate as the diffraction grating. Crystalline solids consist of regular arrays of atoms, ions or molecules with interatomic spacings of the order of 100 pm. For diffraction to take place, the wavelength of the incident light has to be of the same order of magnitude as the spacings of the grating. Because of the periodic nature of the internal structure, it is possible for crystals to act as a three-dimensional diffraction grating to light of a suitable wavelength: a Laue photograph is shown in Figure 2.2.

This discovery was immediately noted by W.H. and W.L. Bragg (father and son), and they started experiments on using X-ray crystal diffraction as a means of structure determination. In 1913 they first determined the crystal structure of NaCl, and they went on to determine many structures including those of KCl, ZnS, CaF₂, CaCO₃ and diamond. W.L. (Lawrence) Bragg noted that X-ray diffraction behaves like ‘reflection’ from the planes of atoms within the crystal and that only at specific orientations of the crystal with respect to the source and detector are X-rays ‘reflected’ from the planes. It is not like the reflection of light from a mirror, as this requires that the angle of incidence equals the angle of reflection and is possible for all angles. With X-ray diffraction the reflection only occurs when the conditions for constructive interference are fulfilled.

Figure 2.3 illustrates the Bragg condition for the reflection of X-rays by a crystal. The array of black points in the diagram represents a section through a crystal and the lines joining the dots mark a set of parallel planes with Miller indices hkl and interplanar spacing d_{hkl} . A parallel beam of monochromatic X-rays ADI (the green lines) is incident to the planes at an angle θ_{hkl} . The ray A is scattered by the atom at B and the ray D is scattered by the atom at F. For the reflected beams to emerge as

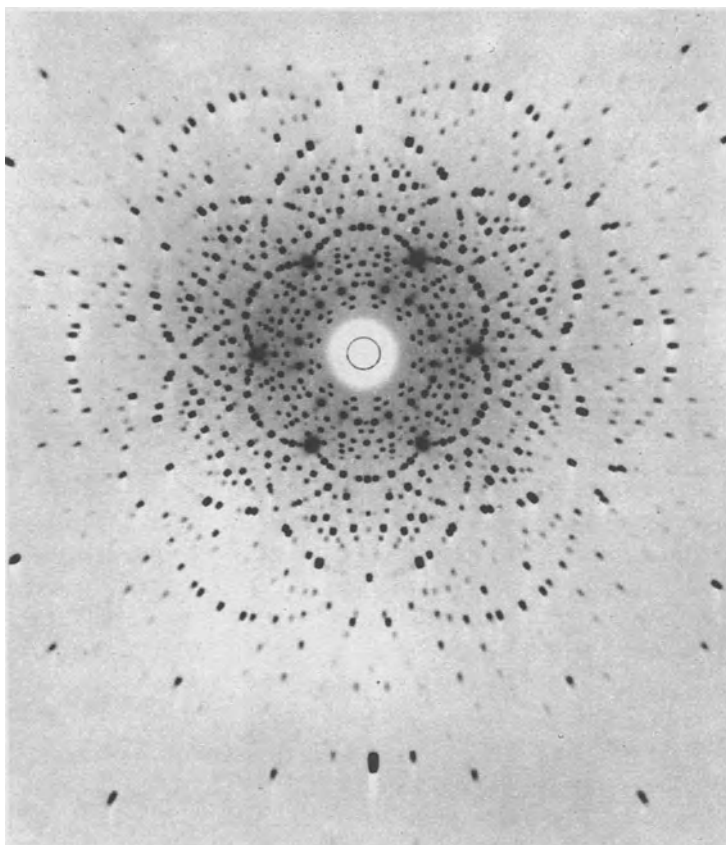


Figure 2.2 X-ray diffraction by a crystal of beryl using the Laue method. (From W.J. Moore (1972) *Physical Chemistry*, 5th edn, Longman. Reprinted courtesy of Eastman Kodak Company.)

a single beam of reasonable intensity, they must reinforce, or arrive in phase, with one another. This is known as constructive interference, and for constructive interference to take place, the path lengths of the interfering beams must differ by an integral number of wavelengths. To find the difference in path length between the two beams in Figure 2.3, ABC and DFH, we have drawn two lines at right-angles to the beam – BE and BG. The difference in path length between the two beams is therefore:

$$\text{difference in path length} = (DF + FH) - (AB + BC)$$

but $AB = DE$ and $BC = GH$, thus

$$\text{difference in path length} = EF + FG.$$

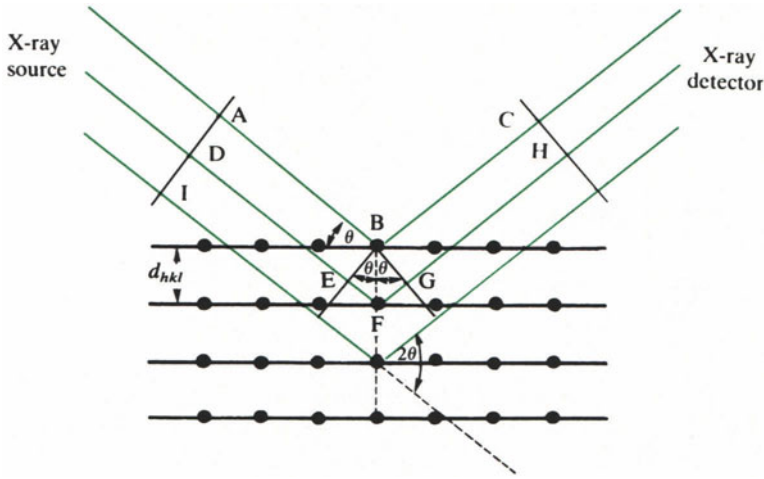


Figure 2.3 Bragg reflection from a set of crystal planes with a spacing d_{hkl} .

From Figure 2.3 it follows that

$$EF = FG = d_{hkl} \sin \theta_{hkl}$$

so that

$$\text{difference in path length} = 2d_{hkl} \sin \theta_{hkl}. \quad (2.1)$$

This must be equal to an integral number, n , of wavelengths. If the wavelength of the X-rays is λ , then

$$n\lambda = 2d_{hkl} \sin \theta_{hkl}. \quad (2.2)$$

This is known as the **Bragg equation**, and it relates the spacing between the crystal planes, d_{hkl} , to the particular Bragg angle, θ_{hkl} , at which reflections from these planes are observed (the subscript hkl can normally be dropped from the Bragg angle, θ , without any ambiguity as the angle is unique for each set of planes, and this will be the practice here).

When $n = 1$, the reflections are called first order, and when $n = 2$ the reflections are second order, and so on. However, the Bragg equation for a second order reflection from a set of planes hkl is

$$2\lambda = 2d_{hkl} \sin \theta, \text{ which can be rewritten as}$$

$$\lambda = 2 \frac{d_{hkl}}{2} \sin \theta. \quad (2.3)$$

Equation (2.3) represents a first order reflection from a set of planes with interplanar spacing $d_{hkl}/2$. The set of planes with interplanar spacing

$d_{hkl}/2$ has Miller indices $2h\ 2k\ 2l$. So, the second order reflection from hkl is indistinguishable from the first order reflection from $2h\ 2k\ 2l$, and the Bragg equation may be written more simply as

$$\lambda = 2d_{hkl} \sin \theta. \quad (2.4)$$

2.4 POWDER DIFFRACTION

2.4.1 Recording a powder diffraction pattern

A finely ground crystalline powder contains a very large number of small crystals, known as crystallites, which are oriented randomly to one another. If such a sample is placed in the path of a monochromatic X-ray beam, diffraction will occur from planes in those crystallites which happen to be oriented at the correct angle to fulfil the Bragg condition. The diffracted beams make an angle of 2θ with the incident beam. Because the crystallites can lie in all directions while still maintaining the Bragg condition, the reflections lie on the surface of cones whose *semi*-apex angles are equal to the deflection angle 2θ (Figure 2.4a). A flat film placed in front of the powder sample would record a photograph consisting of concentric

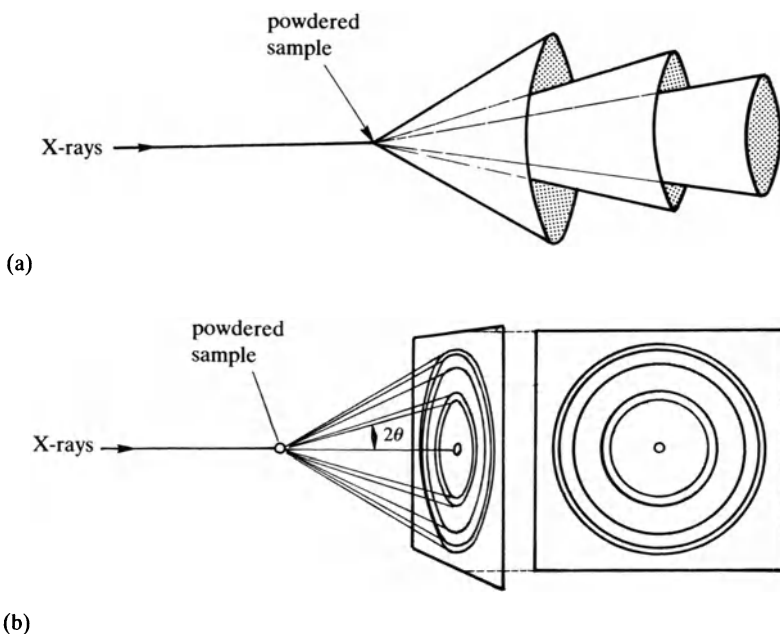


Figure 2.4 (a) Cones produced by a powder diffraction experiment. (b) producing a powder photograph.

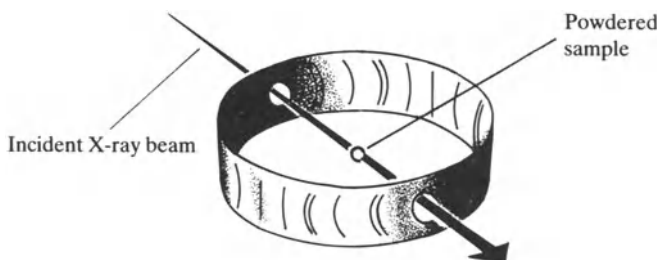
rings (Figure 2.4b). In practice this would severely restrict the maximum angle of 2θ that could be recorded, and so in the **Debye–Scherrer method** a strip of photographic film is wrapped around the inside of the X-ray camera (Figure 2.5a) with a hole to allow in the collimated incident beam and a beam-stop to absorb the undiffracted beam. The sample is rotated to bring as many planes as possible into the diffracting condition, and the cones are recorded as arcs on the film, which when uncoiled looks like Figure 2.5b. If we call the distance between the first pair of equivalent arcs y , we know from Figure 2.4 that they subtend an angle of 4θ at the sample. If the radius of the camera is R and the circumference of the film is $2\pi R$, then

$$\frac{y}{2\pi R} = \frac{4\theta}{360} \quad (2.5)$$

Knowing R , and measuring y for each cone, enables us to calculate the Bragg angle and thus the d_{hkl} spacing for each reflection.

Increasingly, the collection of powder diffraction patterns is performed by automatic diffractometers (Figure 2.6a) and film is not used: a detector records the intensity of the diffracted beams and these can be plotted out (Figure 2.6b).

The difficulty in the powder method lies in deciding which planes are responsible for each reflection: this is known as ‘indexing the reflections’, i.e. assigning the correct hkl index to each reflection. Although this is



(a)



(b)

Figure 2.5 (a) Experimental arrangement for Debye–Scherrer photograph. (b) An uncoiled Debye–Scherrer film of Ni powder. (Photograph kindly supplied by Dr Marten Barker.)

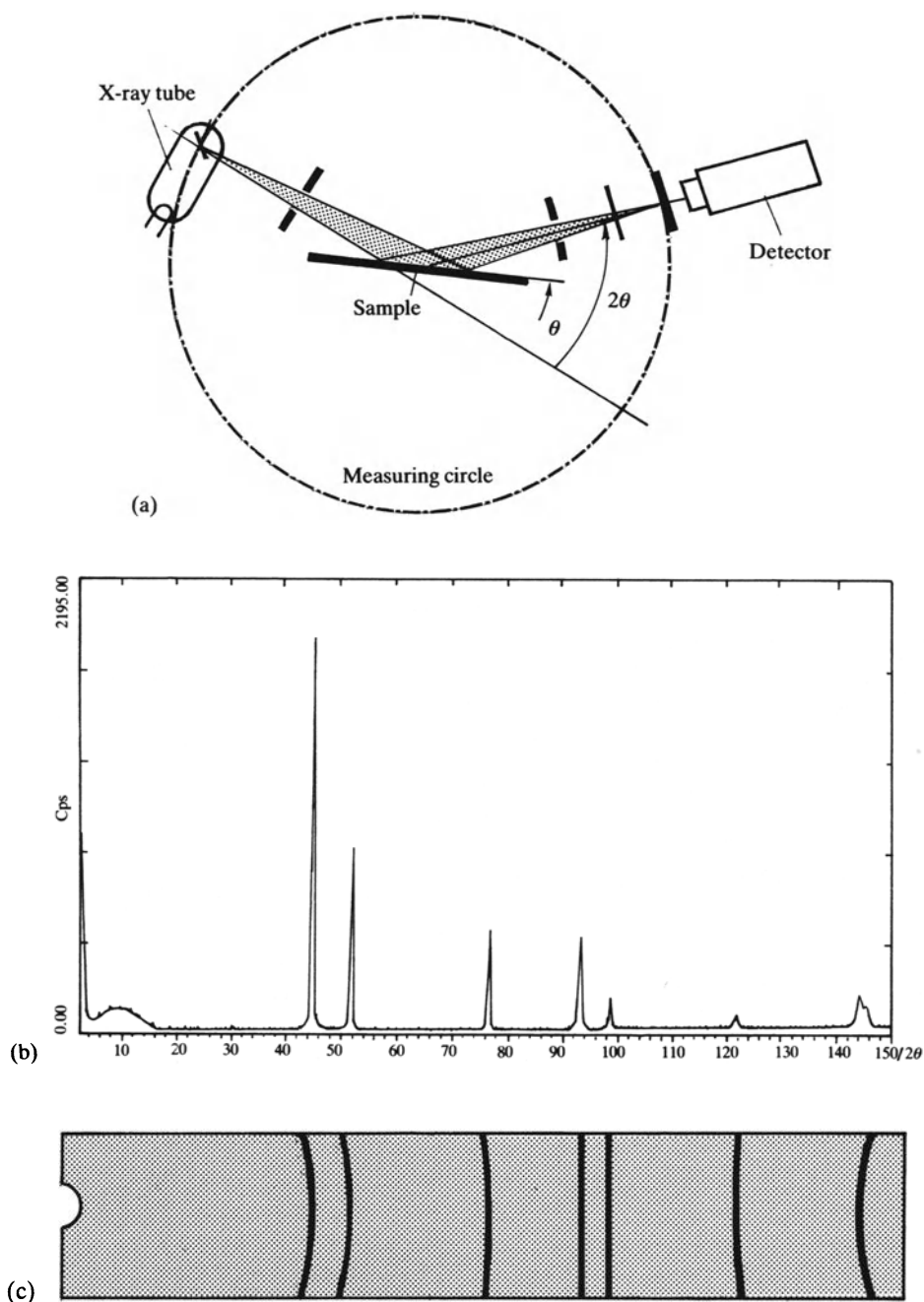


Figure 2.6 (a) Diagram of a powder diffractometer. (b) A diffractometer powder pattern for Ni powder compared with (c) the Debye-Scherrer photograph of Ni powder.

often possible for simple compounds in high symmetry systems (as we shall explain in section 2.4.3) it is extremely difficult to do for many larger and/or less symmetrical systems.

2.4.2 Absences due to lattice centring

First, we will consider a primitive cubic system. The reflection nearest the centre of a powder photograph has the smallest Bragg angle. It follows from equation (2.4) that the planes giving rise to this reflection will have the largest d_{hkl} spacing. In the primitive cubic system the 100 planes have the largest separation and thus give rise to this reflection, and as $a = b = c$ in a cubic system the 010 and the 001 also reflect at this position. For the cubic system, with a unit cell dimension a , the spacing of the reflecting planes is given by equation (2.5):

$$d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}. \quad (2.5)$$

Combining this with the Bragg equation gives

$$\lambda = \frac{2a \sin \theta_{hkl}}{(h^2 + k^2 + l^2)^{1/2}} \quad (2.6)$$

and rearranging gives

$$\sin^2 \theta_{hkl} = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2). \quad (2.7)$$

For the primitive cubic class all integral values of the indices h , k and l are possible. Table 2.1 shows the values of hkl in order of increasing value of $(h^2 + k^2 + l^2)$ and therefore of increasing $\sin \theta$ values. One value in the sequence, 7, is missing: this is because there are no possible integral values for $(h^2 + k^2 + l^2) = 7$. There are also other higher missing values where $(h^2 + k^2 + l^2)$ cannot be an integer: 15, 23, 28, etc., but note that this is only an arithmetical phenomenon and is nothing to do with the structure.

Taking equation (2.7), if we plot the intensity of diffraction of the powder pattern of a primitive cubic system against $\sin^2 \theta_{hkl}$ we would get six equispaced lines with the 7th, 15th, 23rd, etc. missing. Consequently it

Table 2.1 Values of $(h^2 + k^2 + l^2)$

hkl	100	110	111	200	210	211	220	300 = 221
$(h^2 + k^2 + l^2)$	1	2	3	4	5	6	8	9

is easy to identify a primitive cubic system and by inspection to assign indices to each of the reflections. The unit cell dimension a is equal to the spacing of the 100 planes.

The pattern of observed lines for the two other cubic crystal systems, body-centred and face-centred, is rather different from that of the primitive system. The differences arise because the centring leads to destructive interference for some reflections and these extra missing reflections are known as **systematic absences**.

Consider the 200 planes shown shaded in the F face-centred structure in Figure 2.7; they have a spacing $a/2$. Figure 2.8 shows the reflections from four consecutive planes in this structure. The reflection shown in colour is the 100 reflection – the in-phase reflection from the 100 planes. Between these planes the reflection from the 200 planes is exactly out of phase with the 100 reflection. Throughout the crystal there are equal numbers of the two types of planes with the result that complete destructive interference occurs and there is no 100 reflection. Examining reflections from all the planes for the F face-centred system in this way, we find that in order for a reflection to be observed, the indices must be either *all odd* or *all even*.

A similar procedure for the body-centred cubic system finds that for reflections to be observed the *sum of the indices must be even*.

It is possible to characterize the type of Bravais lattice present by the pattern of systematic absences. Although our discussion has centred on cubic crystals, these absences apply to all crystal systems, not only to cubic, and are summarized in Table 2.3.

We saw earlier that for a cubic crystal we could derive the relationship

$$\sin^2\theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2). \quad (2.7)$$

The possible values of $h^2 + k^2 + l^2$ are listed in Table 2.2 for each of the cubic lattices. Using these pieces of information we can see that if the observed $\sin^2\theta$ values for a pattern are in the ratio $1:2:3:4:5:6:8\dots$,

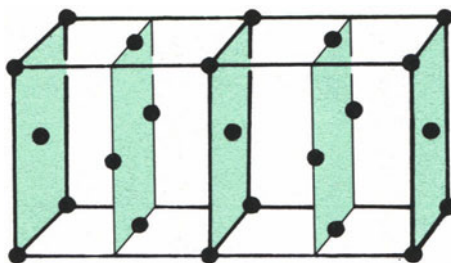


Figure 2.7 Two F-centred unit cells showing the 200 planes shaded.

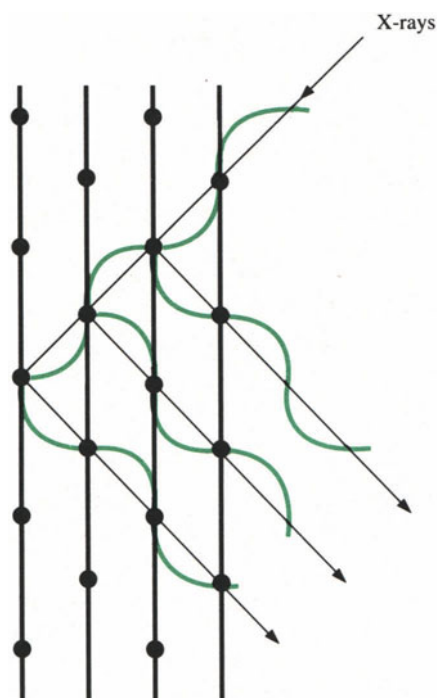


Figure 2.8 The 100 reflection from an F-centred cubic lattice.

Table 2.2 Some values of $h^2 + k^2 + l^2$ for cubic crystals

<i>Forbidden numbers</i>	<i>Primitive, P</i>	<i>Face-centred, F</i>	<i>Body-centred, I</i>	<i>Corresponding hkl values</i>
7	1			100
	2		2	110
	3	3		111
	4	4	4	200
	5			210
	6		6	211
	7			—
15	8	8	8	220
	9			$221, 300$
	10		10	310
	11	11		311
	12	12	12	222
	13			320
	14		14	321
15	15			—
	16	16	16	400

then the unit cell is likely to be primitive cubic, and the common factor is $\lambda/4a^2$.

A face-centred cubic unit cell can also be recognized: if the first two lines have a common factor, A , then dividing all the observed $\sin^2\theta$ values by A gives a series of numbers, 3, 4, 8, 11, 12, 16 . . . , and A is equal to $\lambda/4a^2$.

A body-centred cubic system gives the values of $\sin^2\theta$ in the ratio 1:2:3:4:5:6:7:8 . . . with the values 7 and 15 apparently *not* missing, but now the common factor is $2\lambda^2/4a^2$.

2.4.3 Systematic absences due to screw axes and glide planes

In Chapter 1 we saw two special types of symmetry element that both involve translation – the screw axis and the glide plane. The presence of these symmetry elements in a crystal structure can be detected because they also each lead to a set of systematic absences in the hkl reflections. Figure 2.9 shows a part of a unit cell of a crystal with a twofold screw (2_1) along z . The effect is to introduce a plane of atoms exactly halfway between the $00l$ planes: reflections from these planes will destructively interfere with reflections from the $00l$ planes and the $00l$ reflection will be absent – indeed any reflection for which l is odd will be absent. Similar arguments apply to higher order axes and the results are summarized in Table 2.3.

The effect of a glide plane is effectively to halve the unit cell length in the direction of the glide. Figure 2.10 shows an a glide perpendicular to b and inspection shows the repetition along a : thus the $10l$ reflections will

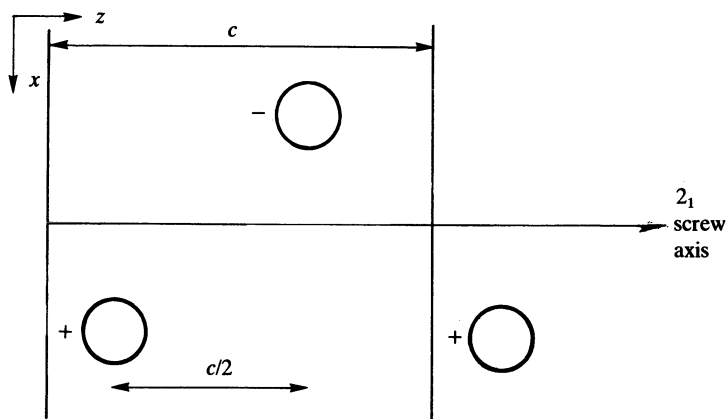
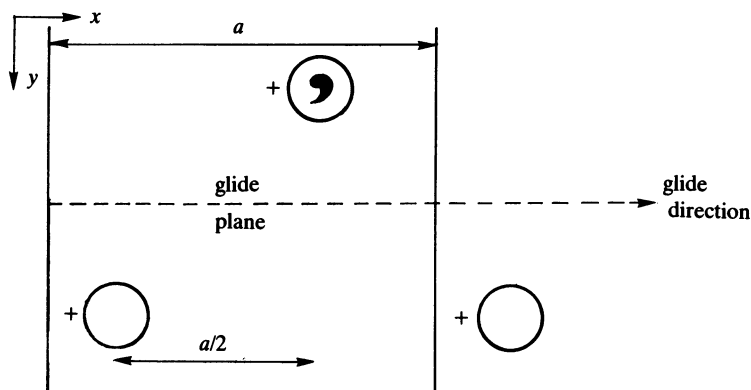


Figure 2.9 A 2_1 screw axis along c .

Table 2.3 Systematic absences due to translational symmetry elements

<i>Symmetry element</i>		<i>Affected reflection</i>	<i>Condition for reflection to be present</i>
Primitive lattice	P	hkl	none
Body-centred lattice	I	hkl	$h + k + l = \text{even}$
Face-centred lattice	A	hkl	$k + l = \text{even}$
	B		$h + l = \text{even}$
	C		$h + k = \text{even}$
Face-centred lattice	F		$h\ k\ l$ all odd or all even
Twofold screw, 2_1 along			
Fourfold screw, 4_2 along	a	$h00$	$h = \text{even}$
Sixfold screw, 6_3 along			
Threefold screw, $3_1, 3_2$ along	c	$00l$	l divisible by 3
Sixfold screw, $6_2, 6_4$ along			
Fourfold screw, $4_1, 4_3$ along	a	$h00$	h divisible by 4
Sixfold screw, $6_1, 6_5$ along	c	$00l$	l divisible by 6
Glide plane perpendicular to b			
translation $\frac{a}{2}$ (a glide)			$h = \text{even}$
translation $\frac{c}{2}$ (c glide)		$h0l$	$l = \text{even}$
$\frac{b}{2} + \frac{c}{2}$ (n glide)			$h + l = \text{even}$
$\frac{b}{4} + \frac{c}{4}$ (d glide)			$h + l$ divisible by 4

**Figure 2.10** An a glide perpendicular to b .

be absent, and in general the $h0l$ reflections will only be present when h is even. Some glide plane absences are summarized in Table 2.3.

There are now fairly powerful computer programmes for indexing in existence, and powder diffraction patterns can be indexed fairly readily for the high symmetry crystal classes such as cubic, tetragonal and hexagonal. For the other systems, the pattern often consists of a large number of overlapping lines, and indexing can be much more difficult or even impossible.

More recently, new methods have been developed for solving crystal structures from powder diffraction data, notably **Rietveld analysis**. The Rietveld method involves an interpretation of not only the line position but also of the line intensities, and because there is so much overlap of the reflections in the powder patterns, the method developed by Rietveld involves analysing the overall line profiles. The method was originally developed for neutron diffraction, and we discuss it further in section 2.9.1.

2.4.4 The number of molecules in a unit cell, Z

Once the reflections in a powder pattern have been indexed, it is possible to calculate the unit cell dimensions. In the case of a cubic crystal we use equation (2.7):

$$\sin^2\theta_{hkl} = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2) \quad (2.7)$$

and from a we can calculate the volume of the unit cell, V . If the density, ρ , of the crystals are known, the mass of the unit cell, M , can also be calculated:

$$\rho = \frac{M}{V}. \quad (2.8)$$

From a knowledge of the molecular mass, the number of molecules, Z , in the unit cell can be calculated. Examples of this kind of calculation are to be found in Questions 2.7–2.10.

The density of crystals can be determined by preparing a mixture of liquids (in which the crystals are insoluble!) such that the crystals neither float nor sink: the crystals then have the same density as the liquid. The density of the liquid can then be determined using a density bottle.

2.4.5 Identification of compounds using powder diffraction

Powder diffraction is difficult to use as a method of determining crystal structures for anything other than simple high-symmetry crystals because

as the structures become more complex the number of lines increases so that overlap becomes a serious problem and it is difficult to index and measure the intensities of the reflections. Accordingly, it is mostly used as a finger-print method for detecting the presence of a known compound or phase in a product. This is made possible by the existence of a huge library of powder diffraction patterns which is regularly updated, known as the JCPDS (Joint Committee for Powder Diffraction Standards) files. When the powder diffraction pattern of your sample has been measured and both the d_{hkl} spacings and intensity of the lines recorded, these can be matched against the patterns of known compounds in the files. With modern diffractometers, the JCPDS files are usually accessible from disc or CD-ROM to the computer which stores the experimentally recorded patterns; the computer can then match the recorded pattern to the ones already on file.

The identification of compounds using powder diffraction can be useful for the qualitative analysis of a product and as rough check of its purity, but powder diffraction will not detect amorphous products, or impurities of less than about 5%.

Powder diffraction can be used where mixtures of small crystals are present, such as in geological samples. It is also a useful method for determining phase diagrams as, by a careful comparison of the intensities of particular lines in standards, not only can the different phases be identified but also the proportions of different phases can be determined.

Powder diffraction can confirm whether two similar compounds, where one metal substitutes for another for instance, give an isomorphous structure.

In favourable cases the Rietveld method can be used to solve a structure from the powder diffraction data. The method works best if a good trial structure is already known, for instance if the unknown structure is a slight modification of a known structure, with perhaps one metal changed for another.

2.4.6 The importance of intensities

So far we have only discussed the effects of using crystals as three-dimensional diffraction gratings for X-rays. But you may have wondered why one goes to all this trouble. If we want to magnify an object to see its structure in more detail then why not use a lens system as in a microscope or a camera? Here a lens system focuses the light which is scattered from an object (which if left alone would form a diffraction pattern) and forms an image. Why not use a lens to focus X-rays and avoid all the complications? The problem is that there is no suitable way in which X-rays can be focused, and so the effect of the lens has to be simulated by a mathematical calculation on the information contained in the diffracted

beams. Much of this information is contained in the intensity of each beam but, as always, there is a snag! The recording methods do not record *all* of the information in the beam because they only record the intensity and are insensitive to the *phase*. Intensity is proportional to the square of the amplitude of the wave, and the phase information is lost. Unfortunately, it is this information which derives from the atomic positions in a structure. When light is focused by a lens this information is retained.

So far we have seen that if we measure the Bragg angle of the reflections and successfully index them, we get information on the size of the unit cell and, if it possesses any translational symmetry elements, also on the symmetry. In addition, we have seen that the intensity of each reflection is different and this too can be measured. In early photographic work the relative intensities of the spots on the film were assessed by eye with reference to a standard, and later a scanning microdensitometer was used. In modern diffractometers the beam is intercepted by a photo-detector, usually a scintillation counter, and the intensity of each reflection is recorded electronically.

The interaction which takes place between X-rays and a crystal involves the electrons in the crystal: the more electrons an atom possesses, the more strongly will it scatter the X-rays. The effectiveness of an atom in scattering X-rays is called the **scattering factor**, and is given the symbol f_0 . The scattering factor depends not only on the atomic number, but also on the Bragg angle, θ , and the wavelength of the X-radiation: as the Bragg angle increases the scattering power drops off. Figure 2.11 depicts some typical curves. The decrease in scattering power with angle is due to the finite size of an atom; the electrons are distributed around the nucleus and as θ increases, the X-rays scattered by an electron in one part of the atom are increasingly out of phase with those scattered in a different part of the electron cloud.

It is probably instructive here to show an example of why intensities are important. We know that the heavier an atom is, the better it is at scattering X-rays. On the face of it then we might think that the planes containing the heavier atoms will give the more intense reflections. While this is true, the overall picture is more complicated because there are interactions with the reflected beams from other planes to take account of, and these may produce destructive interference. We can illustrate this effect by considering the diffraction patterns produced by NaCl and KCl crystals. The NaCl crystal unit cell is shown in Figure 2.12; KCl has the same structure, and the structure was discussed in detail in Chapter 1, p. 30. The structure can be thought of as two interlocking *ccp* arrays of Na^+ and Cl^- ions. The unit cell shown in the figure has close-packed layers of Cl^- ions which lie parallel to a body diagonal, with indices *111* (shown shaded in Figure 2.12). In the figure drawn here, the *111* planes contain

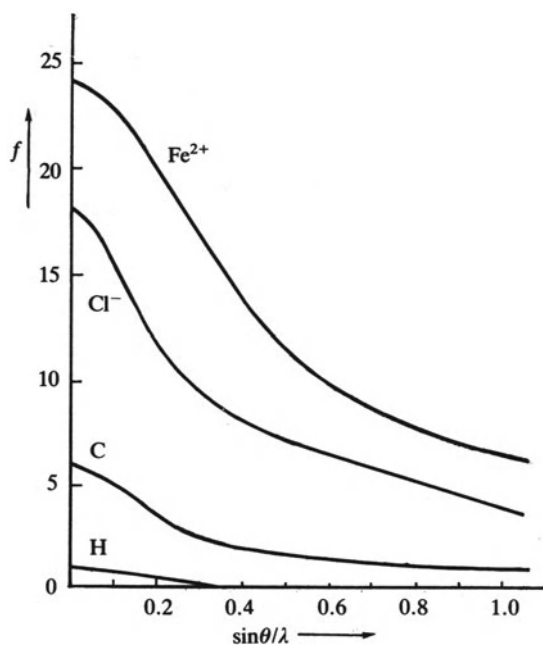


Figure 2.11 Scattering factors for hydrogen, carbon, chloride and ferrous ion, as a function of $\sin \theta / \lambda$.

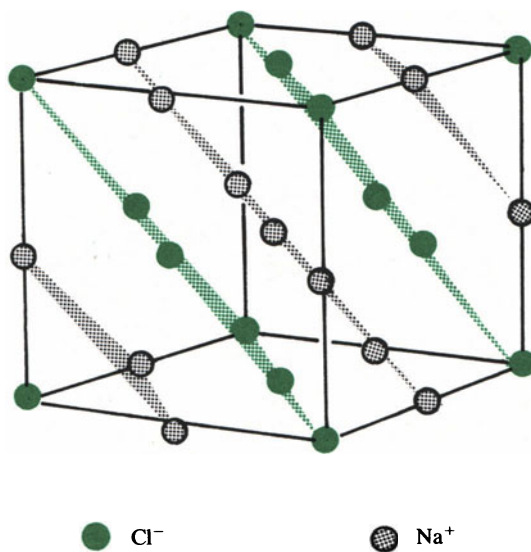


Figure 2.12 NaCl unit cell showing the close-packed III planes shaded in green.

only Cl^- ions. Lying exactly halfway between the 111 layers, and parallel to them, are close-packed layers of Na^+ ions; this means that a reflection from the Cl^- close-packed layers is exactly out-of-phase with that from the equivalent Na^+ layers. Because a chloride ion has 18 electrons and a sodium ion 10 electrons the reflections partially cancel and the intensity of the 111 reflection will be fairly weak. (Note that we could have drawn our NaCl unit cell with a different origin, such that the Na^+ ions were at the corners of the unit cell and the 111 planes contained only Na^+ ions; now the destructive interference is caused by intervening Cl^- ions, but the end result is the same.) The 222 layers contain the close-packed layers of both Na^+ and Cl^- , and this will be a strong reflection because the reflected waves will now reinforce one another. When we come to look at the equivalent situation in KCl , the reflection from the 111 layers containing K^+ ions is exactly out-of-phase with the reflection from the Cl^- close-packed layers. But K^+ and Cl^- are isoelectronic, and so their scattering factors for X-rays are virtually identical. The net effect is that the two reflections cancel and the 111 reflection appears to be absent. This means that the first observed reflection in the diffraction pattern from KCl is the 200 and it would be very easy to make the mistake that this was the 100 reflection from a primitive cubic cell with unit cell length half that of the real face-centred cell.

The resultant of the waves scattered by all the atoms in the unit cell, in the direction of the hkl reflection, is called the **structure factor**, F_{hkl} , and is dependent on both the position of each atom and its scattering factor. It is given by the general expression for j atoms in a unit cell

$$F_{hkl} = \sum_j f_j e^{2\pi i(hx_j + ky_j + lz_j)} \quad (2.9)$$

where f_j is the scattering factor of the j th atom and x_j y_j z_j are its fractional coordinates. Series such as this can also be expressed in terms of sines and cosines, more obviously reflecting the periodic nature of the wave; they are known as **Fourier series**. In a crystal which has a centre of symmetry and n unique atoms in the unit cell (the unique set of atoms is known as the **asymmetric unit**) the expression in equation (2.9) simplifies to

$$F_{hkl} = 2 \sum_n f_n \cos 2\pi(hx_n + ky_n + lz_n). \quad (2.10)$$

The electron density distribution within a crystal can be expressed in a similar way as a three-dimensional Fourier series:

$$\rho(x, y, z) = \frac{1}{V} \sum_h \sum_k \sum_l F_{hkl} e^{-2\pi i(hx + ky + lz)} \quad (2.11)$$

where $\rho(x, y, z)$ is the electron density at a position x, y, z in the unit cell and V is the volume of the unit cell. Notice the similarity between the expressions in equations (2.9) and (2.11). In mathematical terms the electron density is said to be the **Fourier transform** of the structure factors and vice versa. This relationship means that if the structure factors are known, it is possible to calculate the electron density distribution in the unit cell, and thus the atomic positions.

The intensities of the hkl reflections, I_{hkl} , are measured as described above and form the data set for a particular crystal. The intensity of a reflection is proportional to the square of the structure factor:

$$I_{hkl} \propto F_{hkl}^2. \quad (2.12)$$

Taking the square root of the intensity gives a value for the *magnitude* of the structure factor (mathematically, this is known as the *modulus* of the structure factor, denoted by the vertical bars either side):

$$|F_{hkl}| \propto \sqrt{I_{hkl}}. \quad (2.13)$$

Before this information can be used, the data set has to undergo some routine corrections; this process is known as **data reduction**. The two corrections made at this stage are the **Lorentz correction**, L , which relates to the geometry of the collection mode, and the **polarization correction**, p , which allows for the fact that the non-polarized X-ray beam may become partly polarized on reflection.

$$|F_{hkl}| = \sqrt{\frac{KI_{hkl}}{Lp}}, \quad (2.14)$$

where K is a scaling factor.

An **absorption correction** is also often applied to the data, particularly for inorganic structures, because the heavier atoms absorb some of the X-ray beam, rather than just scatter it. As the pathlength of the beam through the crystal is different for each reflection (except in the special case of a spherical crystal) so will the absorption of the X-ray beam affect some reflections more than others. If the shape, size and orientation of the crystal is known precisely, it is possible to work out a pathlength and thence a correction for each reflection; alternatively there are some empirical techniques available for modelling the crystal shape and making the appropriate correction.

Corrections can also be made for **anomalous dispersion** which affects the scattering power of an atom when the wavelength of the incident X-ray is close to its absorption edge. These corrections are applied to the scattering factor, f_0 , of the atom.

The structure factor (and thus the intensity of a reflection) is dependent on both the position of each atom and its scattering factor. The structure factor can be *calculated*, therefore, from a knowledge of the types of

atoms and their positions using equations such as (2.9) and (2.10). It is the great problem of X-ray crystallography that we need to be able to do the reverse of this calculation – we have the measured magnitudes of the structure factors, and from them we want to calculate the atomic positions. But there is the snag, which we mentioned earlier, known as **the phase problem**. When we take the square root of the intensity we only obtain the modulus of the structure factor, and so we only know its magnitude and not its sign. The phase information is unfortunately lost and we need it in order to calculate the electron density distribution and thus the atomic positions.

On the face of it then, it looks like an unresolvable problem – to calculate the structure factors we need the atomic positions and to get the atomic positions we need both the amplitude and the phase of the resultant waves, and we only have the amplitude. Fortunately, many scientists over the years have worked at finding ways around this problem, and have been extremely successful, to the extent that for many systems the solving of the structure has become a routine and fast procedure. We will look at some of these methods in section 2.6, but before that we need to know a little more about diffraction from single crystals.

2.5 SINGLE CRYSTAL X-RAY DIFFRACTION

Diffraction patterns can be collected from one single crystal instead of the many thousands of randomly oriented crystals which are found in a powder. From a single crystal it is possible to measure the position and intensity of the hkl reflections accurately and from this data determine not only the space group of the crystal but also the precise atomic positions. In most cases this can be done with speed and accuracy, and it is one of the most powerful structural techniques available to a chemist.

Single crystal X-ray diffraction data is nowadays collected using a computer-controlled diffractometer, which measures the Bragg angle, θ , and the intensity, I , for each hkl reflection. Not many years ago these data were collected photographically, and although this method is now rarely used, it is instructive to look at some of the photographs because it is just these same reflections that are now being collected and measured by an automatic diffractometer.

If a single crystal is mounted vertically so that it can be rotated about one of the crystallographic axes then the diffraction from each plane will lie on the surface of a set of cones, as described before (Figure 2.13a). Rotating the crystal brings each plane into the diffracting condition, and the reflections can be recorded on a film that is wrapped around the rotating crystal (Figure 2.13b and 2.13d). Such photographs are called **rotation** or (if the angle of rotation is restricted) **oscillation** photographs.

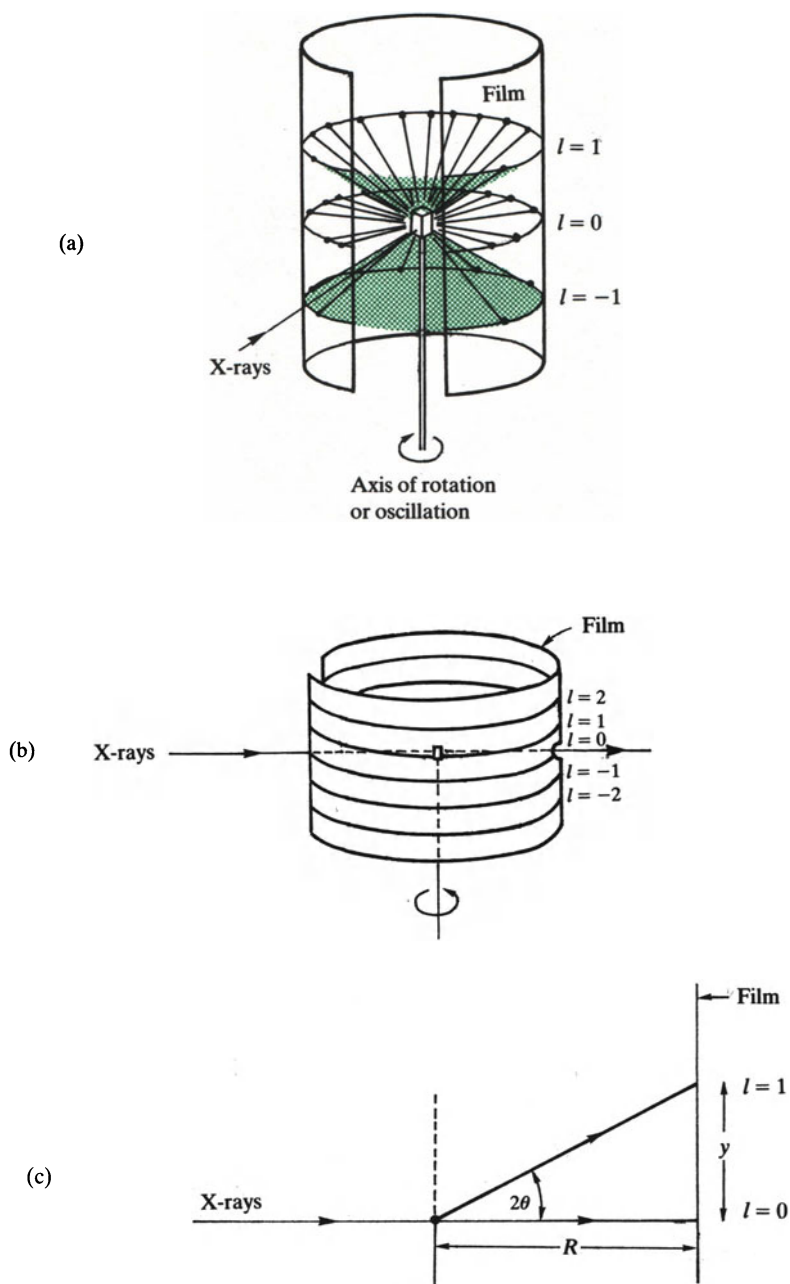
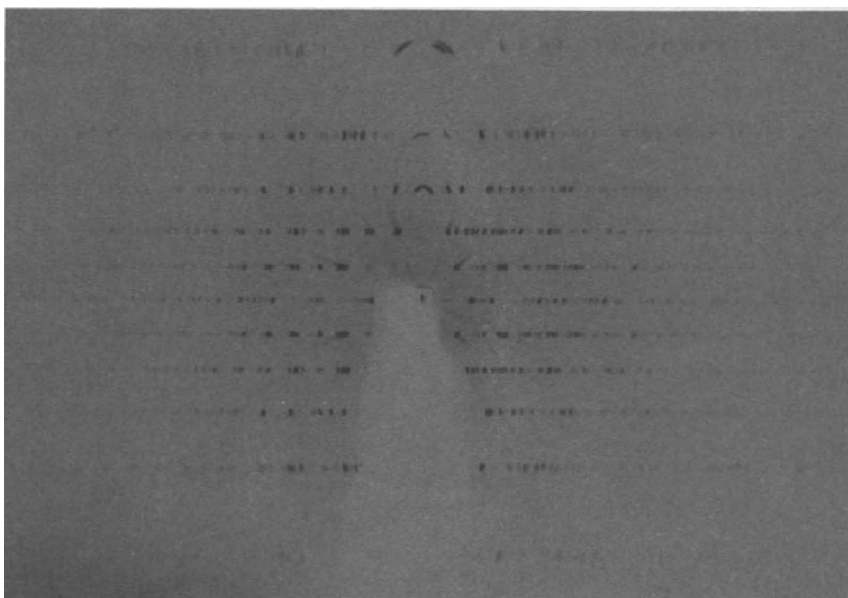


Figure 2.13 (a) Cones of diffracted rays produced by a single crystal. (b) Layer lines produced by the intersection of the cones with a cylindrical film. (c) Calculating the unit cell dimension of the mounted axis.



(d)

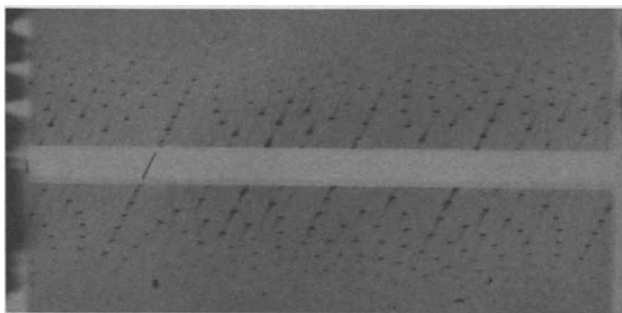
Figure 2.13 Continued (d) A single crystal rotation photograph.

If the crystal is mounted about the z axis, then the separation of the planes in that direction depends only on c , and all the reflections on the zero layer have $l = 0$, and on the first layer, $l = 1$, and so on. The c dimension can also be calculated: if the distance between the zero and first layer is y , and the radius of the camera is R , then

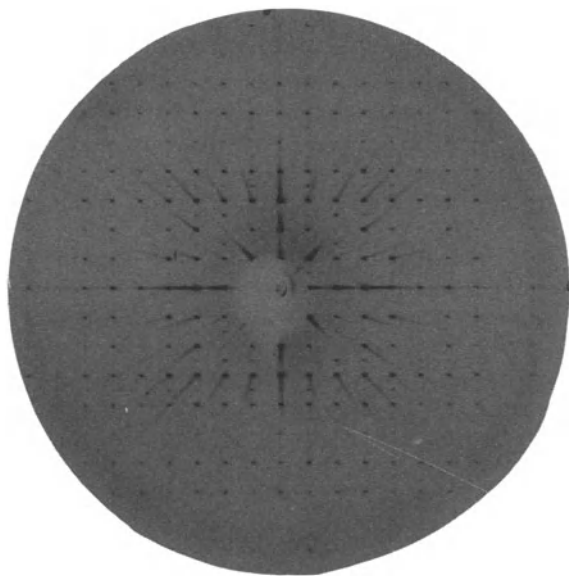
$$\tan 2\theta = \frac{y}{R}. \quad (2.15)$$

θ can thus be calculated and used in the Bragg equation (2.4).

As you can see from Figure 2.13d, the reflections still overlap considerably, and there are two methods of separating them; the first is to translate the camera parallel to the rotation axis as the crystal rotates, this produces a **Weissenberg** photograph; the second is to use a **precession** technique. Examples of both types of photograph are shown in Figure 2.14. From these photographs it is possible to measure the two other unit cell dimensions and the unit cell angles. It is now an easy job to index each reflection and, from the systematic absences observed, determine both the Bravais lattice and the translational symmetry elements present; the combination of this symmetry information often pinpoints the space group unequivocally or narrows the possibilities down to a choice of two or three.



(a)



(b)

Figure 2.14 (a) A Weissenberg photograph. (b) A precession photograph.

The final job is to measure the intensity of each reflection and this then provides all the data necessary to solve the crystal structure. Measuring the intensities of the reflections from film is not easy and although methods were developed which gave good results for many years, they are tedious and less accurate than modern methods and no longer used. Intensities are always collected now using some kind of automatic diffractometer.

A modern automatic four-circle diffractometer collects the intensities of all the reflections by driving the detector into the correct Bragg position. The machine is named after the four arcs which permit relative movement of the crystal and the detector – the X-ray tube does not move because of all its electrical and water cooling connections, and so the beam comes from a fixed direction (Figure 2.15). The crystal can move on the ϕ and χ and ω circles and the detector on the 2θ circle. A single crystal can be set in any orientation, and from a knowledge of the unit cell size and shape (the unit cell parameters are either determined *in situ* or by the photographic methods discussed above) the diffractometer calculates the position in space of all the hkl reflections, defining each position using the four angles. The diffractometer then drives the crystal and detector to bring each set of planes into the reflecting position in turn and measures the intensity by scanning the detector across the reflection: the data is then stored on a computer. Typical data sets consist of a few thousand reflections and can be collected in a day or two. Most

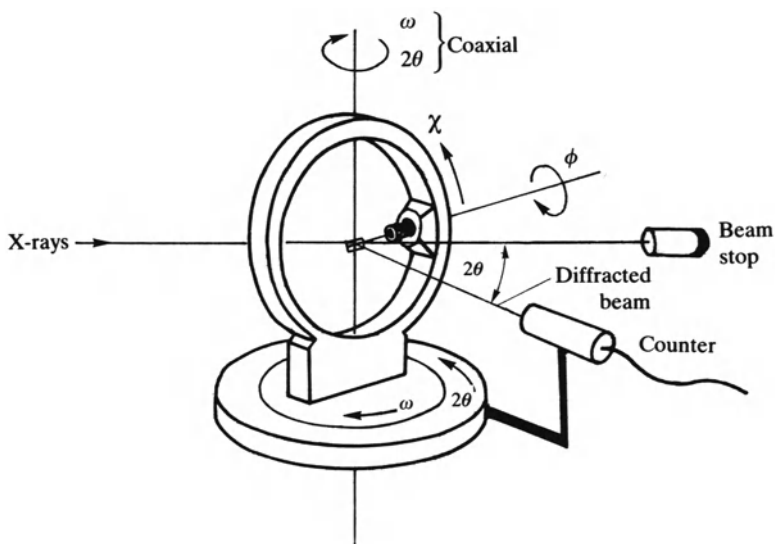


Figure 2.15 Schematic diagram of a four-circle diffractometer.

crystallographic laboratories are currently equipped with four-circle diffractometers.

A new generation of X-ray diffractometers is now (1995) becoming available; these are using various types of 'area detector', so that many reflections can be collected at the same time. This is a system that has been employed by protein crystallographers for some time. There are various systems available on the market, one of which is the imaging plate detector diffractometer. The basic principle behind this system is the use of an automated oscillation camera that diffracts on to a flat plate. The imaging plate employs reusable film, and an integral scanner determines the diffracted intensities. The plate uses a europium-doped barium halide, BaFBr(Eu²⁺), to record the diffracted beams. When X-rays strike the plate Eu²⁺ is oxidized to Eu³⁺ together with a trapped electron forming a colour centre (section 5.6). The plate is scanned by a He-Ne laser which causes the trapped electron to reduce the Eu³⁺ back to Eu²⁺, at the same time releasing radiation: this luminescence can be detected and measured by a photomultiplier. This process only takes a few minutes and a whole data set can be collected in a matter of hours. Another modern diffractometer employs a charge-coupled device (CCD) to record the diffracted intensities. Again, the machine employs a flat-plate detector, so that many reflections can be collected and measured at the same time, but the X-ray intensities here are measured electronically using a scientific grade CCD chip similar to that used in video cameras, and transmitted via a fibreoptics connection. Again, a full data set can be collected in hours rather than days.

2.6 SOLVING SINGLE CRYSTAL STRUCTURES

First, we'll summarize what we have said so far.

- The size and shape of the unit cell is determined. This can be done using the single crystal photographic techniques we have described, but more commonly these days crystallographers can find this information more quickly from rotation photographs and scanning routines directly on the diffractometer.
- The reflections can be indexed, and from the systematic absences the Bravais lattice and the translational symmetry elements of the structure can be determined: this information often determines the space group unequivocally, but even if it doesn't, it usually narrows the possibilities down to a choice of two or three.
- The intensities of the indexed reflections are measured and stored as a data file.
- The intensity data are corrected for geometric and polarization effects.

- Finally, the square roots of the corrected data are taken to give a set of observed structure factor moduli. These are known as F_{obs} or F_o .
- In order to calculate the electron density distribution in the unit cell, we need to know not only the magnitudes of the structure factors but also their phase.

Crystal structures are solved by creating a set of trial phases for the structure factors. There are two main methods for doing this. The first is known as the **Patterson** method, and relies on the presence of at least one, but not many, heavy atoms in the unit cell and so is useful for solving structures of organometallic compounds, for instance. The second way is to use so-called **direct methods** and this is used when there are no heavy atoms in the cell and is useful, for example, in solving the structures of organic, biological and cluster compounds.

2.6.1 Patterson maps

Patterson pointed out that a Fourier synthesis using F_{hkl} values as the coefficients produces a three-dimensional electron density map (equation (2.11)), but that a similar Fourier synthesis using $|F_{hkl}|^2$ as the coefficients has peaks corresponding to all the interatomic vectors:

$$P(u, v, w) = \frac{1}{V} \sum_h \sum_k \sum_l |F_{hkl}|^2 \cos 2\pi(hu + kv + lw). \quad (2.16)$$

So, in the Patterson method a synthesis is performed on the data set, from which a three-dimensional map of the unit cell is calculated from values of $P(u, v, w)$, not directly of the electron density in the unit cell (unfortunately!) but such that the values of $P(u, v, w)$ correspond to the *vectors* between all pairs of atoms in the cell. Figure 2.16 shows a simple example of how this can work. The diagram shows a projection of a

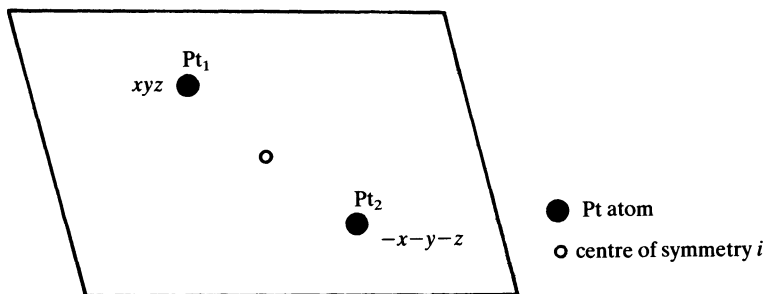


Figure 2.16 Projection of a unit cell containing two platinum atoms related by a centre of symmetry.

centrosymmetric triclinic unit cell, which contains two platinum atoms, Pt₁ and Pt₂ (the other atoms are not shown). Their atomic coordinates are x, y, z and $-x, -y, -z$ respectively, and are related by the centre of symmetry. The direction of the *vector* between these two atoms is $u, v, w = [(x, y, z) - (-x, -y, -z)] = 2x, 2y, 2z$. This vector appears in the Patterson map, and from it we can calculate the positions of the two Pt atoms very easily – simply by dividing by two!

How do we know which peak in the Patterson map belongs to these two atoms – because of course all the vectors for all the pairs of atoms are present? The reason why the Patterson method works so well for heavy atoms is that the size of the vector is proportional to the product of the atomic numbers of the atoms concerned. Thus, in a structure containing platinum and carbon atoms for instance, the height of the Pt–Pt vector is proportional to $(78 \times 78) = 6084$, that of a Pt–C vector is proportional to $(78 \times 6) = 468$, and that of a C–C vector $(6 \times 6) = 36$. So we can see that the Pt – Pt peak stands out head and shoulders above the rest. (You will find a couple of Patterson problems at the end of the chapter – Questions 13 and 14 – notice how much more difficult the problem becomes as the numbers of atoms increases.)

The heavy atoms in a structure determine most of the phases, and so once they have been located these phases can be used to calculate a preliminary electron density map, and this usually then shows the positions of the other lighter atoms in the unit cell.

2.6.2 Direct methods

Direct methods are used when all the atoms in the molecule have similar scattering power. Direct methods use the facts that the electron density in a structure cannot take any value but must always be positive, and that the structure consists of discrete spherically symmetric atoms, to calculate mathematical probabilities for the phase values and thus to calculate an electron density map of the unit cell. Theoreticians have worked on the mathematics of these methods for many years and have produced accessible computer programs that employ them – two of the best known are MULTAN and SHELX.

2.6.3 Difference maps

Once some of the atomic positions in the structure have been located by one of the methods it is then possible to *calculate* the structure factors, and this gives a set of values known as F_{calc} or F_c . A difference synthesis or difference Fourier compares the values of F_o and F_c by calculating a function where the coefficients are $\Delta F = |F_o| - |F_c|$:

$$\Delta\rho(x, y, z) = \frac{1}{V} \sum_h \sum_k \sum_l \Delta F e^{-2\pi i(hx + ky + lz)}. \quad (2.17)$$

This produces an extremely useful three-dimensional map because it effectively subtracts out the atoms that have been located and plots the remaining electron density in the unit cell, thereby enabling the crystallographer to find the positions of the other atoms. As the structure is solved and more and more atoms are located the difference map shows less and less remaining electron density and so gets flatter and flatter. In these later stages, with a good data set, it is often possible to locate hydrogen atoms. When all the atoms have been located the difference map should of course be completely flat, and this is one of the tests of whether a structure has been correctly solved.

2.7 REFINING A STRUCTURE

Once all the atoms in a structure have been located, the final part of the process is to **refine** it, i.e. get it as accurate as possible. The positions of the atoms are refined using **least-squares methods**, for which standard computer programs are available; these procedures allow systematic variation of the atomic positions until the best agreement between the calculated and observed structure factors, F_c , and F_o , is achieved. (It is often not possible to refine hydrogen atom positions, and in this case they are left fixed in sensible calculated positions, based on known geometries and bond lengths.)

Also at this stage, the electron density around each nucleus may be allowed to become non-spherical; this allows for the fact that atoms are not stationary, but vibrate about their equilibrium positions. Other corrections may also be made to the data.

A final residual index, the **R factor**, is computed for the structure, which gives an overall measure of how correct the structure is.

2.7.1 Displacement parameters

When we looked at the scattering power of an atom earlier, we saw that the scattering factor, f_0 , falls off with $\sin \theta / \lambda$ due to the finite size of the atom. The plots that we showed in Figure 2.11 assumed that the atoms were stationary. In practice atoms vibrate about their equilibrium positions; this is often called **thermal motion**, although it depends not only on the temperature but also on the mass of the atom and the strengths of the bonds holding it. The higher the temperature, the bigger the amplitude of vibration and the electron density becomes spread out over a larger volume, thus causing the scattering power of the atom to fall off more quickly. The scattering factor can be corrected for this effect:

$$f = f_0 e^{-B(\sin 2\theta)/\lambda^2} \quad (2.18)$$

where $e^{-B(\sin 2\theta)/\lambda^2}$ is the correction factor and B is an adjustable parameter known as the **isotropic displacement parameter** (also called the **isotropic temperature factor**). This correction allows the electron density of each atom to be refined in a sphere around the nucleus.

The ultimate refinement for thermal motion is to allow the electron density of each atom to lie within an ellipsoid around its nucleus, when an **anisotropic displacement parameter** correction is applied which has six adjustable parameters.

2.7.2 The R factor

The residual index, R , gives a measure of the difference between the observed and calculated structure factors and therefore of how well the structure has been refined. It is defined as

$$R = \frac{\sum (|F_o| - |F_c|)}{\sum |F_o|} \quad (2.19)$$

and is used to give a guide to the correctness and precision of a structure. In general, the lower the R value, the better the structure determination. R values have to be used with caution as it is not unknown for structures to have a low R value and still be wrong, although fortunately this doesn't happen often. There are no hard and fast rules for the expected value of R , and interpreting them is very much a matter of experience. If the correct number and kinds of atom are placed randomly in a centrosymmetric unit cell the R value can be calculated to be 0.67. It is usually taken as a rule of thumb for small molecule structures, that a correct structure for a reasonable quality data set would refine to below an R of 0.1, anything above should be viewed with some degree of suspicion. That said, most structures nowadays, if collected from good quality crystals on modern diffractometers, would usually refine to $R < 0.05$ and often to $R < 0.03$.

A good structure determination, as well as having a low R value, will also have low standard deviations on both the atomic positions and the bond lengths calculated from these positions. This is probably a more reliable guide to the quality of the refinement.

2.8 X-RAY CRYSTAL STRUCTURES IN THE LITERATURE

When a single crystal of a solid can be produced, X-ray diffraction provides an accurate, definitive structure, with bond lengths determined to tenths of a picometre. In recent years the technique has been trans-

formed from a very slow method reserved only for the most special structures to a method of almost routine analysis: with modern machines, suites of computer programs and fast computers, several crystal structures a week can be processed.

Many papers in the chemical literature contain reports of single crystal structure determinations. In the experimental section of a paper you will find listed the unit cell dimensions, a , b , c , α , β , γ , the volume, V , the space group, the number of molecules in the unit cell, Z , and the density of the crystals, ρ or d . A paper will usually describe how the data was collected (what kind of diffractometer was used and the temperature at which the data was collected, etc.), how many reflections were observed and what corrections have been applied. It will go on to say what methods were used to solve and refine the structure and finally quote an R value. In the results section of the paper you will find a table listing the atomic positions of all the atoms in the asymmetric unit and these positions are given as fractional coordinates of the unit cell; the displacement parameters of each atom are also usually listed in this table. Next to this table you will find a perspective diagram of the molecule, plotted from these atomic coordinates, and the atoms will be labelled to correspond with those in the table of coordinates; this plot often puts the displacement ellipsoids on each atom as well. A packing diagram of the structure is sometimes included as well, but with pressure on space in the literature these are less common, and are only given for extended structures like polymers where the interactions between adjacent molecules or asymmetric units are important. A second table lists the bond lengths and angles for the molecule, calculated from the atomic positions. Estimated errors or standard deviations are usually given in parentheses. An example of the kind of results you might expect to see is given in Figure 2.17.

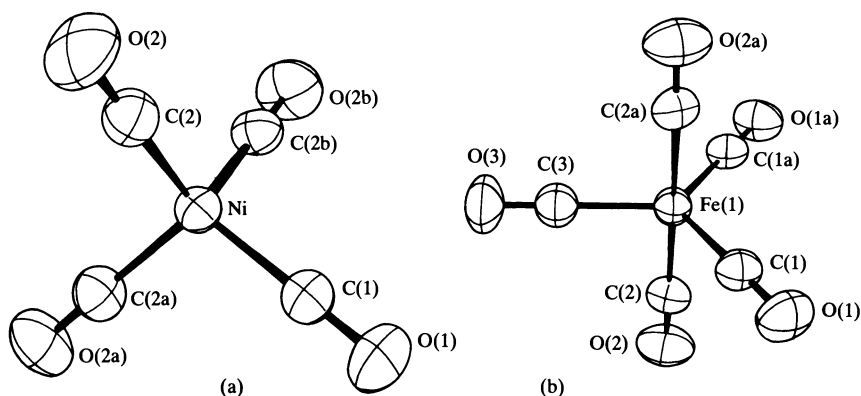
2.9 NEUTRON DIFFRACTION

The vast majority of crystal structures published in the literature have been solved using X-ray diffraction. However, it is also possible to use neutron diffraction for crystallographic studies. It is a much less commonly used technique because there are very few sources of neutrons available, whereas X-ray diffractometers can be housed in any laboratory. It does, however, have advantages for certain structures.

The de Broglie relationship states that any beam of moving particles will display wave properties according to the formula

$$\lambda = \frac{h}{p}, \quad (2.18)$$

where λ is the wavelength, p is the momentum of the particles ($p = mv$, mass $\times$ velocity), and h is Planck's constant. Neutrons are released in



Atomic Coordinates for $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$

Atom	x	y	z
$\text{Ni}(\text{CO})_4$			
Ni	0.12184(2)	0.12184(2)	0.12184(2)
C1	0.21878(15)	0.21878(15)	0.21878(15)
O1	0.27872(12)	0.27872(12)	0.27872(12)
C2	0.0231(2)	0.02757(15)	0.2190(2)
O2	-0.03870(14)	-0.03102(13)	0.27895(15)
$\text{Fe}(\text{CO})_5$			
Fe1	0.0000	0.16650(4)	0.2500
C1	0.08312(13)	0.3035(2)	0.4136(2)
C2	0.12939(15)	0.1640(2)	0.1828(2)
C3	0.0000	-0.0981(4)	0.2500
O1	0.13541(12)	0.3912(3)	0.5158(2)
O2	0.20922(13)	0.1609(2)	0.1413(2)
O3	0.0000	-0.2639(3)	0.2500

Bond Lengths (Å) and Angles (deg)

$\text{Ni}(\text{CO})_4$			
Ni–C2	1.815(2)	C1–O1	1.125(3)
Ni–C1	1.819(3)	C2–O2	1.128(2)
C2–Ni–C2a	109.65(6)	O1–C1–Ni	180.0
C2–Ni–C1	109.29(6)	O2–C2–Ni	179.66(15)
$\text{Fe}(\text{CO})_5$			
Fe1–C3	1.801(3)	C1–O1	1.136(2)
Fe1–C1	1.804(2)	C2–O2	1.117(2)
Fe1–C2	1.811(2)	C3–O3	1.128(4)
C3–Fe1–C1	121.11(5)	C2–Fe1–C2a	178.94(10)
C1–Fe1–C1a	117.78(10)	O1–C1–Fe1	179.4(2)
C3–Fe1–C2	89.47(5)	O2–C2–Fe1	179.43(15)
C1–Fe1–C2	90.38(7)	O3–C3–Fe1	180.0

Figure 2.17 Crystal structure determinations of $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$ as reported in the literature by D. Braga, F. Grepioni and A.G. Orpen, *Organometallics* (1993) **12**, 1481–3. (a) Displacement ellipsoid plot (50%) of the molecular structure of $\text{Ni}(\text{CO})_4$. The crystallographic threefold axis passes through atoms Ni, C(1), and O(1). (b) Displacement ellipsoid plot (50%) of the molecular structure of $\text{Fe}(\text{CO})_5$. The crystallographic twofold axis passes through atoms Fe(1), C(3) and O(3).

atomic fission processes, when they have very high velocities and a very small wavelength. The neutrons generated in a nuclear reactor can be slowed using heavy water so that they have a wavelength of about 100 pm and are thus suitable for structural diffraction experiments. The neutrons generated have a spread of wavelengths, and a monochromatic beam is formed using reflection from a single crystal monochromator.

Structural studies need a high flux of neutrons and this usually means that the only appropriate source is a high-flux nuclear reactor which is both very expensive to build and to run; there are only a few in the world, notable sources being Brookhaven and Oak Ridge in the USA and Grenoble in France. Alternative spallation sources are becoming available, where the neutrons are produced by bombarding metal targets with high-energy protons.

The difference between the X-ray and neutron diffraction techniques lies in the scattering process: X-rays are scattered by the electrons around the nucleus, whereas neutrons are scattered by the nucleus. The scattering factor for X-rays increases linearly with the number of electrons in the atom, so that heavy atoms are much more effective at scattering than light atoms, but the scattering factor decreases with $\sin \theta / \lambda$ due to the destructive interference associated with the size of the atom (see section 2.4.6 and Figure 2.11). Neutron scattering factors cannot be predicted but have to be determined experimentally and they vary for different atoms and indeed for different isotopes. Neutron scattering factors have several important differences: they are all fairly similar in value; the scattering factor is dependent on the particular isotope; and because the nucleus is very small they do not decrease with $\sin \theta / \lambda$.

2.9.1 Uses of neutron diffraction

The fact that neutron scattering factors are similar for all elements means that light atoms scatter neutrons as effectively as heavy atoms and can therefore be located in the crystal structure. This property is particularly useful for locating hydrogen atoms in a structure, which can sometimes be difficult to do in an X-ray determination, especially if the hydrogen atoms are in the presence of a heavy metal atom. Accordingly, many neutron studies in the literature have been done with the express purpose of locating hydrogen atoms, or of exploring hydrogen bonding.

Neutrons are not absorbed by the crystals, so they are also useful for studying systems containing heavy atoms that absorb X-rays very strongly.

Atoms near each other in the Periodic Table have very similar X-ray scattering factors and cannot always be distinguished in an X-ray structure determination. A neutron structure determination may be able to identify atoms with similar atomic numbers.

As well as the scattering of the neutrons by the nuclei, there is ad-

ditional magnetic scattering of the neutrons from paramagnetic atoms. This arises because a neutron has spin and so possesses a magnetic moment which can interact with the magnetic moment of an atom. The atomic magnetic moment is due to the alignment of the electron spins, and so this interaction, like the scattering of X-rays, falls off with increasing Bragg angle due to the size of the electron cloud. As you will see later in Chapter 9, the magnetic moments of a paramagnetic crystal are arranged randomly, but in ferromagnetic, ferrimagnetic, and antiferromagnetic substances the atomic magnetic moments are arranged in an ordered fashion. In ferromagnetic substances the magnetic moments are arranged so that they all point in the same direction and so reinforce one another; in antiferromagnetic substances the magnetic moments are ordered so that they completely cancel one another out, and in ferrimagnetic substances the ordering leads to a partial cancellation of magnetic moments. Magnetic scattering of a polarized beam of neutrons from these ordered magnetic moments gives rise to magnetic Bragg peaks. For instance, the structure of NiO, as determined by X-ray diffraction is the same as NaCl. In the neutron study, however, below 120 K extra peaks appear due to the magnetic interactions; these give a magnetic unit cell which has a cell length *twice* that of the standard cell. This arises (Figure 2.18) because the alternate close-packed layers of Ni atoms have their magnetic moments aligned in opposing directions, giving rise to antiferro-

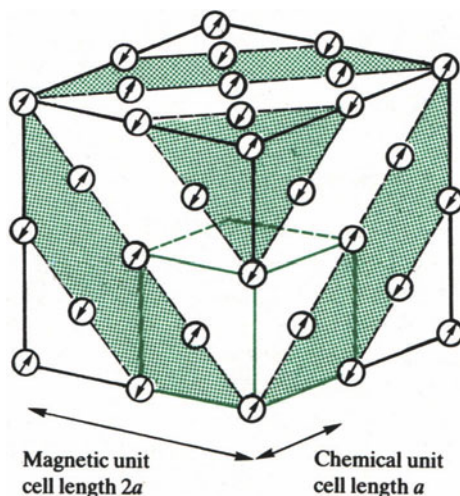


Figure 2.18 The magnetic ordering in NiO. The diagram shows only the Ni atoms, and alternate close-packed layers have opposing magnetic moments. Also indicated is the magnetic unit cell length, which is double that of the chemical unit cell length, and the chemical unit cell is picked out in colour.

magnetic behaviour. (This phenomenon is discussed in more depth in Chapter 9.)

We have already mentioned the technique of Rietveld profile analysis in the context of X-ray powder diffraction, but it was with neutron powder diffraction that this technique originated. The fact that the neutron scattering factors are almost invariant with $\sin \theta/\lambda$ means that the intensity of the data does not drop off at high angles of θ , as is the case with X-ray patterns, and so a neutron powder pattern tends to yield up considerably more data.

In a high symmetry crystal system there are very few peaks in the powder pattern, and they are often well resolved and well separated. It is then possible to measure their position and intensity with accuracy, and by the methods we described earlier, index the reflections and solve the structure. For larger and less symmetrical structures there are far more reflections which overlap considerably, and it becomes impossible to measure the intensities of individual peaks with any accuracy. Rietveld formulated a method of assigning each peak a gaussian shape and then allowing the gaussians to overlap so that an overall line profile could be calculated. A calculated line profile for the complete powder pattern is computed, based on a trial structure, and then this is compared with the experimental profile. Least-squares methods are then used to refine the model. The main difficulties with this method compared with single crystal methods are twofold: a complicated powder pattern cannot be indexed easily unless the structure is already known, so a good trial structure is imperative, and there are far fewer data collected, so the refinement is likely to be less accurate. However, the technique can be extremely useful in solid state chemistry if, for instance, a known structure is modified slightly by doping with a different element.

2.9.2 Disadvantages of neutron diffraction

We have already mentioned both the difficulty and expense of obtaining a source of neutrons, so that is the first problem. But this is not the only one. The flux of a monochromatic source of neutrons is small, and this necessitates the use of large single crystals and long counting times for the experiment, in order to get sufficient intensity. Crystals typically have needed to be at least 1 mm in each direction, and it can be extremely difficult if not impossible to grow such large, perfect crystals. However, new high-energy neutron sources are becoming available, such as the one at Grenoble, and the need for these large single crystals in neutron studies is receding.

Because the neutron scattering factor of each atom is similar, it is not usually possible to base the initial phasing model on the heavy atoms alone, and direct methods have to be used to solve the structure.

The bond lengths from neutron and X-ray diffraction studies of the same system will not be identical. This is because neutron diffraction locates the positions of the nuclei, whereas X-ray diffraction finds the positions of maximum electron density, and the two are not necessarily the same. These positions will be very similar for ionic structures and heavy atoms with many electrons, but for light atoms forming covalent bonds the electron cloud may be displaced quite considerably from the position of the nucleus.

In summary, then, neutron diffraction is usually reserved for particular problems involving the location or bonding of light atoms, especially hydrogen, and for magnetic ordering. Its expense and the difficulty of growing large single crystals precludes its use except in special cases.

FURTHER READING

General

Cheetham, A.K. and Day, P. (1987) *Solid State Chemistry: techniques*, Oxford University Press.

This has a very good chapter on diffraction techniques, but also gives comprehensive coverage of all the other major techniques employed in unravelling solid state structures. Aimed at higher level undergraduates and postgraduates.

Ebsworth, E.A.V., Rankin, D.W.H. and Cradock, S. (1987) *Structural Methods in Inorganic Chemistry*, Blackwell Scientific Publications.

An excellent book covering many different structural techniques, including diffraction. It is not, however, specific to the solid state. It is aimed at higher level undergraduates and postgraduates.

X-ray diffraction

Luger, P. (1980) *Modern X-ray Analysis on Single Crystals*, Walter de Gruyter.

An excellent text outlining modern methods in X-ray crystallography. It is aimed at those starting out in crystallographic research.

Dent Glasser, L.S. (1977) *Crystallography and its Applications*, Van Nostrand Reinhold.

A clearly written text, aimed at the advanced undergraduate. It covers both single crystal and powder diffraction, and emphasizes relevance to solid state and materials chemistry.

Glusker, J.P. and Trueblood, K.N. (1985) *Crystal Structure Analysis*, 2nd edn, Oxford University Press.

A well-written text explaining the X-ray single crystal technique in detail. It is aimed at higher level undergraduates and those starting out in crystallographic research.

Stout, G.H. and Jensen, L.H. (1968) *X-ray Structure Determination*, The Macmillan Company.

One of the classic texts, it explains single crystal X-ray diffraction methods in detail. Aimed at those starting crystallographic research.

Klug, H.P. and Alexander, L.E. (1974) *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, John Wiley and Sons.

Neutron diffraction

Bacon, G.E. (1975) *Neutron Diffraction*, Clarendon Press, Oxford.

Windsor, C.G. (1981) *Pulsed Neutron Scattering*, Taylor and Francis, London.

QUESTIONS

1. What are the spacings of the 100 , 110 and 111 planes in a cubic crystal system of unit cell dimension a ? In what sequence would you expect to find these reflections in a powder diffraction photograph?
2. What is the sequence of the following reflections in a primitive cubic crystal: 220 , 300 and 211 ?
3. Nickel crystallizes in a cubic crystal system. The first reflection in the powder pattern of nickel is the 111 . What is its Bravais lattice?
4. The $\sin^2\theta$ values for Cs_2TeBr_6 are listed in Table 2.4 for the observed reflections. To which cubic class does it belong? Calculate its unit cell length assuming Cu-K_α radiation of wavelength 154.2 pm .
5. X-ray powder data for NaCl is listed in Table 2.5. Determine the Bravais lattice, assuming that it is cubic.
6. Use the data given in Question 5 to calculate a unit cell length for the NaCl unit cell.
7. If the unit cell length of NaCl , $a = 563.1\text{ pm}$ and the density of NaCl is measured to be $2.17 \times 10^3\text{ kg m}^{-3}$, calculate Z , the number of formula units in the unit cell. (The atomic masses of sodium and chlorine are 22.99 and 35.45 respectively.)

Table 2.4 $\sin^2\theta$ values for Cs_2TeBr_6

$\sin^2\theta$
0.0149
0.0199
0.0399
0.0547
0.0597
0.0799
0.0947

Table 2.5 $\sin^2\theta$ values for NaCl

θ_{hkl}
13°41'
15°51'
22°44'
26°56'
28°14'
33°7'
36°32'
37°39'
42°0'
45°13'
50°36'
53°54'
55°2'
59°45'

8. A powder diffraction pattern establishes that silver crystallizes in a face-centred cubic unit cell. The 111 reflection is observed at $\theta = 19.1^\circ$ using $\text{Cu-K}\alpha$ radiation. Determine the unit cell length, a .
If the density of silver is $10.5 \times 10^3 \text{ kg m}^{-3}$ and $Z = 4$, calculate the value of the Avogadro constant. (The atomic mass of silver is 107.9.)
9. Calcium oxide crystallizes with a face-centred cubic lattice, $a = 481 \text{ pm}$ and a density $\rho = 3.35 \times 10^3 \text{ kg m}^{-3}$: calculate a value for Z . (Atomic masses of Ca and O are 40.08 and 15.999 respectively.)
10. Thorium diselenide, ThSe_2 , crystallizes in the orthorhombic system with $a = 442.0 \text{ pm}$, $b = 761.0 \text{ pm}$, $c = 906.4 \text{ pm}$ and a density, $\rho = 8.5 \times 10^3 \text{ kg m}^{-3}$: calculate Z . (Atomic masses of Th and Se are 232.03 and 78.96 respectively.)
11. Cu crystallizes with a cubic close-packed structure. The Bragg angles of the first two reflections in the powder pattern collected using $\text{Cu-K}\alpha$ radiation are 21.6° and 25.15° . Calculate the unit cell length, a , and estimate a radius for the Cu atom.
12. Arrange the following atoms in order of their ability to scatter X-rays: Na, Co, Cd, H, Tl, Pt, Cl, F, O.
13. A triclinic unit cell containing two Pt atoms related by a centre of symmetry has a Patterson map showing one very large vector maximizing at the coordinates, u, v, w : 0.52, 0.04, 0.48. What are the fractional coordinates of the two Pt atoms in the unit cell?

14. A triclinic unit cell contains four Pt atoms. Pt_1 and Pt'_1 have the coordinates x_1, y_1, z_1 and $-x_1, -y_1, -z_1$ and are related by a centre of symmetry; similarly for Pt_2 and Pt'_2 with coordinates x_2, y_2, z_2 and $-x_2, -y_2, -z_2$. A Patterson map shows two peaks of height 200 (arbitrary units) at 0.24, 0.50, 0.58 and 0.80, 0.76, 0.44 respectively and two peaks of height 400 at 0.28, 0.13, -0.07 and 0.48, 0.37, 0.59 respectively. Locate the platinum atoms. (Remember that the Patterson function will calculate *all* the vectors between the atoms.)

3.1 INTRODUCTION

The interest in properties of solids has given rise to the development of a variety of methods of preparing them. The method chosen for any solid will depend not only on the composition of the solid but also on the form in which it is required for its proposed use. For example, silica glass for fibre optics needs to be much freer of impurities than silica glass used to make laboratory equipment. Some methods may be particularly useful for producing solids in forms that are not the stable form under normal conditions, for example the synthesis of diamond employs high pressures. Other methods may be chosen because they favour the formation of unusual oxidation states, for example the preparation of chromium dioxide by the hydrothermal method, or because they promote the production of fine powders or, by contrast, large single crystals. For industrial use a method that does not employ high temperatures could be favoured because of the ensuing energy savings.

We do not have space here to discuss all the ingenious syntheses that have been employed, so we shall concentrate on those that are commonly used with a few examples of techniques used for solids with particularly interesting properties. The preparation of organic solid state compounds is not covered as generally they involve organic synthesis techniques which are a whole field in themselves and are covered in many organic text books. Instead we concentrate on the less well-known methods of inorganic solid preparation. We start with one of the simplest methods, widely used in industry, and then look at methods devised to get around some of the disadvantages of this basic method and some methods used to produce particularly pure solids which are important in the semiconductor industry.

3.2 CERAMIC METHODS

In its simplest form, the **ceramic method** consists of heating together two solids which react to form the required product. This method is used widely both industrially and in the laboratory; the first high-temperature superconductors were, for example, made by a ceramic method. An illustrative example of a laboratory preparation is given below.

3.2.1 Samarium sulphide

An example of the use of this method is the preparation of samarium sulphide. Samarium sulphide, SmS , is of interest because it contains samarium (a lanthanide element) in an unusual oxidation state, +2, rather than the more common state, +3. Samarium metal in powder form and powdered sulphur were mixed together and heated to about 1000 K in an evacuated silica tube. Silica is a common choice for the reaction tube. Other materials frequently used are platinum and alumina. The material chosen must be stable at high temperatures and chemically inert so that it does not take part in the reaction. Evacuated tubes are used when the products or reactants are sensitive to air or water or are volatile. In this case, sulphur has a low boiling temperature (717 K) and an evacuated tube is necessary to prevent it boiling off and being lost from the reaction vessel. The product from the initial heating was then homogenized and heated to about 2300 K in a sealed tantalum tube by passing an electric current through the tube. The resistance of the tantalum results in electrical energy being converted to heat as in an electric fire. This is a common method of heating up to 2300 K but above this other methods have to be employed. One such method is to direct an electric arc at the reaction mixture. For very high temperatures, a carbon dioxide laser (with output in the infrared) is used.

3.2.2 Disadvantages

Despite its widespread use, the simple ceramic method has several disadvantages. Firstly, high temperatures are generally required (2300 K in the example we gave). This requires a large input of energy. In addition, the phase or compound desired may be unstable or decompose at such high temperatures. A second disadvantage is the slowness of solid state reactions. In general, the solids are not raised to their melting temperatures, and so the reaction occurs in the solid state. Solid state reactions only take place at the interface of the two solids and once the surface layer has reacted, reaction can only continue as reactants diffuse from the bulk to the interface. Raising the temperature enables reaction at the interface and diffusion through the solid to proceed faster than they do at

room temperatures. Even so, diffusion is often the limiting step. Because of this, it is important that the starting materials are ground to give a small particle size, and very well mixed to maximize the surface contact area and minimize the distance that the reactants have to diffuse. To achieve a homogeneous mix of small particles with the ceramic method it is necessary to be very thorough in grinding the reactants. Commonly the reaction mixture is removed during the heating process and reground to bring fresh surfaces in contact and so speed up the reaction. Nevertheless the reaction time is measured in hours; the oxide CuFe_2O_4 , for example, takes 23 h. A third disadvantage is that the product is often not homogeneous in composition.

Many methods have been developed to overcome some or all of these disadvantages. Use of microwave ovens rather than conventional heating leads to a speeding up of reaction in favourable cases. To obtain more homogeneous products, methods involving particles smaller than those obtained by grinding have been introduced. One of these is the sol-gel method. Increased homogeneity is also obtained with the precursor and hydrothermal methods and in addition these operate at lower temperatures than conventional methods.

3.3 MICROWAVE SYNTHESIS

Cooking food is just one example of the use of microwave radiation to increase the speed of reaction. Recently this method has been used to synthesize solid state materials such as mixed oxides. Initially experiments were performed in modified domestic ovens, and these are still used but more specialized ovens have also been developed giving more control over the conditions. We shall briefly consider how microwaves heat solids and liquids because this gives us insight into which reactions will be good candidates for this method.

In a liquid or solid the molecules or ions are not free to rotate and so the heating is *not* the result of the absorption of microwaves by molecules undergoing rotational transitions as they would in the gas phase. In a solid or liquid the alternating electric field of the microwave radiation can act in two ways. If there are charged particles present that can move freely through the solid or liquid then these will move under the influence of the field, producing an oscillating electric current. Resistance to their movement causes energy to be transferred to the surroundings as heat. This is conduction heating. If there are no particles that can move freely but there are molecules or units with dipole moments then the electric field acts to align the dipole moments. This produces **dielectric heating**. It is this effect acting upon water molecules that is generally responsible for the heating of food. The electric field of microwave radiation, like that of

all electromagnetic radiation, is oscillating at the frequency of the radiation. The electric dipoles in the solid do not change their alignment instantaneously but with a characteristic time, τ . If the oscillating electric field changes its direction slowly so that the time between changes is much greater than τ then the dipoles can follow the changes. A small amount of energy is transferred to the surroundings as heat each time the dipole realigns but this is only a small heating effect. If the electric field of the radiation oscillates very rapidly then the dipoles cannot respond fast enough and do not realign. The frequency of microwave radiation is such that the electric field changes sign at a speed that is the same order of magnitude as τ . Under these conditions the dipole realignment lags slightly behind the change of electric field and the solid absorbs microwave radiation. This absorbed energy is converted to heat. The quantities governing this process are the dielectric constant (Chapter 9), which determines the extent of dipole alignment, and the dielectric loss, which governs how efficiently the absorbed radiation is converted to heat.

To use microwave heating in solid state synthesis at least one component of the reaction mixture must absorb microwave radiation. The speed of the reaction process is then increased by both increasing the rate of the solid state reaction and by increasing the rate of diffusion, which as we mentioned earlier is often the rate-limiting step.

3.3.1 The superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$

High-temperature superconductors were first prepared using a conventional ceramic method; in this case by baking together yttrium oxide, copper(II) oxide and barium carbonate. The synthesis however takes 24 h to complete. A microwave method has been reported that can prepare the superconductor in under 2 h. A stoichiometric mixture of copper(II) oxide, CuO, barium nitrate, $\text{Ba}(\text{NO}_3)_2$, and yttrium oxide, Y_2O_3 , was placed in a microwave oven which had been modified to allow safe removal of the nitrogen oxides formed during the reaction. The mixture was treated with 500 W of microwave radiation for 5 min then reground and exposed to microwave radiation at 130–500 W for 15 min. Finally the mixture was ground again and exposed to microwave radiation for a further 25 min. The microwaves in this example couple to the copper(II) oxide. This is one of a range of oxides, mostly non-stoichiometric, which are efficiently heated by microwave radiation. For example, a 5–6 g sample of CuO exposed to 500 W of microwave radiation for 30 s attained a temperature of 1074 K. Other oxides which absorb microwave radiation strongly include ZnO, V_2O_5 , MnO_2 , PbO_2 , Co_2O_3 , Fe_3O_4 , NiO and WO_3 . Carbon, SnCl_2 and ZnCl_2 are also strong absorbers. By contrast a 5–6 g sample of calcium oxide, CaO, exposed to 500 W microwave radiation only attained a temperature of 356 K after half an hour. Other

oxides which do not absorb strongly include TiO_2 , CeO_2 , Fe_2O_3 , Pb_3O_4 , SnO , Al_2O_3 and La_2O_3 .

Although microwave synthesis dramatically decreases reaction time, it does not solve the problem of chemical inhomogeneity and temperatures in the reaction are high. It does however have some other advantages. One of these is that there are less problems with cracking because the heating is from inside, not absorbed from outside.

3.4 THE SOL-GEL METHOD

This method was developed in the 1950s and 1960s after it was realized that colloids, which contain small particles (1–1000 nm in diameter), can be highly chemically homogeneous, although the first investigation of a sol-gel process for synthesis was in the mid-nineteenth century. This early investigation studied the preparation of silica glass from a sol made by hydrolysing an alkoxide of silicon. Unfortunately, in order to prevent the product cracking and forming a fine powder, a drying period of a year or more was required!

A sol is a colloidal suspension of particles in a liquid; for the materials being discussed here, these particles will typically be 1–100 nm in diameter. A gel is a semi-rigid solid in which the solvent is contained in a framework of material which is either colloidal (essentially a concentrated sol) or polymeric.

To prepare solids using the sol-gel method, a sol is first prepared of reactants in a suitable liquid. Sol preparation can either be simply the dispersal of an insoluble solid or addition of a precursor which reacts with the solvent to form a colloidal product. A typical example of the first is the dispersal of oxides or hydroxides in water with the pH adjusted so that the solid particles remain in suspension rather than precipitate out. A typical example of the second method is the addition of metal alkoxides to water. The alkoxides are hydrolysed giving the oxide as a colloidal product.

The sol is then either treated or simply left to form a gel. To obtain the final product, the gel is heated. This heating serves several purposes – it removes the solvent, it decomposes anions such as alkoxides or carbonates to give oxides, it allows rearrangement of the structure of the solid and it allows crystallization to occur. The main steps in the sol-gel process are outlined in Figure 3.1. Of course, not all of these functions are needed in any one preparation. To illustrate the method, two examples are given which have been chosen because they have interesting properties and uses discussed later on in this book. Many other materials have been prepared by the sol-gel method and other sol-gel preparations have been employed

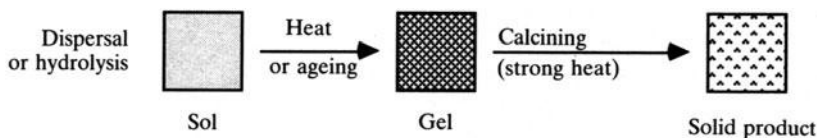
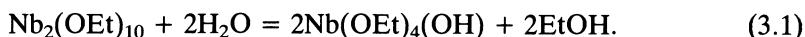


Figure 3.1 Steps in the sol-gel synthesis route.

for the materials chosen, and so these examples should be taken as illustrative and not as the main uses of the method.

3.4.1 Lithium niobate, LiNbO_3

Lithium niobate is a ferroelectric material used as an optical switch (Chapter 8). Preparation by the simple ceramic method leads to problems obtaining the correct stoichiometry and a mixture of phases often results. Several sol-gel preparations have been described, their advantage being the lower temperature required for the preparation. One such preparation starts with lithium ethoxide (LiOC_2H_5 , LiOEt) and niobium ethoxide $\text{Nb}_2(\text{OEt})_{10}$. Each ethoxide was dissolved in absolute ethanol and the two solutions mixed. The addition of water leads to partial hydrolysis giving hydroxy-alkoxides, for example



The hydroxy-alkoxides condense to form a polymeric gel with metal–oxygen–metal links. Lithium niobate is then formed when the gel is heated. Heating removes any remaining ethanol and any water formed during the condensation. It will also pyrolyse (that is, oxidize to carbon dioxide and water) any remaining ethyl groups, leaving just the oxides.

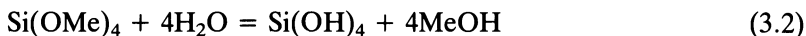
3.4.2 Doped tin dioxide

Tin dioxide, SnO_2 , is an oxygen-deficient *n*-type semiconductor (Chapter 5) whose conductivity is increased by the addition of dopants such as Sb^{3+} ions. One use of doped tin dioxide is to form a transparent electrode. For this it is deposited onto glass and must have a large surface area with a controlled distribution of dopants. Sol-gel methods have proved suitable for the preparation of such coatings because gels can be finely sliced. In one reported preparation of titanium-doped tin dioxide, the sol was prepared by adding titanium butoxide ($\text{Ti}(\text{OC}_4\text{H}_9)_4$, $\text{Ti}(\text{OBu})_4$) to a solution of tin dichloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in absolute ethanol. Tin(II) salts are easily hydrolysed to give hydroxy complexes and can be oxidized to tin(IV) by oxygen in the air. The sol was left in an open container for 5 days, during which time it formed a gel. The gel was dried by heating at

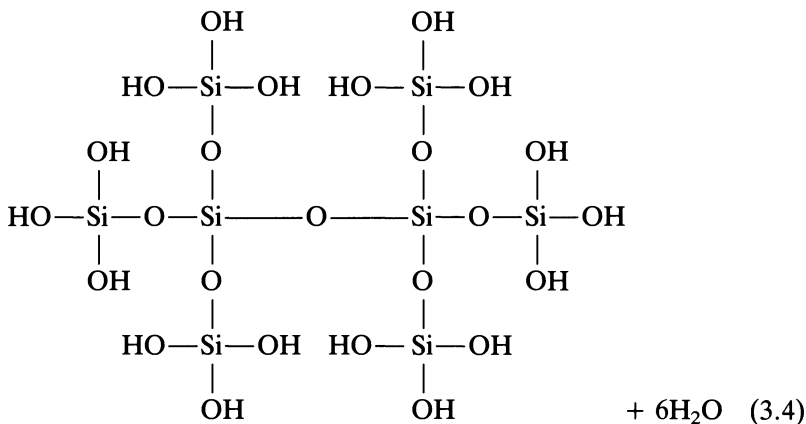
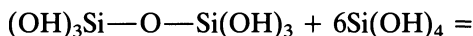
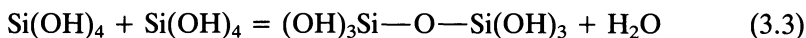
333 K under reduced pressure for 2 h. Finally it was heated to around 600 K for 10 min to produce a layer of tin dioxide doped with Ti^{4+} ions.

3.4.3 Silica for optical fibres

Optical fibres need to be free of impurities such as transition metal ions (Chapter 8) and conventional methods of preparing silica glasses are inadequate. The sol-gel process is one way of forming fibres of sufficient purity; chemical vapour deposition (section 3.7) is another. These processes use volatile compounds of silicon which are more easily purified, for example by fractional distillation, than silica. It is possible to produce silica fibres using a method similar to that studied in the nineteenth century but with the gel-drying time reduced from a year to a few days. Liquid silicon alkoxide, $\text{Si}(\text{OR})_4$, where R is methyl, ethyl or propyl, is hydrolysed by mixing with water (equation 3.2).



The product $\text{Si}(\text{OH})_4$ condenses forming Si-O-Si bonds. Gradually more and more SiO_4 tetrahedra are linked eventually forming SiO_2 . Early stages of this process are shown in equations (3.3) and (3.4):



As the condensed species reach a certain size, they form colloidal particles. The resulting sol is cast into a mould where further cross-linking results in gel formation. Fibres can be pulled as gelation occurs. Condensation continues as the gel ages. During ageing it remains immersed in liquid. The gel is porous and the alcohol and water produced by hydrolysis and condensation are trapped in the pores. Some is expelled as the gel shrinks during ageing but the rest has to be removed in a drying process.

It is at this stage that cracking occurs, but if fibres are drawn with a diameter of less than about 1 cm, the stresses produced by drying are reduced and cracking is not a problem. For gels of larger cross-section, cracking can be reduced by the use of surfactants. Finally the silica is heated to about 1300 K to increase the density of the glass.

3.4.4 A biosensor

An interesting application of the sol-gel method is in manufacturing biosensors. A **biosensor** uses a substance of biological origin, often an enzyme, to detect the presence of a molecule. To be of use as a sensor, the biological substance must be in a form which can easily be carried around and placed in a solution, in a stream of gas or on a patient's skin. Biological materials such as enzymes are potentially extremely useful as sensors because they can be very specific; where a chemical test may be positive for any oxidizing gas, for example, an enzyme may only give a positive test for oxygen. Enzymes are however easily denatured by removing them from their aqueous environment or by altering the pH of their environment. One way round this problem is to trap the enzyme with its microenvironment in a silica gel. In one such preparation, a sol of silica was first prepared by acid hydrolysis of tetramethylorthosilicate ($\text{Si}(\text{OMe})_4$). In a typical sol-gel synthesis this compound would be dissolved in methanol, but in this case methanol was avoided because alcohols denature proteins and so the solvent used was water. The sol was then buffered to be at a suitable pH for the enzyme and the enzyme was added. As the sol formed a gel by condensing, the enzyme was trapped in cavities in the gel surrounded by an aqueous medium of the correct pH.

In this last case, the product was left as a gel, but if the product is to be a glass, a powder or crystalline material, a high temperature calcining step is required after formation of the gel. Thus the sol-gel method improves the homogeneity of the product but reaction times are still long (note the 5 day gelling time in the tin dioxide synthesis) and high temperatures (1300 K for silica) are still needed. The next two methods operate at lower temperatures.

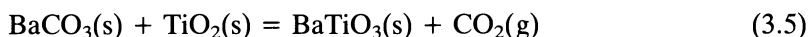
3.5 PRECURSOR METHOD

The **precursor method** achieves mixing at the atomic level by forming a solid, the precursor, in which the metals of the desired compound are present in the correct stoichiometry. For example, if an oxide $\text{MM}'_2\text{O}_4$ is required a mixed salt of an oxyacid, such as an acetate, containing M and M' in the ratio of 1:2 is formed. The precursor is then heated to decompose it to the required product. Homogeneous products are formed at

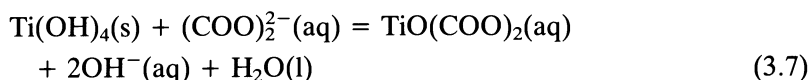
relatively low temperatures. A disadvantage is that it is not always possible to find a suitable precursor.

3.5.1 Barium titanate

Barium titanate, BaTiO_3 , is a ferroelectric material (Chapter 9) widely used in capacitors because of its high dielectric constant. It was initially prepared by heating barium carbonate and titanium dioxide at high temperature.



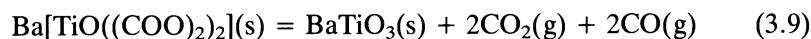
However, for modern electronic circuits it is important to have a product of controlled grain size and the precursor method is one way to achieve this. Another way is the sol-gel method, which has also been applied to this material. The precursor used is an oxalate. The first step in the preparation is to prepare an oxo-oxalate of titanium. Excess oxalic acid solution is added to titanium butoxide, which initially hydrolyses to give a precipitate which then redissolves in the excess oxalic acid.



Barium chloride solution is then added and barium titanyl oxalate precipitates.



This precipitate contains barium and titanium in the correct ratio and is easily decomposed by heat to the oxide. The temperature used for this final heating is 920 K.



The products of the precursor method are usually crystalline solids, often containing small particles of large surface area. For some applications, such as catalysis or barium titanate capacitors, this is an advantage. Other applications need single crystals. The hydrothermal method, which also increases homogeneity and lowers operating temperatures, can be used to grow single crystals.

3.6 HYDROTHERMAL METHODS

The original **hydrothermal method** involves heating the reactants in a closed vessel (an autoclave) with water. In a closed vessel the pressure

increases and the water remains liquid above its normal boiling temperature of 373 K – ‘super-heated water’. These conditions, in which the temperature is raised above the boiling temperature of water but not to as high a temperature as used in the methods described previously, and in which the pressure is raised above atmospheric pressure, are known as hydrothermal conditions. Hydrothermal conditions exist in nature and numerous minerals, including naturally occurring zeolites, are formed by this process. Synthetic emeralds are also made under hydrothermal conditions. The term has been extended to other systems with moderately raised pressures and temperatures lower than those typically used in ceramic and sol-gel syntheses. The lower temperatures used are one of the advantages of this method. Others include the preparation of compounds in unusual oxidation states or phases which are stabilized by the raised temperature and pressure. It is useful in metal oxide systems where the oxides are not soluble in water at atmospheric pressure but dissolve in the super-heated water of the hydrothermal set-up. Where even these temperatures and pressures are insufficient to dissolve the starting materials, alkali or metal salts can be added, whose anions form complexes with the solid and render it soluble. The examples below are chosen to illustrate these advantages and also the different variations of the method.

3.6.1 Quartz

The first industrial process to use hydrothermal methods of synthesis was the production of quartz crystals for use as oscillators in radios. Quartz, SiO_2 , can be used to generate a high-frequency alternating current via the piezoelectric effect (Chapter 9). The hydrothermal growth of quartz crystals employs a **temperature gradient**. In this variant of hydrothermal processing, the reactant dissolves at a higher temperature, is transported up the reaction tube by convection and crystallizes out at a lower temperature. A schematic diagram of the apparatus is shown in Figure 3.2. One end of the autoclave is charged with silica and an alkaline solution. When the autoclave is heated, the silica dissolves in the solution and is transported along the autoclave to the cooler part, where it crystallizes out. The alkaline solution is returned to the hotter region where it can dissolve more silica. In this particular case the autoclave, which is made of steel, can act as the reaction vessel. Because of the corrosive nature of superheated solutions and the possibility of contamination of the product with material from the autoclave walls, it is generally necessary to either line the autoclave with an inert substance such as teflon or to perform the reaction in a sealed ampoule in the autoclave.

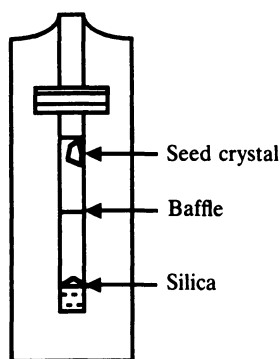


Figure 3.2 Growth of quartz crystals in an autoclave under hydrothermal conditions.

3.6.2 Chromium dioxide

Chromium dioxide, which is used on audio tapes because of its magnetic properties (Chapter 9), contains chromium in the unusual oxidation state of +4. It is prepared by the oxidation of chromium(III) oxide, Cr_2O_3 , which is the stable oxide of chromium under normal laboratory conditions. Chromium(III) oxide and chromium trioxide (chromium(VI) oxide, CrO_3) are placed in an autoclave with water and heated to 623 K. Oxygen is produced during the reaction and, because the autoclave is sealed, it builds up a high partial pressure. (The pressure in the reaction vessel is 440 bar). This high oxygen partial pressure favours the formation of chromium dioxide through the reactions (3.9) and (3.10) given below.



3.6.3 Zeolites

Naturally occurring zeolite minerals are formed through a hydrothermal process and it was shown in the 1940s and 1950s that they could be synthesized in the laboratory under hydrothermal conditions. A general method of preparing zeolites involves mixing an alkali, aluminium hydroxide and silica sol or an alkali, a soluble aluminate and silica sol. The silica and aluminate condense to form a gel as in the sol-gel method but the gel is then heated in a closed vessel at temperatures close to 373 K. Under these conditions zeolites rather than other alumino-silicate phases crystallize out. For example, in the synthesis of a typical zeolite, zeolite

A $(\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot 27\text{H}_2\text{O})$; Chapter 7), hydrated alumina, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, is dissolved in concentrated sodium hydroxide solution. The cooled solution is then mixed with a solution of sodium metasilicate, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, and a thick white gel forms. The gel is then placed in a closed teflon bottle and heated to about 363 K over 6 h. The reaction time can be reduced by using microwave radiation for this final step. Zeolite A has been made by heating for 45 min using pulses of 300 W microwave radiation.

Changes in the form of the alumina, in the pH of the solution and in the proportions of alkali, aluminium compound and silica lead to the production of different zeolites. The alkali can be a simple metal hydroxide such as sodium hydroxide but organic bases can also be used and these lead to some interesting structures. Large cations, such as tetramethylammonium (NMe_4^+) and tetrapropylammonium ($\text{N}(\text{C}_3\text{H}_7)_4^+$), become trapped in the zeolite which crystallizes with large cavities to accommodate the ion. On heating the cation is pyrolysed but the structure retains the cavities, giving the structures discussed in Chapter 7.

3.6.4 Yttrium aluminium garnet

The preparation of yttrium aluminium garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$, YAG) illustrates a variation of the hydrothermal method used if the starting materials have very different solubilities from each other. In this case yttrium oxide, Y_2O_3 , was placed in a cooler section of the autoclave and aluminium oxide as sapphire in a hotter section to increase its solubility (Figure 3.3). YAG forms where the two zones meet.



So far we have discussed improvements on the ceramic method; we end this chapter by looking at some methods used to form crystalline solids from the gas phase.

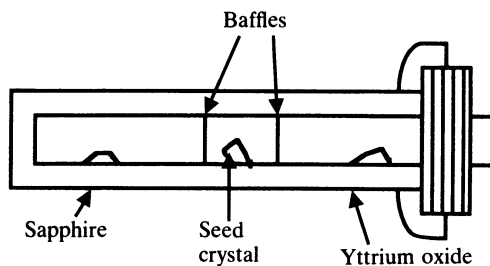


Figure 3.3 Hydrothermal arrangement for synthesis starting from two reactants of differing solubilities.

3.7 CHEMICAL VAPOUR DEPOSITION (CVD)

So far the methods we have looked at involve reactants that are in the solid state or in solution. The methods in the next sections form crystals from reactants in the vapour or gas phase. The simplest of these is **chemical vapour deposition (CVD)** where volatile starting materials are mixed at a suitable temperature and the solid product crystallizes out. Typical starting materials are hydrides, halides and organometallic compounds, as these compounds tend to be volatile. The volatile reactants, sometimes with a carrier gas, are passed into a reaction vessel. The whole vessel may be heated but in this case the product tends to be deposited all over the walls of the vessel. More commonly, energy to initiate the reaction is supplied at the point where a substrate is ready to build on. Figure 3.4 shows a schematic set-up for chemical vapour deposition.

Lithium niobate

The sol-gel method of preparing lithium niobate used lithium and niobium alkoxides. Alkoxides are often used in CVD methods and in principle these could be used to prepare lithium niobate. Unfortunately, lithium alkoxides are much less volatile than niobium alkoxides and to get the two metals deposited together it is better to use compounds of similar volatility. One way round this is to use a more volatile compound of lithium. One reported synthesis uses a β -diketonate of lithium in which lithium is coordinated to 2,2,6,6-tetramethylheptane-3,5-dione ($\text{Me}_3\text{CCOCH}_2\text{COCMe}_3$):

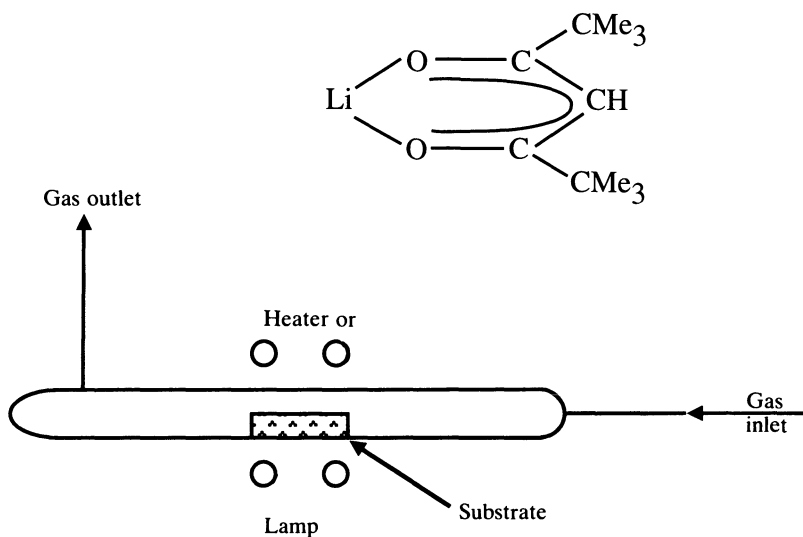


Figure 3.4 Chemical vapour deposition reactor.

The lithium compound was heated at about 520 K and niobium pentamethoxide at 470 K in a stream of argon containing oxygen. Lithium niobate was deposited on the reaction vessel, which was heated to 720 K.

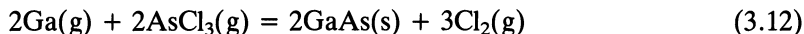
In this example the volatile precursor compounds were heated to obtain the product. Other energy sources are also used, notably electromagnetic radiation. An example of vapour phase deposition involving photo decomposition is given in the next section on vapour phase epitaxy.

3.7.1 Vapour phase epitaxial (VPE) growth

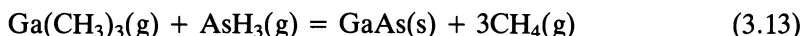
In epitaxial growth a single crystal is built up layer by layer on a substrate, adopting the same crystal structure as the substrate. This is an important method for semiconductor applications where single crystals of controlled composition are needed. Gallium arsenide, GaAs, for example, has been prepared by several vapour phase epitaxial methods.

Gallium arsenide

In one method arsenic(III) chloride, AsCl_3 , (boiling temperature 376 K) is used to transport gallium vapour to the reaction site where gallium arsenide is deposited in layers. The reaction involved is



An alternative to gallium vapour is an organometallic compound of gallium. One preparation reacts trimethyl gallium, $\text{Ga}(\text{CH}_3)_3$, with the highly volatile (although toxic) arsine, AsH_3 .



Mercury telluride

Mercury telluride, HgTe , was first made by vapour phase epitaxy in 1984. This preparation illustrates the use of ultraviolet radiation as the energy source for decomposition. Diethyltellurium ($(\text{C}_2\text{H}_5)_2\text{Te}$) vapour in a stream of hydrogen carrier gas was passed over heated mercury, where it picked up mercury vapour. As the gas passed over the substrate it was subjected to ultraviolet illumination and mercury telluride was deposited. The substrate was heated to 470 K, which is about 200 K lower than the temperature needed for thermal decomposition. The use of the lower temperature enabled later workers to build up a crystal of alternating mercury telluride and cadmium telluride because diffusion of one layer into the other was slowed by the lower temperature.

Production of single crystals with carefully controlled varying composition is vital to make semiconductor devices. The production of crystals for quantum well lasers illustrates how carefully such syntheses can be controlled.

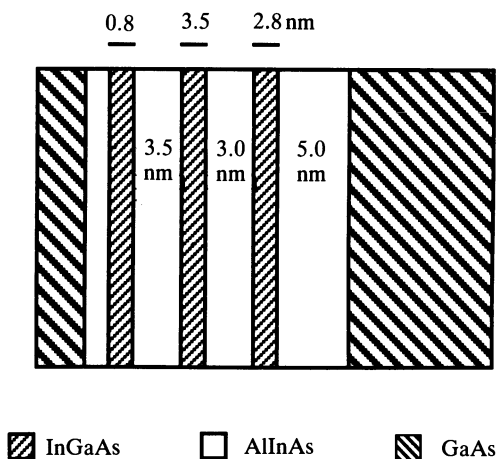


Figure 3.5 The layers of an active region of a quantum cascade laser.

3.7.2 Molecular beam epitaxy (MBE)

A molecular beam is a narrow stream of molecules formed by heating a compound in an oven with a hole which is small compared to the mean free path of the gaseous molecules produced. Very thin layers can be built up by directing a beam of precursor molecules onto the substrate. The system is kept under ultra-high vacuum. Because of the very low pressure, the reactants need not be as volatile as in other CVD methods. An application of this method is the growth of single crystals for quantum cascade lasers (Chapter 8) where the crystal must contain nanometre thickness layers of $\text{Al}_{0.48}\text{In}_{0.52}\text{As}$ and $\text{Ga}_{0.47}\text{In}_{0.53}\text{As}$. The layers of the laser material are shown in Figure 3.5. Beams of aluminium, gallium, arsenic and indium were directed onto a heated InP crystal. The substrate needs to be heated to allow the atoms deposited from the beams to migrate to their correct lattice position. The relative pressures of the component beams were adjusted for each layer to give the desired compositions.

3.8 CHEMICAL VAPOUR TRANSPORT

In chemical vapour deposition, solids are formed from gaseous compounds. In **chemical vapour transport**, a solid or solids interact with a volatile compound and a solid product is deposited in a different part of the apparatus. It is used both for preparing compounds and for growing crystals from powders or less pure crystalline material.

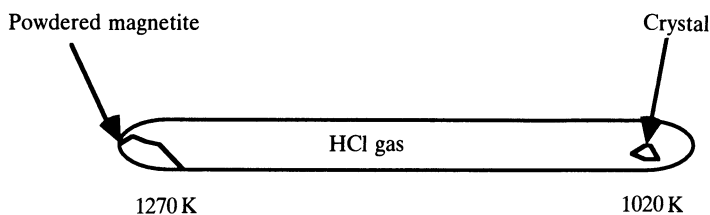
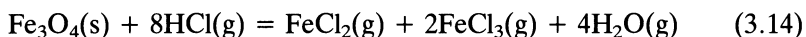


Figure 3.6 Growth of magnetite crystals using chemical vapour transport.

3.8.1 Magnetite

Chemical vapour transport has been used to grow magnetite crystals using the reaction of magnetite with hydrogen chloride gas:



Powdered magnetite is placed at one end of the reaction vessel and the tube is evacuated. HCl gas is introduced and the tube is sealed and then heated. Reaction (3.14) is endothermic ($\Delta H_m^\ominus$ positive) and so the equilibrium moves to the right as the temperature is raised. Thus, at the hotter end of the tube magnetite reacts with the hydrogen chloride gas and is transported down the tube as gaseous iron chlorides. At the cooler end of the tube the equilibrium shifts to the left and magnetite is deposited (Figure 3.6).

3.9 CHOOSING A METHOD

Our choice of methods is not exhaustive. We have not for example covered high-pressure methods, used for substances such as diamond which are not the stable phase at normal pressures, or shock or ultrasonic methods. Nor have we covered the electrolytic methods used to produce some intercalation compounds (Chapter 6). Our aim here, therefore, is not to provide a way of choosing the method for a particular product. (Indeed, several of the examples given in this chapter show that several methods can be suitable for one substance.) Instead we hope to give a few pointers to deciding whether a particular method is suitable for a particular material.

It is important that you consider the stability of compounds under the reaction conditions and not at normal temperature and pressure. As we have illustrated in this chapter, a particular method may be chosen because the desired product is stable only at raised pressures or because it decomposes if the reaction temperature is too high.

What form do you want the product to be in? You might for example

choose vapour phase epitaxy because an application requires a single crystal, or a method such as the precursor method or hydrothermal synthesis because you need a homogeneous product.

How pure must your product be? If you require high purity you could choose a method that involves a volatile compound as starting material because these are generally easier to purify than solids.

You should consider the availability of reactants required for a particular method. If you are considering a precursor method, is there a suitable precursor with the right stoichiometry? The CVD method needs reactants of similar volatility; do your proposed reactants meet this requirement? In microwave synthesis does at least one of your starting materials absorb microwaves strongly?

FURTHER READING

General

Cheetham, A.K. and Day, P. (1987) *Solid-state Chemistry: Techniques*, Chapter 1, Oxford University Press, Oxford.

A more detailed assessment than can be given here on the factors that govern choice of synthetic method. Written for final year undergraduate/first year graduate students.

Wold, A. and Dwight, K. (1993) *Solid State Chemistry: Synthesis, Structure and Properties of Selected Oxides and Sulfides*, Chapter 6, Chapman and Hall, London.

This chapter covers a wide range of synthetic methods for oxides, including some not covered in this book, and methods of crystal growth. Each topic is covered briefly.

Solid state syntheses are not covered in many text books at an appropriate level and so we include review articles on several of the topics.

Microwave synthesis

Mingos, D.M.P. and Baghurst, D.R. (1991) Application of microwave dielectric heating effects to synthetic problems in chemistry, Tilden lecture, *Chemical Society Reviews*, **20**, 1–47.

A thorough review of the principles of microwave synthesis with a wide range of examples including synthesis of organometallic compounds and organic materials as well as solid state applications.

Sol-gel method

Lakeman, C.D.E. and Payne, D.A. (1994) Sol-gel processing of electrical and magnetic ceramics, *Materials Chemistry and Physics*, **38**, 305–24.

A readable review of the use of sol-gel methods in producing commercially important ceramics with a large number of examples.

Hydrothermal synthesis

Rabenau, A. (1985) The role of hydrothermal synthesis in preparative chemistry, *Angewandte Chemie (Int. edn)*, **24**, 1026–40.
An interesting and readable review including historical and industrial applications.

Vapour phase epitaxy

Cole-Hamilton, D.J. (1990) Precursors for growing new materials, *Chemistry in Britain*, September, 852–6.
The emphasis in this review is on purifying volatile precursors for metal organic vapour phase epitaxy (MOVPE).

Almond, M.J., Rice, D.A. and Yates, C.A. (1988) Photoepitaxy – a new light on inorganic materials, *Chemistry in Britain*, November, 1130–2.
A short, readable article on the use of photo reactions in MOVPE.

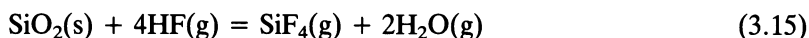
Barium titanate preparation

Morell, A. and Niepce, J.-C. (1991) BaTiO₃-based materials for M.L.C. capacitors applications, *Journal of Materials Education*, **13**, 173–232.
A readable review of the use of barium titanate in capacitors, written for materials scientists. It contains very clear sections on the preparative methods for BaTiO₃ and the qualities needed in the product.

QUESTIONS

1. The Chevrel phase CuMo₆S₈ was prepared by a ceramic method. What would be suitable starting materials and what precaution would you have to take?
2. Which synthetic methods would be suitable for producing the following characteristics: (a) a thin film of material; (b) a single crystal; (c) a single crystal containing layers of different material with the same crystal structure; (d) a powder of homogeneous composition?
3. What are the advantages and disadvantages of using the sol-gel method to prepare barium titanate for use in a capacitor?
4. A compound (NH₄)₂Cu(CrO₄)₂ · 2NH₃ is known. How could this be used to prepare CuCr₂O₄? What would be the advantage of this method over a ceramic method? Suggest which solvent was used to prepare the ammonium compound.
5. β-TeI is a metastable phase formed at 465–470 K. Suggest an appropriate method of preparation.

6. In hydrothermal processes involving alumina, Al_2O_3 , such as the synthesis of zeolites, alkali is added to the reaction mixture. Suggest a reason for this addition.
7. Which of the following oxides would be good candidates for microwave synthesis: CaTiO_3 , BaPbO_3 , ZnFe_2O_4 , $\text{Zr}_{1-x}\text{Ca}_x\text{O}_{2-x}$, KVO_3 ?
8. Crystals of silica can be grown using the chemical vapour transport method with hydrogen fluoride as a carrier gas. The reaction involved is



This reaction is exothermic. In a temperature gradient method, will the silica crystals grow at the hotter or cooler end of the reaction vessel?

9. In the preparation of lithium niobate by CVD, argon-containing oxygen is used as a carrier gas. In the preparation of mercury telluride the carrier gas was hydrogen. Suggest reasons for these choices of carrier gas.

Bonding in solids and electronic properties

4.1 INTRODUCTION

In the first chapter we introduced the physical structure of solids – how their atoms are arranged in space. We now turn to a description of the bonding in solids – the electronic structure. Some solids consist of molecules bound together by very weak forces. We shall not be concerned with these because their properties are essentially those of the molecules. Nor shall we be much concerned with ‘purely ionic’ solids bound by electrostatic forces between ions as discussed in Chapter 1. The solids considered here are those in which all the atoms can be regarded as bound together. To illustrate how this bonding is reflected in the properties of the solids, we explore electronic properties of various types of solid.

Solids display a wide variety of interesting and useful electronic properties. Good electronic conductivity is one of the characteristic properties of metals; semiconductors are the foundation of the ‘silicon revolution’. But why is tin a metal, silicon a semiconductor and diamond an insulator? Many solid state devices (transistors, photocells, light-emitting diodes (LEDs), solid state lasers, solar cells) are based on semiconductors containing carefully controlled amounts of impurity. How do these impurities affect the conductivity? These are some of the questions to be addressed, but first the basic bonding theory will be introduced.

4.2 BONDING IN SOLIDS – BAND MODEL

Traditionally bonding in metals has been approached through the idea of free electrons, a sort of electron gas. We discuss this model briefly in this chapter when we come to consider simple metals such as sodium and aluminium. However, for most purposes it is more fruitful to think of

solids as a very large collection of atoms bonded together. For chemists this has the advantage that solids are not treated as totally different species from small molecules.

The theory most often used by chemists to describe the way electrons bind nuclei together to form molecules is the molecular orbital theory. This assumes that electrons have wave-like properties and are described by wave functions that result from the interaction of the electrons with all the nuclei in the molecule. The equation that is used to calculate the wave functions is the **Schrödinger equation**. Solving such an equation for a solid is something of a tall order, however, since exact solutions have not yet been found for small molecules and even a small crystal could well contain of the order of 10^{20} atoms. An approximation often used for smaller molecules is that the molecular wave functions can be formed by combining atomic wave functions. This **linear combination of atomic orbitals (LCAO)** approach can also be applied to solids.

We shall start by reminding the reader how to combine atomic orbitals for a very simple molecule, H_2 . For H_2 we assume that the molecular orbitals are formed by combining $1s$ orbitals on each of the hydrogen atoms. These can combine in phase to give a bonding orbital or out of phase to give an anti-bonding orbital. The bonding orbital is lower in energy than the $1s$ and the anti-bonding orbital higher in energy. The amount by which the energy is lowered for a bonding orbital depends on the amount of overlap of the $1s$ orbitals on the two hydrogens. If the hydrogen nuclei are pulled further apart, for example, the overlap decreases and so the decrease in energy is less. (If the nuclei are pushed together, the overlap will increase but the electrostatic repulsion of the two nuclei becomes important and counteracts the effect of increased overlap.)

Suppose we form a chain of hydrogen atoms. For N hydrogen atoms there will be N molecular orbitals. The lowest energy orbital will be that in which all the $1s$ orbitals combine in phase, and the highest energy orbital will be that in which the orbitals combine out of phase. In between are $(N - 2)$ molecular orbitals in which there is some in-phase and some out-of-phase combination. Figure 4.1 shows a plot of the energy levels as the length of the chain increases. Note that as the number of atoms increases, the number of levels increases but the spread of energies seems to increase only slowly and is levelling off for long chains. Extrapolating to crystal length chains, one can see that there would be a very large number of levels within a comparatively small range of energies. A chain of hydrogen atoms is a very simple and artificial model; as an estimate of the energy separation of the levels, let us take a typical band in an average size metal crystal. A metal crystal might contain 10^{20} atoms and the range of energies be only 10^{-19} J. The average separation between levels would thus be only 10^{-39} J. The lowest energy levels in the

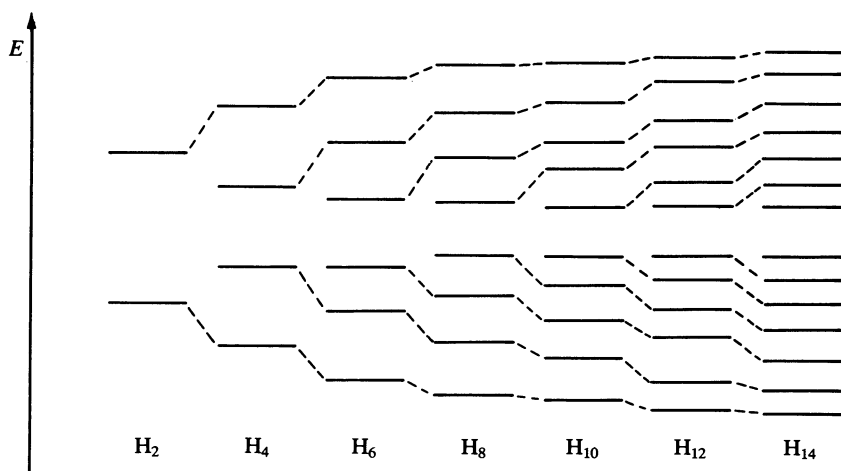


Figure 4.1 Orbital energies for a chain of N hydrogen atoms as N increases.

hydrogen atom are separated by energies of the order of 10^{-18} J, showing that the energy separation in a crystal is minute compared to the difference between energy levels in a gaseous molecule. The separation is in fact so small that we can think of the set of levels as a continuous range of energies. Such a continuous range of allowed energies is known as an **energy band**.

In place of a set of discrete levels, then, we have an energy band. The hydrogen chain orbitals were made up from only one sort of atomic orbital, $1s$, and one energy band was formed. For most of the other atoms in the Periodic Table it is necessary to consider other atomic orbitals in addition to $1s$. Aluminium for example has the atomic configuration $1s^2 2s^2 2p^6 3s^2 3p^1$ and would be expected to form a $1s$ band, a $2s$ band, a $2p$ band, a $3s$ band and a $3p$ band. In fact the lower energy bands, those formed from the core orbitals $1s$, $2s$ and $2p$, are very narrow and for most purposes can be regarded as a set of localized atomic orbitals. This arises because these orbitals are concentrated very close to the nuclei and so there is little overlap between orbitals on neighbouring nuclei. In small molecules the greater the overlap, the greater the energy difference between bonding and anti-bonding orbitals. Likewise for continuous solids, the greater the overlap, the greater the spread of energies or **band width** of the resulting band. For aluminium, then, $1s$, $2s$ and $2p$ electrons can be taken to be core orbitals and only $3s$ and $3p$ bands considered.

Just as in small molecules, the available electrons are assigned to levels in the energy bands starting with the lowest. Each orbital can take two electrons of opposed spin. Thus if N atomic orbitals were combined to make the band orbitals, then $2N$ electrons are needed to fill the band. For

example, the $3s$ band in a crystal of aluminium containing N atoms can take up to $2N$ electrons because each atom contributes one s orbital, whereas the $3p$ band can accommodate up to $6N$ electrons because each atom has three $3p$ orbitals. As aluminium has only one $3p$ electron per atom, however, there would only be N electrons in the $3p$ band and only $N/2$ levels would be occupied. Similarly, sodium with electronic configuration $1s^2 2s^2 2p^6 3s^1$ would have N electrons in the $3s$ band filling $N/2$ levels and vanadium with electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$ would have $3N$ electrons filling only $3N/2$ of the available $10N$ levels of the d band.

The highest occupied level at 0 K is called the **Fermi level**. At temperatures above 0 K, some electrons just below the Fermi level will be excited to levels just above the Fermi level, but the number is small compared to the number of electrons in the band and so for most purposes we make the approximation that electrons occupy all levels from the bottom of the band up to the Fermi level. Now we look at some examples of solids and see how we can apply the concept of energy bands to understanding some of their properties.

4.3 ELECTRONIC CONDUCTIVITY – SIMPLE METALS

The elements on the far left of the Periodic Table – Group 1 (sodium, potassium, etc.), Group 2 (magnesium, calcium, etc.) and aluminium – are often described as simple metals. The crystal structures of these metals are such that the atoms have high coordination numbers. For example, the Group 1 elements have body-centred cubic structures with each atom surrounded by eight others. This high coordination number increases the number of ways in which the atomic orbitals can overlap. The ns and np bands of the simple metals are very wide, due to the large amount of overlap and, since the ns and np atomic orbitals are relatively close in energy, the two bands merge. For the simple metals we then do not have an ns band and an np band but rather one continuous band which we shall label ns/np . For a crystal of N atoms this ns/np band contains $4N$ energy levels and can hold up to $8N$ electrons.

The simple metals have far fewer than $8N$ electrons available however; they have only N , $2N$ or $3N$. Thus the band is only partly full. In a partly full band, it requires very little energy to promote an electron to a higher energy level and because this promoted electron is delocalized it can transport its energy to other positions in the crystal. This ease of promotion is crucial in explaining characteristic properties of metals such as high electronic and thermal conductivity which involve the ease of transport of energy through a solid. The high electrical conductivity of metals was however first explained in terms of a simpler theory than the band

model, the free electron model. A fuller explanation of the electronic conductivity of simple metals will be left until after this latter model has been introduced.

4.3.1 Free electron theory

The free electron model regards a metal as a box in which electrons are free to roam unaffected by the atomic nuclei or by each other. The simple metals provide the nearest approximation to this model as the electrons in the *ns*/*np* band spend most of their time between the nuclei and can keep well away from each other.

The model assumes that the nuclei stay fixed on their lattice sites surrounded by the inner or core electrons whilst the outer or valence electrons travel freely through the solid. If we ignore the cores then the quantum mechanical description of the outer electrons becomes very simple. Taking just one of these electrons the problem becomes the well-known one of the '**particle in a box**'. We start by considering an electron in a one-dimensional solid. The electron is confined to a line of length a (the length of the solid) which we shall call the x -axis. Since we are ignoring the cores, there is nothing for the electron to interact with and so it experiences zero potential within the solid. The Schrödinger equation for the electron is

$$-\hbar^2/2m_e d^2\psi/dx^2 = (E - V)\psi \quad (4.1)$$

where $\hbar$ is Planck's constant divided by 2π , m_e is the mass of the electron, V is the electrical potential, ψ is the wave function of the electron and E is the energy of an electron with that wave function. When $V = 0$, the solutions to this equation are simple sine or cosine functions, and this can be verified by substituting $\psi = \sin\sqrt{2m_e E/\hbar^2} x$ into equation (4.1), as follows.

If $\psi = \sin\sqrt{2m_e E/\hbar^2} x$ then differentiating once gives

$$d\psi/dx = \sqrt{2m_e E/\hbar^2} \cos\sqrt{2m_e E/\hbar^2} x.$$

Differentiating twice gives $d^2\psi/dx^2 = -2m_e E/\hbar^2 \sin\sqrt{2m_e E/\hbar^2} x$,

which is $d^2\psi/dx^2 = -2m_e E/\hbar^2 \psi$ corresponding to (4.1) rearranged and with $V = 0$.

The electron is not allowed outside the box and to ensure this we put the potential to infinity outside the box. Since the electron cannot have infinite energy, the wave function must be zero outside the box and since it cannot be discontinuous, it must be zero at the boundaries of the box. If we take the sine wave solution, then this is zero at $x = 0$. To be zero at $x = a$, there must be a whole number of half waves in the box. Sine

functions have a value of zero at angles of $n\pi$ radians where n is an integer and so $a\sqrt{2m_e E/\hbar^2} = n\pi$. The energy is thus quantized, $E = n^2\hbar^2/(8m_e a^2)$, with quantum number n . Since n can take all integral values this means there are an infinite number of energy levels with larger and larger gaps between each level. Most solids of course are three-dimensional (although we shall meet some later where conductivity is confined to one or two dimensions) and so we need to extend the free electron theory to three dimensions.

For three dimensions the metal can be taken as a rectangular box $a \times b \times c$. The appropriate wave function is now the product of three sine or cosine functions and the energy is given by

$$E = \hbar^2(n_a^2/a^2 + n_b^2/b^2 + n_c^2/c^2)/8m_e \quad (4.2)$$

Each set of quantum numbers n_a, n_b, n_c will give rise to an energy level. However in three dimensions there are many combinations of n_a, n_b and n_c that will give the same energy, whereas for the one-dimensional model there were only two levels of each energy (n and $-n$). For example, the following sets of numbers all give $(n_a^2/a^2 + n_b^2/b^2 + n_c^2/c^2) = 108$:

n_a/a	n_b/b	n_c/c
6	6	6
2	2	10
2	10	2
10	2	2

and hence the same energy. The number of states with the same energy is known as the **degeneracy**. For small values of the quantum numbers, it is possible to write out all the combinations that will give rise to the same energy. If we are dealing with a crystal of say 10^{20} atoms it becomes difficult to work out all the combinations especially near the Fermi level. To estimate the degeneracy of any level in a band of this size we introduce a quantity called the wave vector. If we substitute k_x, k_y and k_z for $n_a\pi/a, n_b\pi/b$ and $n_c\pi/c$, then the energy becomes

$$E = (k_x^2 + k_y^2 + k_z^2)\hbar^2/2m_e. \quad (4.3)$$

k_x, k_y and k_z can be considered as the components of a vector, $\mathbf{k}$; the energy is proportional to the square of the length of this vector. $\mathbf{k}$ is called the **wave vector** and is related to the momentum of the electron wave as can be seen by comparing the classical expression $E = p^2/2m$, where p is the momentum, with the expression above. This gives the electron momentum as $\pm\hbar\mathbf{k}$.

All the combinations of quantum numbers giving rise to one particular energy correspond to a wave vector of the same length $|\mathbf{k}|$. Thus all possible combinations leading to a given energy produce vectors whose ends lie on the surface of a sphere of radius $|\mathbf{k}|$. The total number of wave

vectors with energies up to and including that with the given energy is given by the volume of the sphere, that is $4k^3\pi/3$ where $|\mathbf{k}|$ is written as k . The number of states with energies up to the given energy depend on n_a , etc., rather than k_x , etc., and so we have to multiply by abc/π^3 . But how many states are there with the particular energy? Well, it is actually more useful to define the number of states in a narrow range. Let us take a range of k values dk . The number of states up to and including those of wave vector length $k + dk$ is $4/3\pi^2V(k + dk)^3$, where $V (= abc)$ is the volume of the crystal. So the number with values between k and $k + dk$ is $4/3\pi^2V((k + dk)^3 - k^3)$ which when $(k + dk)^3$ is expanded gives a leading term $4/\pi^2 V k^2 dk$. This quantity is the **density of states**, $N(k) dk$. In terms of the more familiar energy, the density of states $N(E) dE$ is given by $(2m_e)^{3/2} V E^{1/2} / 2\pi^2 \hbar^3 dE$. A plot of $N(E) dE$ against E is given in Figure 4.2.

The concepts of wave vectors and density of states are not confined to free electron theory. In the orbital theory the energy levels within a band have varying degeneracies and so we can plot the number of levels with a particular range of energy against energy just as for the free electron model. The density of states diagram produced by the orbital theory will not, however, obey a simple formula like the one shown in Figure 4.2, but will vary from band to band. In general though, orbital density of states diagrams show fewer energy levels, that is a lower density of states, at the top and bottom of the band and more, that is a higher density of states, in the middle.

Experimentally, the density of states can be determined by X-ray emission spectroscopy. A beam of electrons or high-energy X-rays hitting

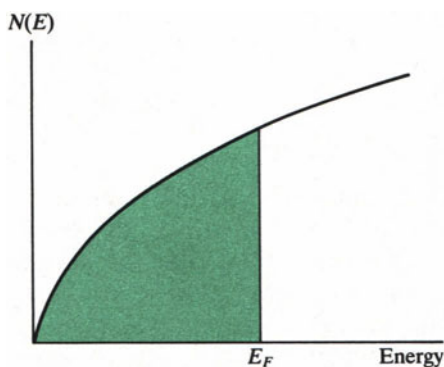


Figure 4.2 A density of states curve based on the free electron model. The levels occupied at 0 K are shaded. Note that later in the book, energy is plotted on the vertical axis. In this figure energy is plotted along the horizontal axis for comparison with the experimental results in Figure 4.3.

a metal can remove core electrons. In sodium, for example, the $2s$ or $2p$ electrons might be removed. The core energy levels are essentially atomic levels and so electrons have been removed from a discrete well-defined energy level. Electrons from the conduction band can now jump down to this energy level, emitting X-rays as they do so. The X-ray energy will depend on the level of the conduction band from which the electron has come. A scan across the emitted X-rays will correspond to a scan across the filled levels of the conduction band. The intensity of the radiation emitted will depend on the number of electrons with that particular energy, that is the intensity depends on the density of states of the conduction band. Figure 4.3 shows some X-ray emission spectra for sodium and aluminium and one can see that the shape of these curves resembles approximately the occupied part of Figure 4.2, so that the free electron model appears to describe these bands quite well.

These bands are, however, less than half full and if we looked at the unoccupied part or at a metal with a band that was more than half full, we should find that instead of continuing to increase as in Figure 4.2, the density of states would start to decrease with energy and reach zero at the top of the band. This is shown, for example, in the nearly full $3d$ band of Ni given in Figure 4.4.

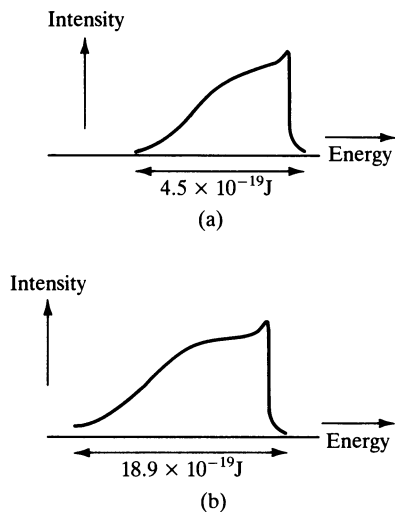


Figure 4.3 X-ray emission spectra obtained from (a) sodium metal and (b) aluminium metal when conduction electrons fall into the $2p$ level. The slight tail at the high energy end is due to thermal excitation of electrons close to the Fermi level.

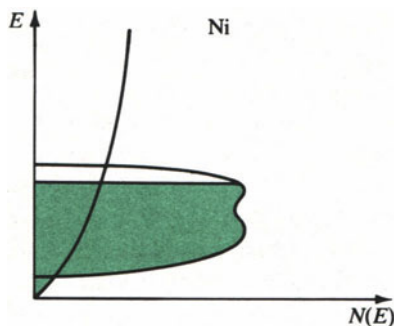


Figure 4.4 The band structure of nickel. Note the shape of the 3d band.

4.3.2 Electronic conductivity

To explain electronic conductivity it is necessary to turn to the wave vector. This concept was derived for a free electron in a box, but it can also be used in the orbital method. The combinations of atomic orbitals forming crystal orbitals form periodic patterns like the sine waves that were needed to fit into the box of the free electron model. For example, along a particular direction the phase of the atomic orbital might change sign every other atom or every third or fourth atom.

Such combinations can be represented by a term in the coefficient $e^{i\mathbf{k}\cdot\mathbf{r}}$, where $\mathbf{r}$ is the position vector of a nucleus in the lattice and $\mathbf{k}$, as in free electron theory, represents the momentum of the electron. The LCAO expression for the orbitals

$$\Psi(i) = \sum_n c_{ni} \phi_n$$

(where the sum is over all n atoms and $\Psi(i)$ is the i th orbital and c_{ni} is the coefficient of the orbital on the n th atom for the i th molecular orbital) is replaced by

$$\Psi(\mathbf{k}) = \sum_n e^{i\mathbf{k}\cdot\mathbf{r}_n} a_{n\mathbf{k}} \phi_n$$

where $\Psi(\mathbf{k})$ is the wave function with wave vector $\mathbf{k}$ and c_{ni} is replaced by $e^{i\mathbf{k}\cdot\mathbf{r}_n} a_{n\mathbf{k}}$.

Whichever model of bonding we use, $\mathbf{k}$ represents a quantized electron momentum, and for explaining electronic conductivity it is important to note that it is a vector with direction as well as magnitude. Thus there may be many different orbitals with the same value of k and hence the same value of the energy, but with different components, k_x , k_y , k_z , giving a different direction to the momentum. In the absence of an electric field, all directions of the wave vector $\mathbf{k}$ are equally likely and so there are equal numbers of electrons moving in all directions (Figure 4.5).

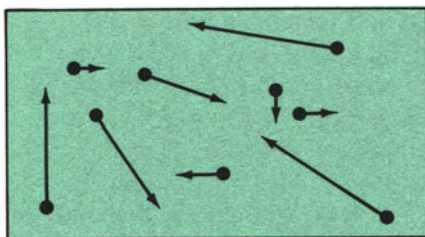


Figure 4.5 Electrons in a metal in the absence of an electric field. They move in all directions but overall there is no net motion in any direction.

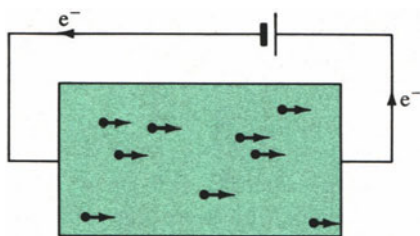


Figure 4.6 The sample of Figure 4.5 in a constant electric field, established by placing the rod between the terminals of a battery. The electrons continue to move in all directions but now their velocities are modified so that each also has a net movement or drift velocity in the left to right direction.

If we now connect our metal to the terminals of a battery producing an electric field, then an electron travelling in the direction of the field will be accelerated and the energies of those levels with a net momentum in this direction will be lowered. Electrons moving the other way will have their energies raised and so some of these electrons will drop down into levels of lower energy corresponding to momentum in the opposite direction. There will thus be more electrons moving one way than the other. This is an electric current. The net velocity in an electric field is shown in Figure 4.6.

The electronic conductivity, σ , is given by the expression

$$\sigma = nZe\mu,$$

where n is the number of charge carriers per unit volume, Ze is their charge (in the case of an electron this is simply e , the electronic charge) and μ is a measure of the velocity in the electric field.

The electrons in the levels of higher energy can only move into levels of lower energy if these are empty, and there will only be empty levels if the band is partly full. Thus *only solids with partly occupied energy bands are good electronic conductors*. Note also that only electrons near the Fermi

level can be promoted and hence only these carry the current. Thus the factor n in the expression above, and hence the conductivity, will depend on the density of states near the Fermi level in the partly filled band.

Although the possession of a partly full band provides an explanation of electronic conductivity, it does not explain all the features of this phenomenon. For example, it does not account for the finite resistance of metals. The current, I , flowing through a metal for a given applied electric field, V , is given by **Ohm's law**, $V = IR$, where R is the resistance. It is characteristic of a metal that R increases with increasing temperature (or putting it another way, σ decreases with increasing temperature), i.e. for a given field, the current decreases as the temperature is raised. There is nothing in our theory yet that will impede the flow of electrons. To account for electrical resistance it is necessary to introduce the ionic cores. If these were arranged periodically on the lattice sites of a perfect crystal and did not move, they would not interrupt the flow of electrons. Most crystals contain some imperfections however and these can scatter the electrons. If the component of the electron's momentum in the field direction is reduced then the current will drop. In addition, even in perfect crystals the ionic cores will be vibrating. There are a set of crystal vibrations in which the ionic cores vibrate together. These vibrations are called **phonons**. An example of a crystal vibrational mode would be one in which each ionic core would be moving out of phase with its neighbours along one axis. (If they moved in phase, the whole crystal would move.) Like vibrations in small molecules, each crystal vibration has its set of quantized vibrational levels. The conduction electrons moving through the crystal are scattered by the vibrating ionic cores and lose some energy to the phonons. As well as reducing the electron flow, this mechanism increases the crystal's vibrational energy. The effect then is to convert electrical energy to heat. This ohmic heating effect is put to good use in, for example, the heating elements of kettles.

4.4 SEMICONDUCTORS – SILICON AND GERMANIUM

Carbon (as diamond polymorph), silicon and germanium, instead of forming structures of high coordination like the simple metals, form structures in which the atoms are tetrahedrally coordinated. With these structures, the ns and np bands still overlap but the ns/np band splits into two. Each of the two bands contains $2N$ orbitals and so can accommodate up to $4N$ electrons. Think of the two bands as an analogy of bonding and anti-bonding; the tetrahedral symmetry not giving rise to any non-bonding orbitals. Carbon, silicon and germanium have electronic configurations $ns^2 np^2$ and so they have available $4N$ electrons, just the right number to fill the lower band. This lower band is known as the **valence**

band, the electrons in this band essentially bonding the atoms in the solid together.

Why do these elements adopt the tetrahedral structure rather than one of the higher coordination structures? Well, if these elements adopted a structure like that of the simple metals, then the ns/np band would be half full. The electrons in the highest occupied levels would be virtually non-bonding. In the tetrahedral structure, however, all $4N$ electrons would be in bonding levels. This is illustrated in Figure 4.7. Elements with few valence electrons will thus be expected to adopt high coordination structures and be metallic. Those with larger numbers (four or more) will be expected to adopt lower coordination structures in which the ns/np band is split and only the lower bonding band is occupied.

Tin (in its most stable room temperature form) and lead, although in the same group as silicon and germanium, are metals. For these elements the atomic s - p energy separation is greater and the overlap of s and p orbitals is much less than in silicon and germanium. For tin the tetrahedral structure would have two s/p bands but the band gap is almost zero. Below 291 K tin undergoes a transition to the diamond structure, but above this temperature it is more stable for tin to adopt a higher coordination structure. The advantage of having no non-bonding levels in the diamond structure is reduced by the small band gap. In lead the diamond structure would give rise to an s band and a p band rather than ns/np bands since the overlap of s and p orbitals is even smaller. It is more favourable for lead to adopt a cubic close-packed structure and, because lead has only $2N$ electrons to go in the p band, it is metallic. This

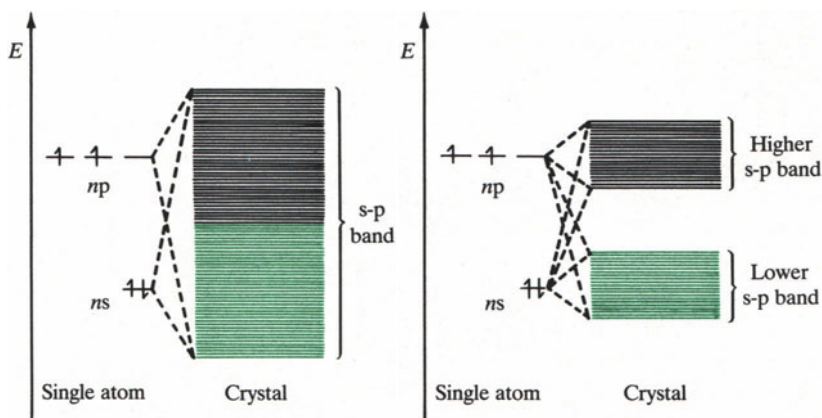


Figure 4.7 Energy bands formed from ns and np atomic orbitals for (a) a body-centred cubic crystal and (b) a crystal of diamond structure, showing filled levels for $4N$ electrons.

is an example of the **inert pair effect**, in which the s electrons act as core electrons, on the chemistry of lead. Another example is the formation of divalent ionic compounds containing Pb^{2+} rather than tetravalent covalent compounds like those of silicon and germanium.

Silicon and germanium have a completely full valence band and would be expected to be insulators. They do, however, belong to a class of materials known as **semiconductors**.

The conductivity of metallic conductors decreases with temperature. As the temperature is raised the phonons gain energy; the lattice vibrations have larger amplitudes. The displacement of the ionic cores from their lattice sites is thus greater and the electrons are scattered more, reducing the net current, by reducing the mobility, μ , of the electrons.

The conductivity of **intrinsic semiconductors** such as silicon or germanium, however, *increases* with temperature. In these solids, conduction can only occur if electrons are promoted to the higher s/p band, the **conduction band**, because only then will there be a partially full band. The current in semiconductors will depend on the number of electrons free to transport charge. This is the number of electrons promoted to the conduction band plus the number in the valence band that have been freed to move by this promotion. As the temperature increases, the number of electrons promoted increases and so the current increases. At any one temperature more electrons will be promoted for a solid with a small band gap than for one with a large band gap so that the solid with the smaller band gap will be a better conductor. The number of electrons promoted varies with temperature in an exponential manner so that, for example, in germanium which has a band gap 10 times smaller than diamond, of the order of 10^{91} more electrons are promoted than in diamond. Germanium has an electrical resistivity of $0.46 \Omega \text{ m}$ at room temperature compared to that of a typical insulator of around $10^{12} \Omega \text{ m}$.

4.4.1 Photoconductivity

Electrons can also be promoted by forms of energy other than heat energy, e.g. light. If the photon energy ($h\nu$) of light shining on a semiconductor is greater than the energy of the band gap, then valence band electrons will be promoted to the conduction band and conductivity will increase. Promotion of electrons by light is illustrated in Figure 4.8.

Semiconductors with band gap energies corresponding to photons of visible light are **photoconductors**, being essentially non-conducting in the dark but conducting electricity in the light. One use of such photoconductors is in **electrophotography**. In the xerographic process there is a positively charged plate covered with a film of semiconductor. (In practice this semiconductor is not silicon but a solid with a more suitable energy band gap such as selenium or the compound As_2Se_3 .) Light reflected

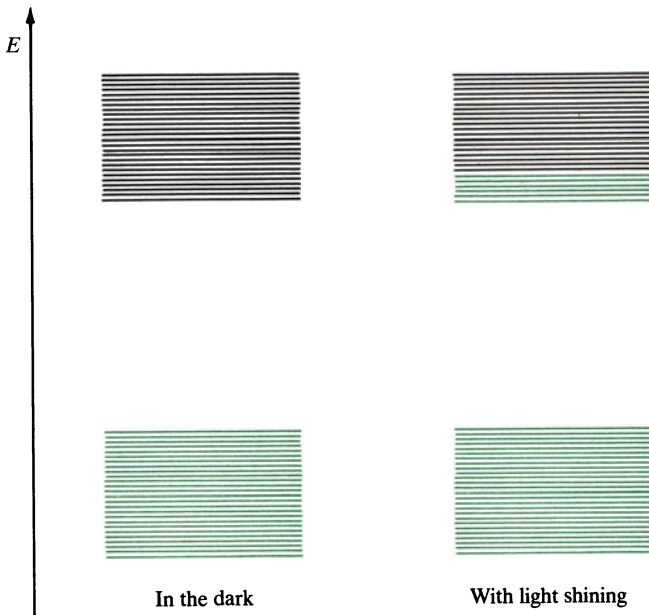


Figure 4.8 Promotion of electrons from the valence to the conduction band by light.

from the white parts of the page to be copied hits the semiconductor film. The parts of the film receiving the light become conducting; an electron is promoted to the conduction band. This electron then cancels the positive charge on the film, the positive hole in the valence band being removed by an electron from the metal backing plate entering the valence band. Now the parts of the film which received light from the original are no longer charged, but the parts underneath the black lines are still positively charged. Tiny negatively charged plastic capsules of ink (toner) are then spread on to the semiconductor film but only stick to the charged bits of the film. A piece of positively charged white paper removes the toner from the semiconductor film and hence acquires an image of the black parts of the original. Finally, the paper is heated to melt the plastic coating and fix the ink.

4.5 DOPED SEMICONDUCTORS

The conductivity of semiconductors can also be increased by introducing a very low concentration of impurity. Such semiconductors are known as doped or extrinsic semiconductors. Consider a crystal of silicon contain-

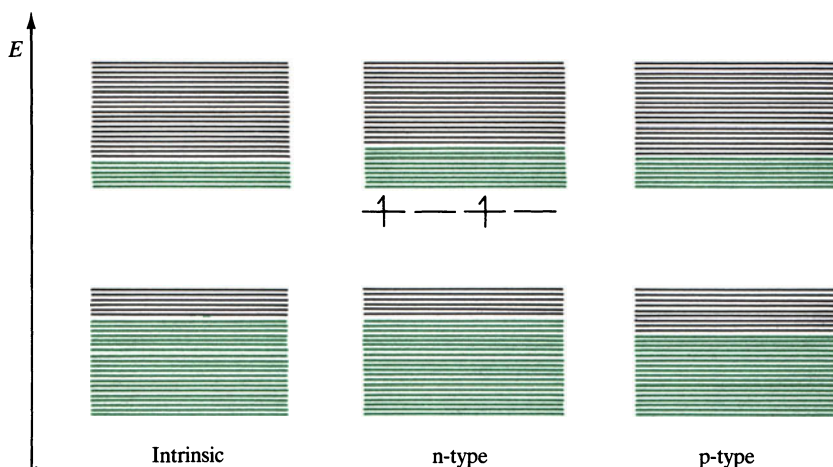


Figure 4.9 Intrinsic, *n*-type and *p*-type semiconductors showing negative charge carriers (electrons in the conduction band) and positive holes.

ing boron as an impurity. Boron has one fewer valence electron than silicon and so for every silicon replaced by boron there is an electron missing from the valence band (Figure 4.9), i.e. there are positive holes in the valence band and these enable electrons near the top of the band to conduct electricity. So the doped solid will be a better conductor than pure silicon. A semiconductor like this doped with an element with fewer valence electrons than the bulk of the material is called a ***p*-type semiconductor** because its conductivity is related to the number of positive holes produced by the impurity.

Suppose instead of boron the silicon was doped with an element with more valence electrons than silicon, e.g. phosphorus. The doping atoms form a set of energy levels that lie in the band gap between the valence and conduction bands. Since the atoms have more valence electrons than silicon, these energy levels are filled. There are therefore electrons present close to the bottom of the conduction band and easily promoted into the band. This time the conductivity increases because of extra electrons entering the conduction band. Such semiconductors are called ***n*-type**; *n* for negative charge carriers or electrons. Figure 4.9 shows schematically energy bands in intrinsic, *p*-type and *n*-type semiconductors.

n- and *p*-type semiconductors in various combinations make up many electronic devices. Rectifiers, field-effect transistors, photo-voltaic cells and light-emitting diodes are made from a crystal doped to be partly *n*- and partly *p*-type. Early transistors were made from *n*-*p*-*n* or *p*-*n*-*p* sandwiches. Other devices use mixtures of *p*- and/or *n*-type semiconductor with metal and insulator layers to produce the required properties.

In the next section we consider what happens at the junction of two differently doped regions, and how such a junction is used as the basis of solar cells.

4.5.1 The p – n junction – photovoltaic (solar) cells

In the region of the crystal (or glass) where n - and p -type meet, there is a discontinuity in electron concentration. Although both n - and p -type are electrically neutral, the n -type has a greater concentration of electrons than the p -type. In order to try and equalize the electron concentrations electrons drift from n - to p -type. However, this produces a positive electric charge on the n -type and a negative electric charge on the p -type. The electric field thus set up encourages electrons to drift back to the n -type. Eventually a state is reached in which the two forces are balanced and the electron concentration varies smoothly across the junction as in Figure 4.10.

This is the situation in the dark. The use of the p – n junction as a solar cell depends on its response to light. If the wavelength is short enough for the photon energy to be greater than the band gap energy then electrons will be promoted across the band gap to the conduction band. The promoted electron will be attracted to the positively charged n -type region. The gap in the valence band will move to the p -type region because an electron from this side would be attracted across to the n -type region to fill any hole there. The promoted electron and the hole are now separated in space and so the conduction electron cannot simply emit light and return to the valence band. It is free, however, to travel through the n -type to an external circuit. The electric current thus produced can be used to do work; the illuminated p – n junction is acting as a battery. Such cells using sunlight as the source of illumination have found widespread application, although their efficiency is not high. They can be used for pocket calculators, for lighting homes and shops in remote areas, and in desert areas even for large-scale power generation. They are attractive because sunlight is a clean, cheap source of power. Semiconductors for these devices need a band gap in or slightly below the range of energies of visible light photons ($2.4 - 5.0 \times 10^{-19}$ J). Silicon has a band gap of 1.9×10^{-19} J and so can use all wavelengths of visible light.

4.6 BANDS IN COMPOUNDS – GALLIUM ARSENIDE

Gallium arsenide (GaAs) is a rival to silicon in some semiconductor applications, including solar cells, and is also used for light-emitting diodes and in a solid state laser (Chapter 8). It has a diamond-type structure and is similar to silicon except that it is composed of two kinds

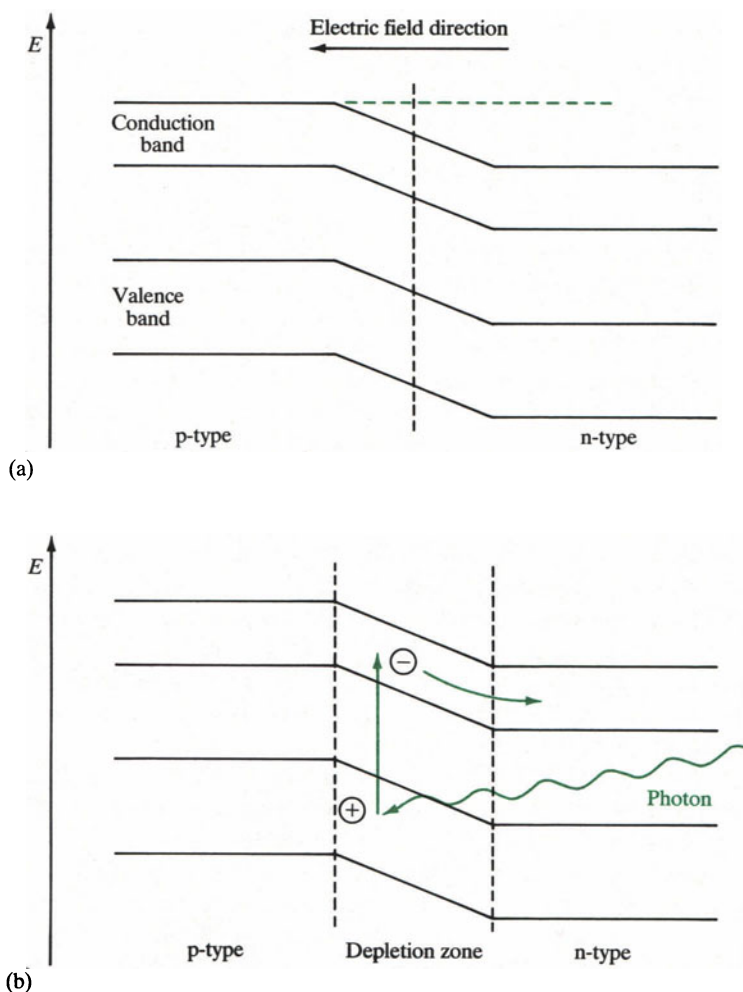


Figure 4.10 (a) Bending of energy levels across a p - n junction and (b) the effect of light on a p - n junction.

of atoms. The valence orbitals in Ga and As are the $4s$ and $4p$ and these will form two bands, each containing $4N$ electrons as in silicon. Because of the different $4s$ and $4p$ atomic orbital energies in Ga and As, however, the lower band will have a greater contribution from As and the conduction band will have a higher contribution from Ga. Thus GaAs can be thought of as having partial ionic character because there is a partial transfer of electrons from Ga to As. The valence band has more As than Ga character and so all the valence electrons end up in orbitals in which the possibility of being near an As nucleus is greater than that of being

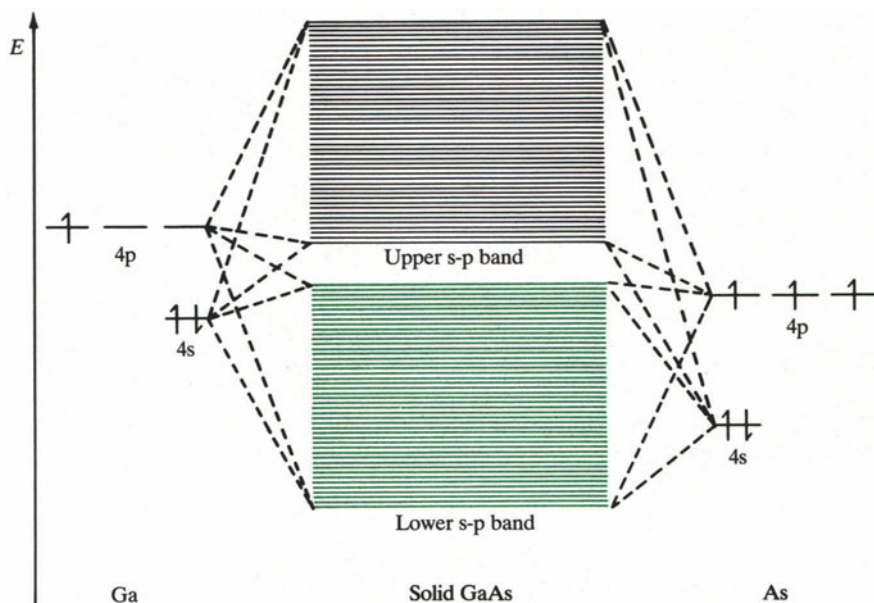


Figure 4.11 Orbital energy level diagram for gallium arsenide.

near a Ga nucleus. The band energy diagram for GaAs is shown in Figure 4.11. GaAs is an example of a class of semiconductors known as III/V semiconductors in which an element with one more valence electron than the silicon group is combined with an element with one less valence electron. Many of these compounds are semiconductors, e.g. GaSb, InP, InAs and InSb. Moving further along the Periodic Table there are II/VI semiconductors such as CdTe and ZnS. Towards the top of the Periodic Table and further out towards the edges, e.g. AlN and AgCl, the solids tend to adopt different structures and become more ionic. For the semiconducting solids the band gap decreases down a group, e.g. GaP > GaAs > GaSb and AlAs > GaAs > InAs.

4.6.1 Semiconductor – liquid junction cells

n-Doped GaAs has been used in an interesting variant of the photovoltaic cell; the semiconductor–liquid junction cell. In these cells the electric field is produced not where the *n*- and *p*-type semiconductors meet but where the *n*-type meets a liquid electrolyte. The cell consists of an electrolyte solution into which dip two electrodes, the *n*-type semiconductor and a metal electrode. When light shines on the *n*-GaAs, an electron is promoted to the conduction band, leaving a hole in the

valence band. The conduction electron drifts towards the bulk of the semiconductor but the hole drifts towards the electrolyte. In the electrolyte solution is an ion that can exist in oxidized and reduced forms, e.g. $\text{Fe}^{2+}/\text{Fe}^{3+}$ or I^-/I . The hole in the valence band is filled by an electron from the reduced form of the ion, the ion being oxidized. Reduction of the ion back to its reduced form takes place at the metal electrode and the circuit is completed by electrons travelling through the external circuit from the semiconductor to the metal. The electrons in the external circuit can do work and so the net result is that light is converted to electrical energy. Examples of electrolyte solutions that have been used include aqueous $\text{Se}^{2-}/\text{Se}_n^{2-}$ and ferrocene/ferrocinium in acetonitrile.

4.7 BANDS IN *d*-BLOCK COMPOUNDS – TRANSITION METAL MONOXIDES

Monoxides (MO) with structures based on sodium chloride¹ are formed by the first row transition elements Ti, V, Mn, Fe, Co and Ni. TiO and VO are metallic conductors, and the others are semiconductors. The O $2p$ orbitals form a filled valence band. The $4s$ orbitals on the metal form another band. What of the $3d$ orbitals?

In the sodium chloride structure, the symmetry enables three of the five d orbitals on different metal atoms to overlap. Because the atoms are not nearest neighbours, the overlap is not as large as in pure metals and the bands are thus narrow. The other two d orbitals overlap with orbitals on the adjacent oxygens. There are thus two narrow $3d$ bands, the lower one, labelled t_{2g} , can take up to $6N$ electrons and the upper one, labelled e_g , up to $4N$ electrons. Divalent titanium has two d electrons and so there are $2N$ electrons to fill the $3N$ levels of the lower band. As in the case of pure metals, a partly filled band leads to metallic conductivity. However, on this basis one would expect MnO, CoO and NiO, which also have partly filled bands, to be metallic. These oxides are semiconductors though.

Going across the first transition series, there is a contraction in the size of the $3d$ orbitals. $3d$ orbital overlap therefore decreases and the $3d$ band narrows. In a wide band such as the s/p bands of the alkali metals, the electrons are essentially free to move through the crystal keeping away from the nuclei and from each other. In a narrow band, by contrast, the electrons are more tightly bound to the nuclei. Interelectron repulsion becomes important; in particular, repulsion between electrons on the same atom. Consider an electron in a partly filled band moving from one nucleus to another. In an alkali metal, the electron would already be in

¹ As explained in Chapter 5, TiO and VO have structures based on sodium chloride but with $\frac{1}{2}$ of each element missing in an ordered manner. The other oxides, when stoichiometric, adopt the sodium chloride structure.

the sphere of influence of surrounding nuclei and would not be greatly repelled by electrons on these nuclei. The $3d$ electron moving from one nucleus to another adds an extra electron near to the second nucleus which already has $3d$ electron density near it. Thus electron repulsion on the nucleus is increased. For narrow bands, therefore, we have to balance gains in energy on band formation against electron repulsion. For MnO , FeO , CoO and NiO electron repulsion wins and it becomes more favourable for the $3d$ electrons to remain in localized orbitals than to be delocalized.

The band gap between the oxygen $2p$ band and the metal $4s$ band is sufficiently wide that the pure oxides would be considered insulators. However, they are almost invariably found to be non-stoichiometric, i.e.

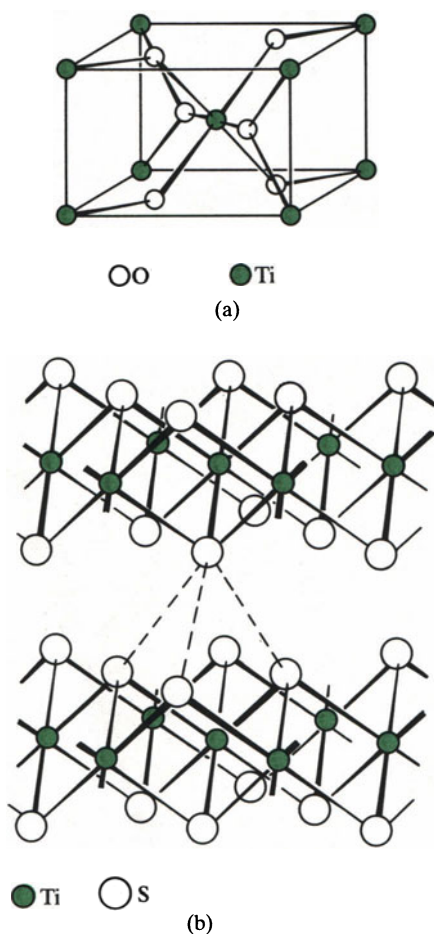


Figure 4.12 Crystal structures of (a) TiO_2 and (b) TiS_2 .

their formulae are not exactly MO , and this leads to semiconducting properties which will be discussed in Chapter 5.

4.7.1 Titanium dioxide and disulphide

The monoxides are not unique in displaying a variation of properties across the transition series. The dioxides form another series and CrO_2 will be discussed later because of its magnetic properties. Several classes of mixed oxides also exhibit a range of electronic properties (e.g. the perovskites LaTiO_3 , SrVO_3 and LaNiO_3 are metallic conductors, LaRhO_3 is a semiconductor and LaMnO_3 is an insulator). Sulphides also show progression from metal to insulator. In general, compounds with broader d bands will be metallic. Broad bands will tend to occur for elements at the beginning of the transition series and for second and third row metals, e.g. NbO and WO_2 . Metallic behaviour is also more common amongst lower oxidation state compounds and with less electronegative anions.

The influence of the anion is illustrated by comparing TiO_2 with TiS_2 . TiO_2 has the rutile structure (Figure 4.12) and is an insulator with a band gap energy just outside the range of photon energies for visible light. n -Doped TiO_2 finds use as a semiconductor, for example, in liquid junction photovoltaic cells. TiS_2 has a different layer structure (CdI_2 type) and is a semiconductor.

The band diagram for TiO_2 is shown in Figure 4.13. The O $2p$ band is

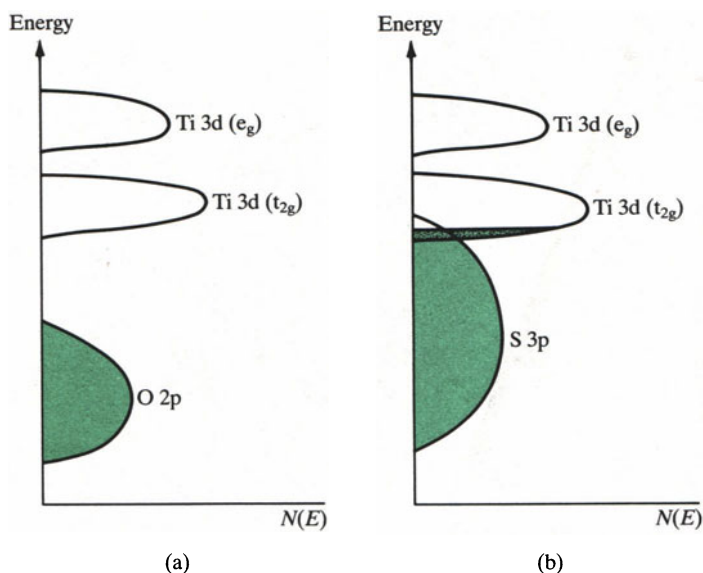


Figure 4.13 Energy bands for (a) TiO_2 and (b) TiS_2 .

full and the $3d(t_{2g})$ band empty. The $3d$ energy levels are delocalized and so the lower $3d$ band forms the conduction band. In TiS_2 the overlap of S and Ti orbitals is greater than that of O and Ti orbitals in TiO_2 and the greater width of the S $3p$ band combined with the smaller S $3p/\text{Ti } 3d$ energy gap means that the $3p$ band is very close to the $3d$ band. The bands either just overlap or are separated by a very small band gap. Since the valence band electrons are thus very easily promoted, the conductivity is much higher than that of a wide band gap semiconductor. Close to a band edge, however, there are relatively few orbitals and hence relatively few electrons available for promotion. Consequently the conductivity is not as high as that of a typical metal.

FURTHER READING

Moore, W.J. (1967) *Seven Solid States*, Chapters II and III, W.A. Benjamin Inc. *Although rather dated, this is an unusual and generally very readable book. Much of it is at introductory level and the style is attractive. In the Silicon chapter, the preparative methods need updating, but the description and basic theory of semiconductors are still very relevant.*

McWeeny, R. (1979) *Coulson's Valence*, Oxford University Press, Oxford. *This well known and standard textbook on quantum chemistry contains a good chapter on band theory from a chemists point of view.*

Cox, P.A. (1987) *Electronic Structure and Chemistry of Solids*, Chapters 1, 4 and 7, Oxford University Press, Oxford. *A good book on solid state theory for chemists at a higher level.*

West, A.R. (1988) *Basic Solid State Chemistry*, Chapters 2 and 7, John Wiley, New York.

This book is a more compact version of the author's Solid State Chemistry and its Applications. Chapter 2 is a survey of types of bonding in solids, but with little detail. Chapter 7 deals with electrical properties mainly from a phenomenological and applications point of view and covers material relevant to Chapters 5 and 9 as well as to this chapter.

Duffy, J.A. (1990) *Bonding, Energy Levels and Bands in Inorganic Solids*, Chapters 4 and 7, Longman, London.

This book is at a fairly advanced level, but is written from a chemist's point of view. Although containing material relevant to this chapter, it is at its most original and useful in its approach to optical properties.

Rosenberg, H.M. (1989) *The Solid State*, Chapters 7–10, Oxford University Press, Oxford.

An elementary solid state physics book. It is one of the most accessible of the solid state texts written for physicists.

Kittel, C. (1986) *Introduction to Solid State Physics*, John Wiley, New York.

A standard text for physics courses.

QUESTIONS

1. In the free electron model, the electron energy is entirely kinetic. Using the formula $E = \frac{1}{2}mv^2$, calculate the velocity of electrons at the Fermi level in sodium metal (Figure 4.3). The mass of an electron is 9.11×10^{-31} kg.
2. The density of sodium metal is 970 kg m^{-3} . A typical crystal has a volume of 10^{-12} m^3 (corresponding to a cube of side 0.1 cm). How many atoms would such a crystal contain? The relative atomic mass of sodium is 23.
3. An estimate of the total number of occupied states can be obtained by integrating the density of states from 0 to the Fermi level.

$$\begin{aligned}
 N &= \int_0^{E_F} N(E) dE = \int_0^{E_F} E^{1/2} (2m_e)^{3/2} V / (2\pi^2 \hbar^3) dE \\
 &= (2m_e E_F)^{3/2} V / 3\pi^2 \hbar^3.
 \end{aligned}$$

Calculate the total number of occupied states for a sodium crystal of volume (a) 10^{-12} m^3 , (b) 10^{-6} m^3 and (c) 10^{-29} m^3 (approximately atomic size). Compare your results with the number of electrons available and comment on the different answers to (a), (b) and (c). $E_F = 2.8 \text{ eV}$ for sodium, and $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$.

4. The energy associated with one photon of visible light ranges from 2.4 to $5.0 \times 10^{-19} \text{ J}$. The band gap in selenium is $2.9 \times 10^{-19} \text{ J}$. Explain why selenium is a good material to use as a photoconductor in applications such as photocopyers.
5. The band gaps of several semiconductors and insulators are given below. Which substances would be photoconductors over the entire range of visible wavelengths?

Substance	Si	Ge	CdS
Band gap (10^{-19} J)	1.9	1.3	3.8

6. Which of the following doped semiconductors will be *p*-type and which will be *n*-type? (a) Arsenic in germanium, (b) germanium in silicon, (c) indium in germanium, (d) boron in indium antimonide (InSb).
7. Would you expect carborundum (SiC) to adopt a diamond structure or one of higher coordination? Explain why.

Defects and non-stoichiometry

5

5.1 INTRODUCTION

In a perfect crystal all atoms would be on their correct lattice positions in the structure. This situation can only exist at the absolute zero of temperature, 0 K. Above 0 K **defects** occur in the structure. These defects may be **extended defects** such as **dislocations**. The strength of a material depends very much on the presence (or absence) of extended defects such as dislocations and **grain boundaries** but discussion of this type of phenomenon lies very much in the realm of materials science and will not be discussed in this book. Defects can also occur at isolated atomic positions; these are known as **point defects**, and can be due to the presence of a foreign atom at a particular site or to a vacancy where normally one would expect an atom. Point defects can have significant effects on the chemical and physical properties of the solid. The beautiful colours of many gemstones are due to impurity atoms in the crystal structure. Ionic solids are able to conduct electricity by a mechanism which is due to the presence of vacant ion sites within the lattice (this is in contrast to the electronic conductivity explored in Chapter 4).

5.2 DEFECTS AND THEIR CONCENTRATION

Defects fall into two main categories: **intrinsic defects** which are integral to the crystal in question – they do not change the overall composition and because of this are also known as **stoichiometric defects**; and **extrinsic defects** which are created when a foreign atom is inserted into the lattice.

5.2.1 Intrinsic defects

Intrinsic defects fall into two categories: **Schottky defects**, which consist of vacancies in the lattice and **Frenkel defects** where a vacancy is created by an atom or ion moving into an interstitial position.

For a 1:1 solid MX, a Schottky defect consists of a *pair* of vacant sites, a cation vacancy and an anion vacancy. This is shown in Figure 5.1a for an alkali-halide-type structure: the number of cation vacancies and anion vacancies have to be equal in order to preserve electrical neutrality. A Schottky defect for an MX_2 -type structure will consist of the vacancy caused by the M^{2+} ion together with *two* X^- anion vacancies, thereby balancing the electrical charges. Schottky defects are more common in 1:1 stoichiometry and examples of crystals that contain them include rock salt (NaCl), wurtzite (ZnS) and CsCl.

A Frenkel defect usually only occurs on one **sublattice** of a crystal, and consists of an atom or ion moving into an interstitial position thereby creating a vacancy. This is illustrated in Figure 5.1c for an alkali-halide-type structure such as NaCl, where one cation is shown as having moved out of the lattice and into an interstitial site. This type of behaviour is seen, for instance, in AgCl where we observe such a **cation Frenkel defect** when Ag^+ ions move from their octahedral coordination sites into tetrahedral coordination (Figure 5.2). The formation of this type of defect is important in the photographic process when they are formed in the light-sensitive AgBr used in the photographic emulsions.

It is less common to observe an **anion Frenkel defect** when an anion moves into an interstitial site. This is because anions are commonly larger than the cations in the structure and so it is more difficult for them to enter a crowded low-coordination interstitial site.

An important exception to this generalization lies in the formation of anion Frenkel defects in compounds with the fluorite structure, such as

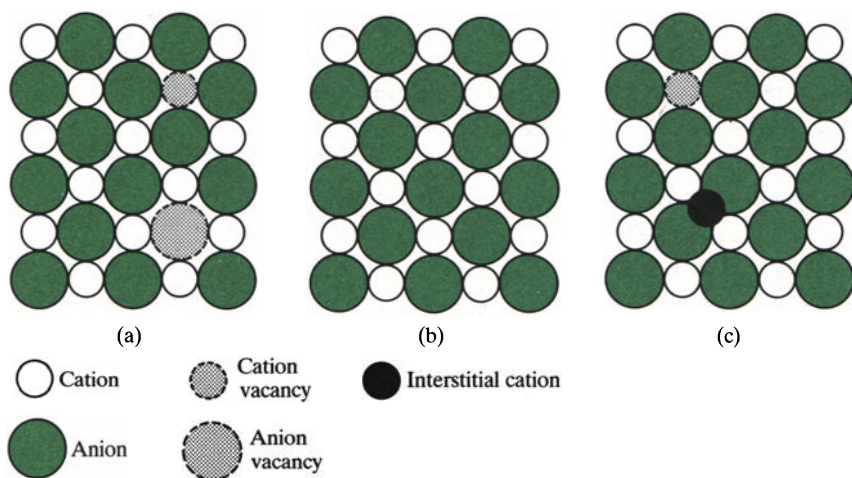


Figure 5.1 Schematic illustration of intrinsic point defects in a crystal of composition MX: (a) Schottky pair; (b) perfect crystal; (c) Frenkel pair.

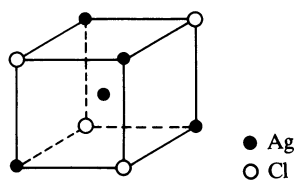


Figure 5.2 The tetrahedral coordination of an interstitial Ag^+ ion in AgCl .

CaF_2 (other compounds adopting this structure are strontium and lead fluorides (SrF_2 , PbF_2) and thorium, uranium and zirconium oxides (ThO_2 , UO_2 , ZrO_2) which we meet again later in this chapter). One reason for this is that the anions have a lower electrical charge than the cations and so do not find it as difficult to move nearer each other. The other reason lies in the nature of the fluorite structure (Figure 5.3). Recall that we can think of it as based on a *ccp* array of Ca^{2+} ions with all the tetrahedral holes occupied by the F^- ions. This of course leaves all of the larger octahedral holes unoccupied – at the centre of the cube in Figure 5.3a – giving a very open structure. This is shown clearly if we redraw the structure as in Figure 5.3c based on a simple cubic array of F^- ions. The unit cell now consists of eight small **octants** with the Ca^{2+} ions only occupying every other octant. The two different views are completely equivalent, but the cell shown in Figure 5.3c shows the possible interstitial sites in the unoccupied octants very clearly.

5.2.2 The concentration of defects

Energy is required to form a defect: this means that the formation of defects is always an **endothermic process**. It may seem surprising that defects exist in crystals at all, and yet they do, even at low temperatures, albeit in very small concentrations. The reason for this is that the formation of defects produces a commensurate gain in entropy. The enthalpy of formation of the defects is thus balanced by the gain in entropy such that, at equilibrium, the overall change in free energy of the crystal due to the defect formation is zero according to the equation

$$\Delta G = \Delta H - T\Delta S.$$

The interesting point is that thermodynamically we do not expect a crystalline solid to be perfect, contrary, perhaps to our ‘commonsense’ expectation of symmetry and order! At any particular temperature there will be an equilibrium population of defects in the crystal.

The number of Schottky defects in a crystal of composition MX is given by

$$n_s \approx N \exp(-\Delta H_s/2kT), \quad (5.1)$$

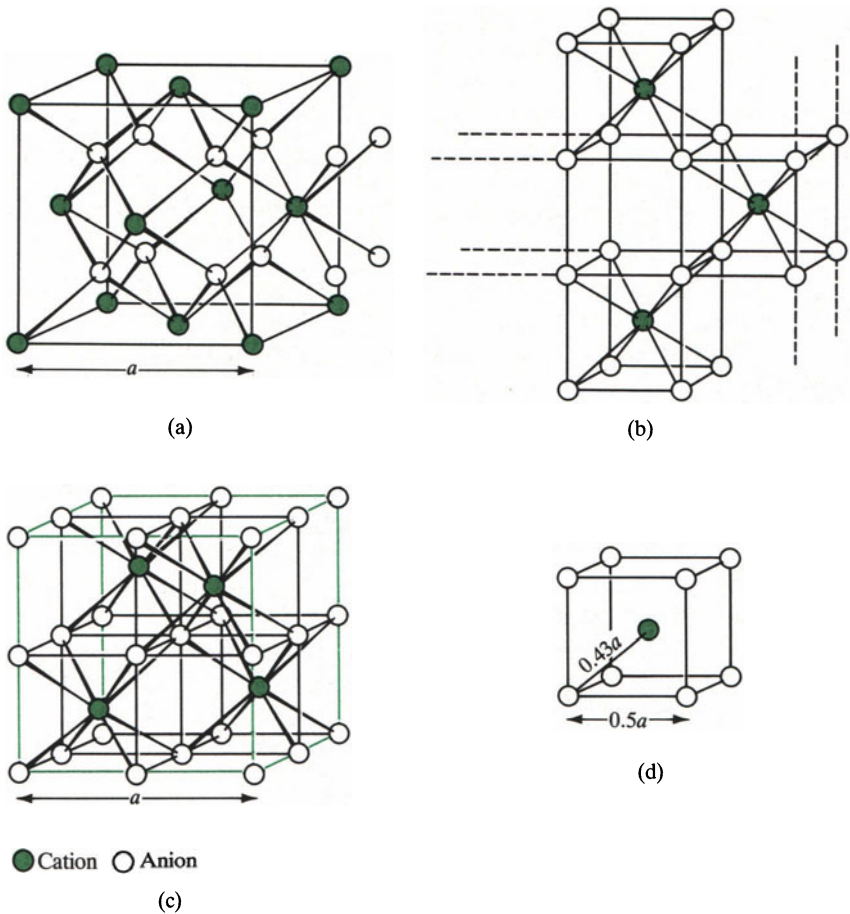


Figure 5.3 The crystal structure of fluorite MX_2 . (a) Unit cell as a *ccp* array of cations. (b) and (c) The same structure redrawn as a simple cubic array of anions: the unit cell is marked by a coloured outline in (c). (d) Cell dimensions.

where n_s is the number of Schottky defects per unit volume, at TK , in a crystal with N cation and N anion sites per unit volume, k is the Boltzmann constant; ΔH_s is the enthalpy required to form one defect. It is quite a simple matter to derive these equations for the equilibrium concentration of Schottky defects by considering the change in entropy of a perfect crystal due to the introduction of defects. The change in entropy will be due to the vibrations of atoms around the defects and also to the arrangement of the defects. It is possible to estimate this latter quantity, the **configurational entropy**, using the methods of statistical mechanics.

If the number of Schottky defects is n_s per unit volume at TK , then there will be n_s cation vacancies and n_s anion vacancies in a crystal

containing N possible cation sites and N possible anion sites per unit volume. The **Boltzmann formula** tells us that the entropy of such a system is given by

$$S = k \ln W, \quad (5.2)$$

where W is the number of ways of distributing n_s defects over N possible sites at random, and k is the Boltzmann constant ($1.380\,622 \times 10^{-23} \text{ J K}^{-1}$). Probability theory shows that W is given by

$$W = \frac{N!}{(N - n)!n!} \quad (5.3)$$

where $N!$ is called 'factorial N ' and is mathematical shorthand for

$$N \times (N - 1) \times (N - 2) \times (N - 3) \dots \times 1.$$

So, the number of ways we can distribute the cation vacancies will be

$$W_c = \frac{N!}{(N - n_s)!n_s!}$$

and similarly for the anion vacancies

$$W_a = \frac{N!}{(N - n_s)!n_s!}$$

The total number of ways of distributing these defects, W , is given by the product of W_c and W_a :

$$W = W_c W_a$$

and the change in entropy due to introducing the defects into a perfect crystal is thus

$$\begin{aligned} \Delta S &= k \ln W = k \ln \left(\frac{N!}{(N - n_s)!n_s!} \right)^2 \\ &= 2k \ln \frac{N!}{(N - n_s)!n_s!} \end{aligned}$$

We can simplify this expression using **Stirling's approximation** that

$$\ln N! \approx N \ln N - N$$

and the expression becomes (after manipulation)

$$\Delta S = 2k \{N \ln N - (N - n_s) \ln (N - n_s) - n_s \ln n_s\}.$$

If the enthalpy change for the formation of a single defect is ΔH_s and we assume that the enthalpy change for the formation of n_s defects is $n_s \Delta H_s$, then the Gibbs free energy change is given by

$$\Delta G = n_s \Delta H_s - 2kT \{N \ln N - (N - n_s) \ln (N - n_s) - n_s \ln n_s\}.$$

At equilibrium, at constant T , the Gibbs free energy of the system must be a minimum with respect to changes in the number of defects n_S ; thus

$$\left(\frac{d\Delta G}{dn_S}\right) = 0.$$

So,

$$\Delta H_S - 2kT \frac{d}{dn_S} [N \ln N - (N - n_S) \ln(N - n_S) - n_S \ln n_S] = 0.$$

$N \ln N$ is a constant and hence its differential is zero; the differential of $\ln x$ is $1/x$ and of $(x \ln x)$ is $(1 + \ln x)$. On differentiating we get

$$\Delta H_S - 2kT [\ln(N - n_S) + 1 - \ln n_S - 1] = 0,$$

hence

$$\Delta H_S = 2kT \ln \left[\frac{(N - n_S)}{n_S} \right]$$

and

$$n_S = (N - n_S) \exp(-\Delta H_S/2kT)$$

as $N \gg n_S$ we can approximate $(N - n_S)$ by N , finally giving

$$n_S = N \exp(-\Delta H_S/2kT). \quad (5.1)$$

If we express this equation in molar quantities it becomes

$$n_S \approx N \exp(-\Delta H_S/2RT), \quad (5.4)$$

where now ΔH_S is the enthalpy required to form one mole of Schottky defects and R is the gas constant, $8.314 \text{ J K mol}^{-1}$: the units of ΔH_S are J mol^{-1} .

By a similar analysis we find that the number of Frenkel defects present in a crystal MX is given by the expression

$$n_F = (NN_i)^{1/2} \exp(-\Delta H_F/2kT) \quad (5.5)$$

where n_F is the number of Frenkel defects per unit volume, N is the number of lattice sites and N_i the number of interstitial sites available. ΔH_F is the enthalpy of formation of one Frenkel defect. If ΔH_F is the enthalpy of formation of one mole of Frenkel defects the expression becomes

$$n_F = (NN_i)^{1/2} \exp(-\Delta H_F/2RT). \quad (5.6)$$

Table 5.1 lists some enthalpy of formation values for Schottky and Frenkel defects in various crystals.

Table 5.1 The formation enthalpy of Schottky and Frenkel defects in some selected compounds

	<i>Compound</i>	$\Delta H(10^{-19} \text{ J})$	$\Delta H(\text{eV})^*$
Schottky defects	MgO	10.57	6.60
	CaO	9.77	6.10
	LiF	3.75	2.34
	LiCl	3.40	2.12
	LiBr	2.88	1.80
	LiI	2.08	1.30
	NaCl	3.69	2.30
	KCl	3.62	2.26
Frenkel defects	UO ₂	5.45	3.40
	ZrO ₂	6.57	4.10
	CaF ₂	4.49	2.80
	SrF ₂	1.12	0.70
	AgCl	2.56	1.60
	AgBr	1.92	1.20
	β -AgI	1.12	0.70

*The literature often quotes values in eV, so these are included for comparison: $1 \text{ eV} = 1.60219 \times 10^{-19} \text{ J}$.

Using the information in Table 5.1 and equation (5.1), we can now get an idea of how many defects are present in a crystal. Assume that ΔH_S has a middle of the range value of $5 \times 10^{-19} \text{ J}$. Substituting in equation (5.1) we find that the proportion of vacant sites n_s/N at 300 K is 6.12×10^{-27} ; at 1000 K this rises to 1.37×10^{-8} . This shows what a low concentration of Schottky defects is present at room temperature. Even when the temperature is raised to 1000 K we still find only of the order of one or two vacancies per hundred million sites!

Whether Schottky or Frenkel defects are found in a crystal depends in the main on the value of ΔH , the defect with the lower ΔH value predominating. In some crystals it is possible for both types of defect to be present.

We will see in a later section that in order to change the properties of crystals, particularly their ionic conductivity, we may wish to introduce more defects into the crystal. It is important, therefore, at this stage to consider how this might be done.

First, we have seen from the above calculation that raising the temperature introduces more defects. We would have expected this to happen because defect formation is an endothermic process and **Le Chatelier's principle** tells us that increasing the temperature of an endothermic reaction will favour the products, in this case defects. Second, if it were possible to decrease the enthalpy of formation of a defect, ΔH_S or ΔH_F , this would also increase the proportion of defects present. A simple

Table 5.2 Values of n_s/N

$T(K)$	$\Delta H_s = 5 \times 10^{-19} J$	$\Delta H_s = 1 \times 10^{-19} J$
300	6.12×10^{-27}	5.72×10^{-6}
1000	1.37×10^{-8}	2.67×10^{-2}

calculation, again using equation (5.1), but now with a lower value for ΔH_s , say $1 \times 10^{-19} J$, allows us to see this. Table 5.2 compares the results. This has had a dramatic effect on the numbers of defects! At 1000 K we are now finding of the order of three in every hundred. It is difficult to see how the value of ΔH could be manipulated within a crystal, but we do find crystals where the value of ΔH is lower than usual due to the nature of the structure, and this can be exploited. This is true for one of the systems that we shall look at in detail later, α -AgI. Third, if we introduce impurities into a crystal selectively we can increase the defect population.

5.2.3 Extrinsic defects

We can introduce vacancies into a crystal by **doping** it with a selected impurity: for instance if we add CaCl_2 to a NaCl crystal, each Ca^{2+} ion replaces two Na^+ ions in order to preserve electrical neutrality, and so one cation vacancy is created. Such created vacancies are known as **extrinsic**. An important example found later in this chapter is that of **zirconia** (ZrO_2); this structure can be stabilized by doping with CaO , when the Ca^{2+} ions replace the Zr(IV) atoms in the lattice. The charge compensation in this case is achieved by the production of anion vacancies on the oxide sublattice.

5.3 IONIC CONDUCTIVITY IN SOLIDS

One of the most important aspects of point defects is that they make it possible for atoms or ions to move through the structure. If a crystal structure were perfect it would be difficult to envisage how the movement of atoms, either **diffusion** through the lattice or **ionic conductivity** (ion transport under the influence of an external electric field), could take place. Setting up equations to describe either diffusion or conductivity in solids is a very similar process, and so we have chosen to concentrate here on conductivity, because many of the examples later in the chapter are of solid electrolytes.

Two possible mechanisms for the movement of ions through a lattice

are sketched in Figure 5.4. In Figure 5.4a an ion hops or jumps from its normal position on the lattice to a neighbouring equivalent but vacant site. This is called the **vacancy mechanism** (it can equally well be described as the movement of a vacancy rather than the movement of the ion). Figure 5.4b shows an **interstitial mechanism** where an interstitial ion jumps or hops to an adjacent equivalent site. These simple pictures of movement in an ionic lattice are known as the **hopping model**, and ignore more complicated cooperative motions.

Ionic conductivity, σ , is defined in the same way as electronic conductivity:

$$\sigma = nZe\mu, \quad (5.7)$$

where n is the number of charge carriers per unit volume, Ze is their charge (expressed as a multiple of the charge on an electron, $e = 1.602\,189 \times 10^{-19}$ C), and μ is their **mobility**, which is a measure of the drift velocity in a constant electric field. Table 5.3 shows the sort of conductivity values one might expect to find for different materials. As we might expect, ionic crystals, although they can conduct, are poor conductors compared with metals. This is a direct reflection of the difficulty the charge-carrier (in this case an ion, although sometimes an electron) has in moving through the crystal lattice.

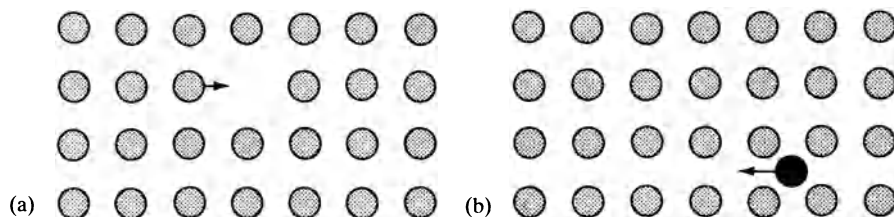


Figure 5.4 Schematic representation of ionic motion by (a) a vacancy mechanism and (b) an interstitial mechanism.

Table 5.3 Typical values of electrical conductivity

	<i>Material</i>	<i>Conductivity ($S\,m^{-1}$)</i>
Ionic conductors	Ionic crystals	$<10^{-16}$ – 10^{-2}
	Solid electrolytes	10^{-1} – 10^3
	Strong (liquid) electrolytes	10^{-1} – 10^3
Electronic conductors	Metals	10^3 – 10^7
	Semiconductors	10^{-3} – 10^4
	Insulators	$<10^{-10}$

Equation (5.7) is a general equation defining conductivity in all conducting materials. In order to understand why some ionic solids conduct better than others it is useful to look at the definition more closely in terms of the hopping model that we have set up. First of all we have said that an electric current is carried in an ionic solid by the defects. In the cases of crystals where the ionic conductivity is carried by the vacancy or interstitial mechanism, n , the concentration of charge carriers, will be closely related to the concentration of defects in the crystal, n_S or n_F . μ will thus refer to the mobility of these defects in such cases.

Let us look more closely at the mobility of the defects. Take the case of NaCl which contains Schottky defects. The Na^+ ions are the ones which move because these are the smallest; however, even these meet quite a lot of resistance (Figure 5.5). We have used dotted lines to illustrate two possible routes that the Na^+ ion could take from the centre of the unit cell to an adjacent vacant site. The direct route (labelled 4) is clearly going to be very unlikely as it leads directly between two Cl^- ions which in a close-packed structure such as this are going to be very close together. The other pathway first passes through one of the triangular faces of the octahedron (point 1), then through one of the tetrahedral holes (point 2), and finally through another triangular face (point 3), before finally arriving at the vacant octahedral site. The coordination of the Na^+ ion will change from $6 \rightarrow 3 \rightarrow 4 \rightarrow 3 \rightarrow 6$ as it jumps from one site to the other.

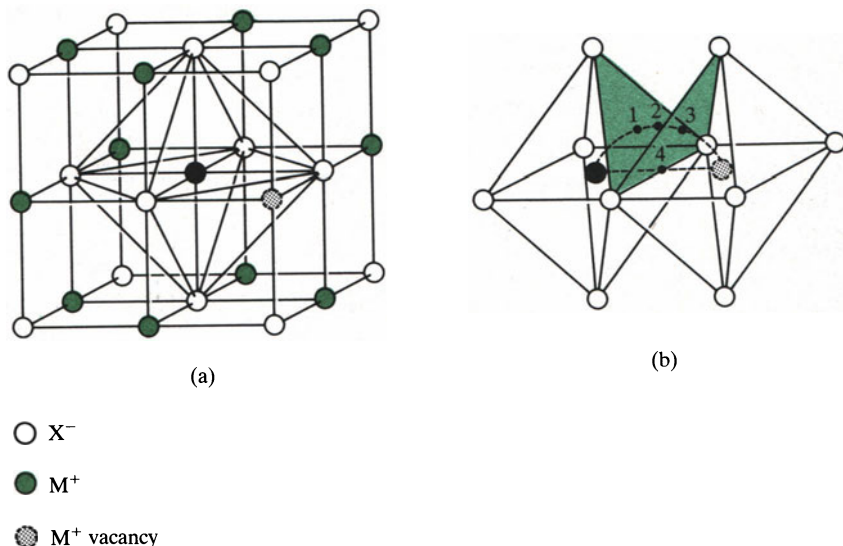


Figure 5.5 Sodium chloride type structure, showing (a) coordination octahedron of central cation, and (b) coordination octahedra of central cation and adjacent vacancy.

While there is clearly going to be an energy barrier to this happening, it will not be as large as for the direct path where the Na^+ ion becomes two-coordinate. In general we would expect the ion to follow the lowest energy path available; a schematic diagram of the energy changes involved in such a pathway is shown in Figure 5.6. Notice that the energy of the ion is the same at the beginning and end of the jump; the energy required to make the jump, E_a , is known as the **activation energy** for the jump. This means that the temperature dependence of the mobility of the ions can be expressed by an **Arrhenius equation**:

$$\mu \propto \exp(-E_a/kT) \quad (5.8)$$

or,

$$\mu = \mu_0 \exp(-E_a/kT), \quad (5.9)$$

where μ_0 is a proportionality constant known as a pre-exponential factor. μ_0 depends on several factors: the number of times per second that the ion attempts the move, ν , called the **attempt frequency** (this is a frequency of vibration of the lattice, of the order of 10^{12} – 10^{13} Hz); the distance moved by the ion; and the size of the external field. If the external field is small (up to about 300 V cm^{-1}) a temperature dependence of $1/T$ is introduced into the pre-exponential factor.

If we combine all this information in equation (5.7), we arrive at an expression for the variation of ionic conductivity with temperature that has the form

$$\sigma = (\sigma_0/T) \exp(-E_a/T). \quad (5.10)$$

The term σ_0 now contains n and Ze , as well as the information on attempt frequency and jump distance. This expression accounts for the fact that ionic conductivity increases with temperature. If we now take logs of equation (5.10) we get

$$\ln \sigma T = \ln \sigma_0 - E_a/T.$$

Plotting $\ln \sigma T$ against $1/T$ should produce a straight line with a slope of

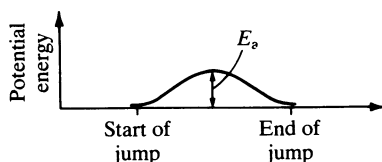


Figure 5.6 Schematic representation of the change in energy during motion of an ion along the lowest energy path.

$-E_a$. The expression in equation (5.10) is sometimes plotted empirically as

$$\sigma = \sigma_0 \exp(-E_a/T)$$

because plotting either $\ln \sigma T$ or $\ln \sigma$ makes little difference to the slope; both types of plot are found in the literature. The results of doing this for several compounds are shown in Figure 5.7.

Ignore the AgI line for the moment, which we discuss in the next section. The other lines on the plot are straight lines apart from the one for LiI, where there are clearly two lines of differing slope. So it appears as though the model we have set up does describe the behaviour of many systems. But how about LiI? In fact other crystals also show this kink in the plot (some experimental data is shown for NaCl in Figure 5.8, where it can also be seen). Is it possible to explain this using the equations that we have just set up? The answer is yes.

The explanation for the two slopes in the plot lies in the fact that even a very pure crystal of NaCl contains some impurities and the line corresponding to low temperatures (on the right of the plot) is due to the **extrinsic vacancies**: at low temperatures the concentration of **intrinsic**

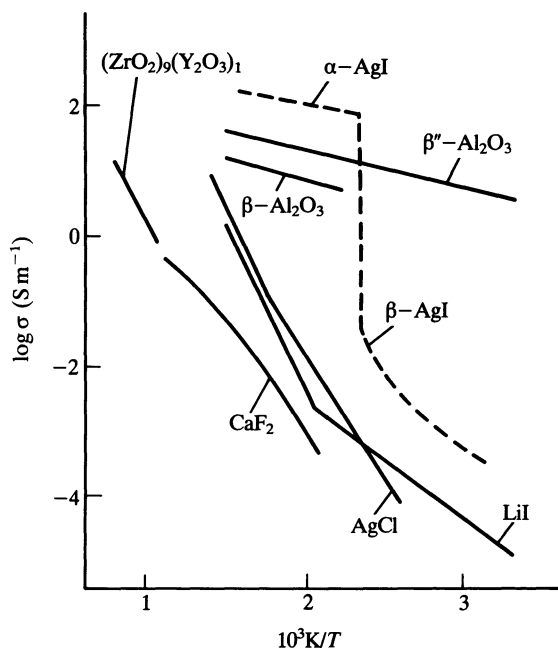


Figure 5.7 The conductivities of selected solid electrolytes over a range of temperatures.

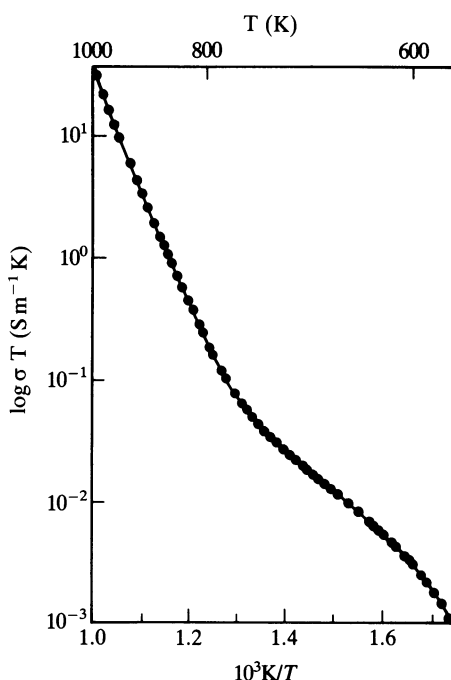


Figure 5.8 The ionic conductivity of NaCl plotted against reciprocal temperature.

vacancies is so small that it can be ignored because it is dominated by the defects created by the impurity. For a particular amount of impurity the number of vacancies present will be essentially constant. μ in this **extrinsic region** thus depends only on the cation mobility due to these extrinsic defects, whose temperature dependence is given by equation (5.9):

$$\mu = \mu_0 \exp(-E_a/kT). \quad (5.9)$$

However, at the higher temperatures on the left-hand side of the graph, the concentration of intrinsic defects has increased to such an extent that it now is similar to or greater than the concentration of extrinsic defects. The concentration of intrinsic defects, unlike that of the extrinsic defects will not be constant; indeed it will vary according to equation (5.1), as we showed earlier:

$$n_s = N \exp(-\Delta H_s/2kT) \quad (5.1)$$

and so the conductivity in this **intrinsic region** on the left-hand side of the plot is given by

$$\sigma = \frac{\sigma'}{T} \exp(-E_a/kT) \exp(-\Delta H_s/2kT). \quad (5.11)$$

A plot of $\ln \sigma T$ versus $1/T$ in this case will give a greater value for the activation energy, E_S , because it will actually depend on two terms: the activation energy for the cation jump, E_a , and the enthalpy of formation of a Schottky defect:

$$E_S = E_a + \frac{1}{2}\Delta H_S. \quad (5.12)$$

Similarly for a system with Frenkel defects:

$$E_F = E_a + \frac{1}{2}\Delta H_F. \quad (5.13)$$

From plots such as these we find that the activation energies lie in the range 0.05–1.1 eV, rather lower than the enthalpies of defect formation. As we have seen, raising the temperature increases the number of defects, and so increases the conductivity of a solid. Better than increasing the temperature to increase conductivity is to find materials that have low activation energies, less than about 0.2 eV. We find such materials in the top right-hand corner of Figure 5.7.

5.4 SOLID ELECTROLYTES

Much of the research in solid state chemistry is related to the electrical conductivity properties of solids; new electrochemical cells and batteries are being developed that contain solid, rather than liquid, electrolytes.

A battery is an electrochemical cell that produces an electric current at a constant voltage as a result of a chemical reaction. The **emf** or voltage produced by the cell under standard open circuit conditions is related to the standard Gibbs free energy change for the reaction by the following equation:

$$\Delta G^\ominus = -nE^\ominus F, \quad (5.14)$$

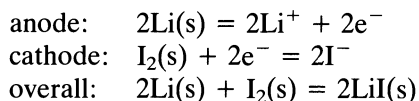
where n is the number of electrons transferred in the reaction, $E^\ominus$ is the standard electromotive force (emf) of the cell (the voltage delivered under standard conditions), and F is the Faraday constant ($96\,485\text{ C mol}^{-1}$ or $96\,485\text{ J V}^{-1}$).

The ions taking part in the reaction pass through an **electrolyte** and are then either oxidized or reduced at an **electrode**; the electrons are released at the positively charged electrode, the **anode**, and pass around an external circuit to the **cathode**. The electric current in the external circuit can be harnessed to do useful work.

The reason that these solid state batteries are potentially useful is that they can perform over a wide temperature range, they have a long shelf life and it is possible to manufacture them so that they are extremely small. There is also interest in solid electrolytes in the production of **secondary** or **storage batteries**; these batteries are reversible because

once the chemical reaction has taken place the reactant concentrations can be restored by reversing the cell reaction using an external source of electricity. Once a **primary battery** has discharged the reaction cannot be reversed and it is useless. If storage batteries can be made to give sufficient power and they are light, they become useful as alternative fuel sources – to power cars for instance; we will look in some detail at the development of the sodium–sulphur battery for this purpose.

To take a simple example, LiI, although it has a fairly low ionic conductivity (Figure 5.7), is used in the manufacture of the batteries that are used in heart pace-makers: LiI is the solid electrolyte that separates the anode (lithium) from the cathode (iodine embedded in a conducting polymer). The cell reaction is:



Because the LiI contains Schottky defects, the small Li^+ cations are able to pass through the solid electrolyte, while the released electrons go round an external circuit.

5.4.1 Fast-ion conductors

Some ionic solids have been discovered that have a much higher conductivity than is typical for such compounds and these are known as **fast-ion conductors**. One of the earliest to be noticed, in 1913 by Tubandt and Lorenz, was a high-temperature phase of silver iodide.

$\alpha\text{-AgI}$

Below 146°C there are two phases of AgI: $\gamma\text{-AgI}$, which has the zinc blende structure, and $\beta\text{-AgI}$ with the wurtzite structure; both are based on a close-packed array of iodide ions with half of the tetrahedral holes filled. However, above 146°C a new phase, $\alpha\text{-AgI}$, is observed where the iodine ions now have a body-centred cubic lattice. A dramatic increase in conductivity is observed for this phase (Figure 5.7): the conductivity of $\alpha\text{-AgI}$ is very high, 131 S m^{-1} , a factor of 10^4 higher than that of $\beta\text{-}$ or $\gamma\text{-AgI}$, comparable with the conductivity of the best conducting liquid electrolytes. How can we explain this startling phenomenon?

The explanation lies in the crystal structure of $\alpha\text{-AgI}$. The structure is based on a body-centred cubic array of I^- ions (Figure 5.9a). Each I^- ion in the array is surrounded by eight equidistant I^- ions. In order to see where the Ag^+ ions fit into the structure we need to look at the *bcc* structure in more detail. Figure 5.9b shows the same unit cell but with the next-nearest neighbours added in; these are the six at the body centres of the surrounding unit cells and are only 15% further away than the eight

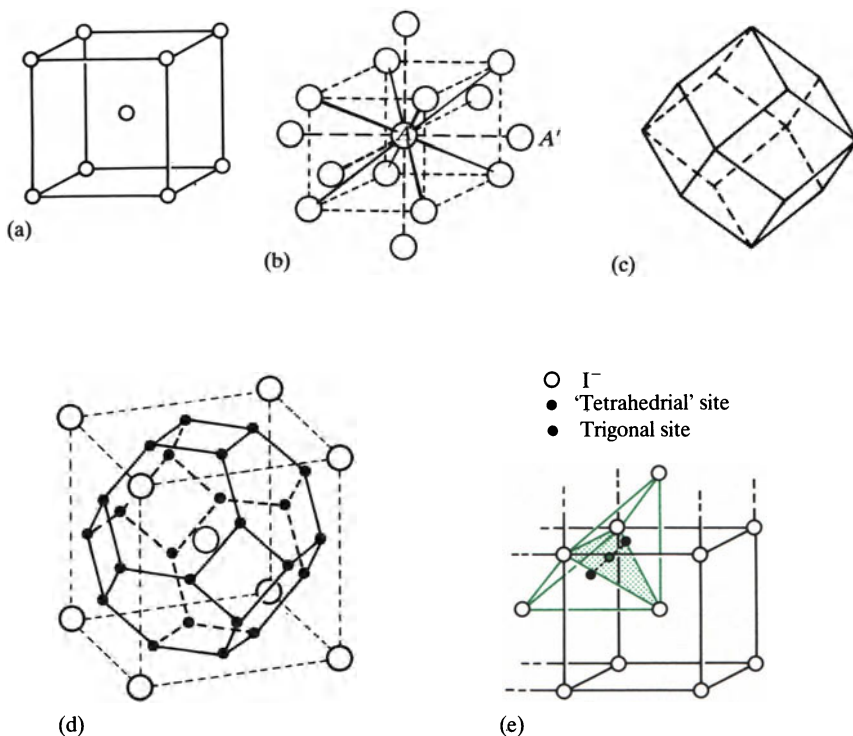


Figure 5.9 Building up the structure of α -AgI. (a) The body-centred cubic array of I^- ions. (b) bcc array extended to next-nearest neighbours. (c) Rhombic dodecahedron. (d) bcc array with enclosed truncated octahedron. (e) The positions of two tetrahedral sites and a trigonal site between them (coloured).

immediate neighbours. This means that the atom marked A is surrounded by 14 other identical atoms, although not in a completely regular way: these 14 atoms lie at the vertices of a **rhombic dodecahedron** (Figure 5.9c). It can be convenient to describe the structure in terms of the space-filling **truncated octahedron** shown in Figure 5.9d, which has six square faces and eight hexagonal faces corresponding to the two sets of neighbours. This is called the **domain** of an atom. Each vertex of the domain lies at the centre of an interstice (like the tetrahedral and octahedral holes found in the close-packed structures), which in this structure is a distorted tetrahedron. Figure 5.9e shows two such adjacent distorted tetrahedral holes, and the 'tetrahedral' site lying on the face of the unit cell. Where the two 'tetrahedra' join, they share a common triangular face; a trigonal site in the centre of this face is also marked in Figure 5.9e. A third type of site in the centre of each face and of each edge of the unit cell can also be defined; these sites have distorted octahedral coordination. The structure thus possesses the unusual feature that there are a great variety of posi-

tions that can be adopted by the Ag^+ ions, and Figure 5.10 sketches many of them. Each AgI unit cell possesses two I^- ions ($(8 \times \frac{1}{8})$ at the corners and one at the body centre) and so positions for only two Ag^+ ions need be found. From the possible sites that we have described there are six distorted octahedral, 12 'tetrahedral' and 24 trigonal, a choice of 42 possible sites – the Ag^+ ions have a huge choice of positions open to them! Structure determinations indicate that the Ag^+ ions are statistically distributed amongst the 12 tetrahedral sites, all of which have the same energy; so, counting these sites alone, we find that there are *five* spare sites per Ag^+ ion. We can visualize the Ag^+ ions moving from tetrahedral site to tetrahedral site by jumping through the vacant trigonal site, following the paths marked with solid lines in Figure 5.10, continually creating and destroying Frenkel defects and able to move easily through the lattice. The paths marked with thin dotted lines in Figure 5.10 require higher energy as they pass through the vacant 'octahedral' sites which are more crowded. The jump that we have described only changes the coordination number from $4 \rightarrow 3 \rightarrow 4$ and experimentally the activation energy is found to be very low, 0.05 eV. This easy movement of the Ag^+ ions through the lattice has often been described as a **molten sublattice** of Ag^+ ions.

The very high conductivity of $\alpha\text{-AgI}$ seems to arise because of a combination of favourable factors. The features that have contributed to this are listed below.

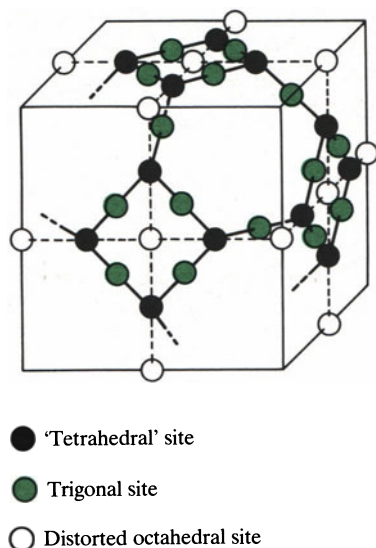


Figure 5.10 Possible cation sites in the *bcc* structure of $\alpha\text{-AgI}$. The thick solid and dashed lines mark possible diffusion paths.

1. The charge on the ions is low; in AgI the mobile Ag^+ ions are monovalent.
2. The coordination around the ions is also low, so that when they jump from site to site the coordination changes only by a little, affording a route through the lattice with a low activation energy.
3. The anion is rather **polarizable**; this means that the electron cloud surrounding it is easily distorted. This makes the passage of a cation past an anion easier.
4. There are a large number of vacant sites for the cations to move into.

These are properties that are known to be important when looking for other fast-ion conductors.

RbAg_4I_5

The special electrical properties of α -AgI inevitably led to a search for other solids exhibiting high ionic conductivity, preferably at temperatures lower than 146°C . The most successful so far (though there are many others) has been the partial replacement of Ag by Rb, forming the compound RbAg_4I_5 . This compound has an ionic conductivity at room temperature of 25 S m^{-1} , with an activation energy of only 0.07 eV . The crystal structure is different from that of α -AgI, but similarly the Rb^+ and I^- ions form a rigid array while the Ag^+ ions are randomly distributed over a network of tetrahedral sites through which they can move.

If a conducting ionic solid is to be useful as a solid electrolyte in a battery, not only must it possess a high conductivity, but it must also have *negligible electronic conductivity*. This is to stop the battery short-circuiting; the electrons must only pass through the external circuit, whence they can be harnessed for work. RbAg_4I_5 has been used as the solid electrolyte in batteries with electrodes made of Ag and RbI_3 . Such cells operate over a wide temperature range (-55 to $+200^\circ\text{C}$), have a long shelf life and can withstand mechanical shock.

Table 5.4 lists ionic conductors that behave in a similar way to α -AgI. Some of these structures are based on a close-packed array of anions and this is noted in the table; the conducting mechanism in these compounds is similar to that in α -AgI. The chalcogenide structures such as silver

Table 5.4 α -AgI related ionic conductors

Anion structure	bcc	ccp	hcp	Other
	α -AgI	α -CuI	β -CuBr	RbAg_4I_5
	α -CuBr	α - Ag_2Te		
	α - Ag_2S	α - Cu_2Se		
	α - Ag_2Se	α - Ag_2HgI_4		

sulphide and selenide tend to show electronic conductivity as well as ionic, although this can be quite useful in an electrode material as opposed to an electrolyte.

Stabilized zirconia

The fluorite structure, as we know from Figure 5.3, has plenty of empty space which can enable a F^- ion to move into an interstitial site. If the activation energy for this process is low enough we might expect compounds with this structure to show ionic conductivity. Indeed PbF_2 has a low ionic conductivity at room temperature, but this increases smoothly with temperature to a limiting value of $\sim 500 \text{ S m}^{-1}$ at 500°C .

Zirconia (ZrO_2) is found as the mineral baddeleyite which has a

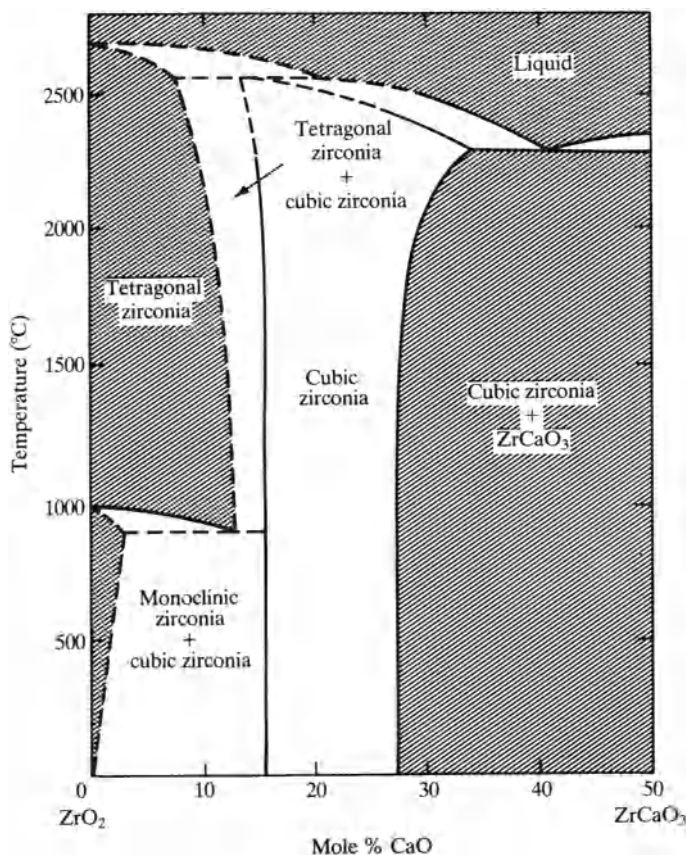


Figure 5.11 Phase diagram of the pseudobinary $CaO-ZrO_2$ system. The cubic calcia-stabilized zirconia phase occupies the central band in the diagram and is stable to about 2400°C .

monoclinic structure. Above 1000°C this changes to a tetragonal form and at high temperatures ZrO_2 adopts the cubic fluorite structure. The cubic form can be stabilized at room temperature, however, by the addition of CaO , which forms a new phase with the ZrO_2 after heating at about 1600°C . The phase diagram is shown in Figure 5.11 and shows that at about 15 mole % CaO the new phase, known as **calcia-stabilized zirconia**, appears alone and persists until about 28 mole % CaO . Above 28 mole % another new phase appears, finally appearing pure as CaZrO_3 . If the Ca^{2+} ions sit on Zr^{4+} sites, compensating vacancies are created in the O^{2-} sublattice: thus for every Ca^{2+} ion taken into the structure *one* anion vacancy is created. The large proportions of CaO mean that such oxides have a huge defect population of oxygen in the structure. Consequently these materials are exceptionally good fast-ion conductors of O^{2-} anions.

There are many materials made with this type of structure based on other oxides such as ThO_2 and HfO_2 as well as ZrO_2 , and doped with oxides of the lanthanide series as well as CaO ; these are also collectively known as stabilized zirconias. They are widely used in electrochemical systems.

One of the most interesting applications is the use of calcia-stabilized zirconia in both **oxygen meters** and **oxygen sensors**, which are based on a specialized electrochemical cell; they work in the following way. Figure 5.12 shows a slab of calcia-stabilized zirconia acting as a solid electrolyte that separates two regions containing oxygen at different pressures. Gas pressures tend to equalize if they can and so, if $p' > p''$, oxygen ions,

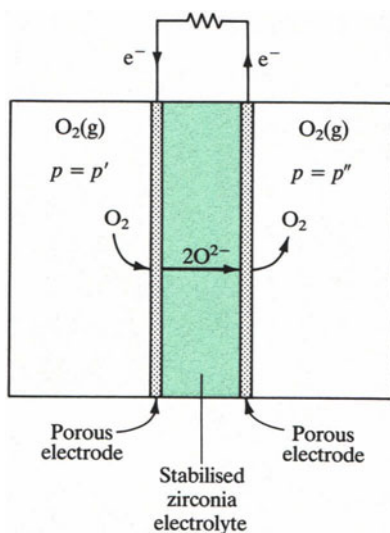


Figure 5.12 Schematic representation of an oxygen meter.

which are able to pass through the stabilized zirconia, tend to pass through the solid from the left-hand side to the right. This tendency produces a potential difference (because the ions are charged), indicating that oxygen is present (in the sensor) and measurement of this potential gives a measure of the oxygen pressure difference (in the oxygen meter).

Oxygen gas is reduced to O^{2-} at the left-hand electrode (LHE), and the oxide ions are able to pass through the doped zirconia and are re-oxidized to oxygen gas at the right-hand electrode (RHE). The equation for the cell reaction is as follows:



Under standard conditions we can relate the change in Gibbs free energy for the above reaction to the standard emf of the cell:

$$\Delta G^\ominus = -nE^\ominus F. \quad (5.14)$$

The **Nernst equation** allows calculation of the cell emf under non-standard conditions, E . If the cell reaction is given by a general equation



then

$$E = E^\ominus - \left(\frac{2.303RT}{nF} \right) \log \left\{ \frac{a_X^x a_Y^y \dots}{a_A^a a_B^b \dots} \right\}. \quad (5.19)$$

where the quantities a_x , etc. are the **activities** of the reactants and products. Applying the Nernst equation to the cell reaction in the oxygen meter we get:

$$E = E^\ominus - \left(\frac{2.303RT}{4F} \right) \log \left(\frac{p''}{p'} \right). \quad (5.20)$$

In this particular case $E^\ominus$ is actually zero because under standard conditions the pressure of the oxygen on each side would be 1 atm and there would be no net potential difference. The pressure of the oxygen on one side of the cell (say p'') is set to be a known reference pressure, usually either pure oxygen at 1 atm or atmospheric oxygen pressure (~ 0.21 atm). Making these two changes we get

$$E = \left(\frac{2.303RT}{4F} \right) \log \left(\frac{p'}{p_{\text{ref}}} \right). \quad (5.21)$$

Clearly, all the quantities in this equation are now known or can be measured, affording a direct measure of the unknown oxygen pressure, p' .

For this cell to operate there must, as we stipulated before, be no electronic conduction through the electrolyte.

Oxygen meters find industrial uses in the detection of oxygen in waste gases from chimneys or exhaust pipes, in investigation into the operation of furnaces, and even in measuring the oxygen content in molten metals during their production.

β -Alumina

β -Alumina is the name given to a series of compounds which show fast-ion conducting properties. The parent compound is sodium β -alumina, $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$ ($\text{NaAl}_{11}\text{O}_{17}$) and is found as a by-product from the glass industry. (The compound was originally thought to be a polymorph of Al_2O_3 and was named as such; it was only later found to contain sodium ions! However, the original name has stuck.) The general formula for the series is $\text{M}_2\text{O} \cdot n\text{X}_2\text{O}_3$, where n can range from 5 to 11; M is a monovalent cation such as (alkali metal)⁺, Cu^+ , Ag^+ , NH_4^+ , and X is a trivalent cation: Al^{3+} , Ga^{3+} or Fe^{3+} .

The real composition of β -alumina actually varies quite considerably from the ideal formula and the materials are always found to be rich in Na^+ and O^{2-} ions to a greater or lesser extent. Two modifications of the structure exist, β - and β'' -alumina, depending on the number of Na^+ ions present; β'' occurs in the more soda-rich crystals where $n = 5-7$ and β occurs for $n = 8-11$.

Interest in these compounds started in 1966 when research at the Ford Motor Co. showed that the Na^+ ions were very mobile both at room temperature and above. The high conductivity of the Na^+ ions in β -alumina is due to the crystal structure. This consists of close-packed layers of oxide ions but every fifth layer has three-quarters of the oxygens missing (Figure 5.13). The four close-packed layers contain the Al^{3+} ions in both octahedral and tetrahedral holes [they are known as the 'spinel blocks' due to their similarity to the crystal structure of the mineral spinel MgAl_2O_4 (discussed in Chapter 1 and illustrated in Figure 1.44)]. The groups of four close-packed oxide layers are held apart by a rigid Al–O–Al linkage; this O atom constituting the fifth oxide layer which contains only a quarter of the number of oxygens of each of the other layers. The Na^+ ions are found in these fifth oxide layers, which are mirror planes in the structure. The overall stoichiometry of the structure is shown layer by layer in Figure 5.13b: the sequence of layers is

C (ABCA) B (ACBA) C . . . ,

where the parentheses enclose the four close-packed layers and the intermediate symbols refer to the fifth oxide layer. The structure of β'' -alumina is not shown here; it is similar, but differs in the stacking sequences of the close-packed layers:

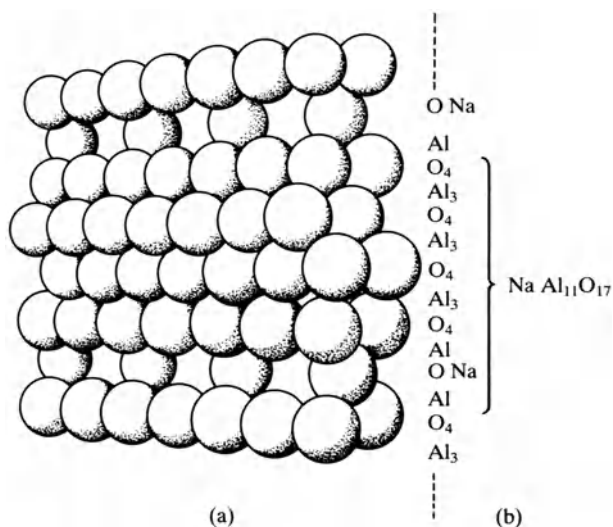


Figure 5.13 (a) Oxide layers in β -alumina. (b) The ratio of atoms in each layer of the structure.

C (ABCA) B (CABC) A (BCAB) C . . .

The crystal structure of β -alumina is shown in Figure 5.14. The Na^+ ions are located in the faces at the top and bottom of the half-cell shown. They can move around easily for two reasons: (i) there are plenty of vacancies, so there is a choice of sites, and (ii) the Na^+ ions are smaller than the O^{2-} ions. Conduction in the β -aluminas only occurs within the planes containing the oxygen vacancies; these are known as the **conduction planes**. The alkali metal cations cannot penetrate the dense 'spinel blocks', but can move easily from site to site within the plane. As stated previously, β -alumina is never found in the stoichiometric form; it is always Na_2O rich. The sodium-rich compounds have a much higher conductivity than stoichiometric β -alumina. The extra sodium ions have to be compensated by a counter defect in order to keep the overall charge on the compound at zero. There is more than one possibility for this but in practice it is found that extra oxide ions provide the compensation and the overall formula can be written as $(\text{Na}_2\text{O})_{1+x} \cdot 11\text{Al}_2\text{O}_3$. The extra sodium and oxide ions both occupy the fifth oxide layer; the O^{2-} ions are locked into position by an Al^{3+} moving out from the spinel block (Figure 5.14), and the Na^+ ions become part of the mobile pool of ions. The Na^+ ions are so fluid that the ionic conductivity in β -alumina at 300°C is close to that of typical liquid electrolytes at ambient temperature.

In general, the β'' -aluminas have even higher conductivities than the β -

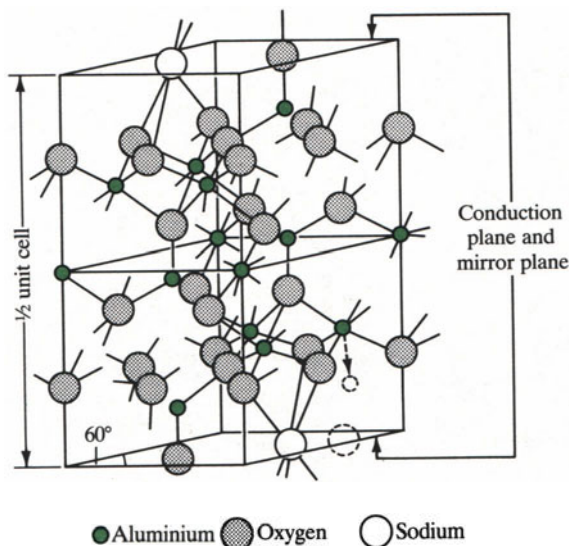


Figure 5.14 Structure of half the unit cell of stoichiometric sodium β -alumina. (The dashed lines indicate the effect of incorporating additional oxygen in the conduction plane.)

aluminas but tend to be more sensitive to moisture. In practice both types of solids are used as electrolytes in the manufacture of electrochemical cells. β -Alumina is used as an electrolyte in cells which are primarily intended as power supplies. From equation (5.14)

$$\Delta G^\ominus = -nE^\ominus F \quad (5.14)$$

we know that in order to obtain a large voltage from a cell we must have a cell reaction with a large negative Gibbs free energy change, such as a reaction between an alkali metal and a halogen might give, for instance. In terms of energy output per unit weight such a reaction can yield about 600 kW per hour per kg of material. Such reactive materials have to be separated by an electrolyte impermeable to electrons but which can be crossed by ions, and β -alumina has proved very useful in these cells.

The **sodium-sulphur** cell uses Na^+ β -alumina as the electrolyte (Figure 5.15). It has a high energy to mass ratio (1030 Wh kg^{-1}) and is being developed for uses such as electric cars. The electrolyte separates molten sodium from molten sulphur which is contained in a graphite felt and is in contact with a current collector connected to the external circuit. The cell operates at 300°C , the heat required to maintain the cell at this operating temperature being supplied by the cell reaction itself.

The cell operates in the following way. At the sodium-electrolyte in-

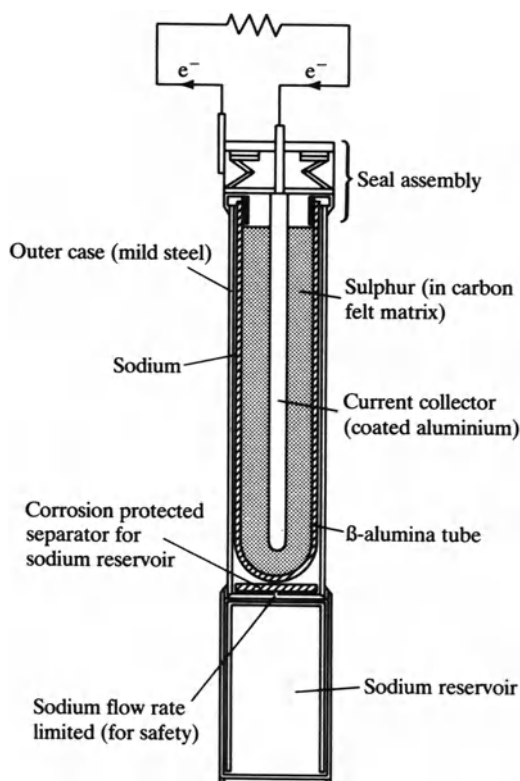


Figure 5.15 Schematic representation of a 'central sulphur' cell. Typically, the electrolyte tube is some 300 mm long and 30 mm in diameter.

terface the sodium atoms each lose an electron and enter the Na^+ layers in the crystal:



At the sulphur-electrolyte interface a complex reaction forming polysulphides of sodium takes place. In the early stages of discharge one such reaction would be



The overall cell reaction is then



Later, low polysulphides are formed, and the discharge is terminated at a composition of about Na_2S_3 . In spite of the complexity of the reactions

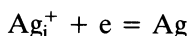
the electrode process can be reversed by applying a current from an external source.

There is much commercial interest in this cell because it incorporates a highly energetic reaction between light substances and so can provide a high **energy density**, and it is reversible so the cells can be recharged. The cells obviously have to incorporate stringent safety features because they contain highly reactive and corrosive chemicals at 300°C! In spite of the restrictions it is hoped that they will become commercially viable.

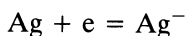
5.5 PHOTOGRAPHY

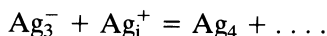
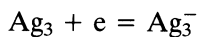
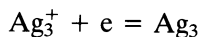
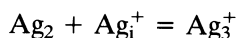
A photographic emulsion consists of very small crystallites of AgBr (or AgBr–AgI) dispersed in gelatin; this is usually supported on paper or thin plastic to form a film. The crystallites are usually small triangular or hexagonal platelets, known as **grains**. They are grown very carefully *in situ* with as few structural defects as possible and range in size from 0.05 to 2×10^{-6} m. During the photographic process light falling on the AgBr produces Ag atoms in some of the grains; these eventually form the dark parts of the negative. The grains which are affected by the light contain the so-called **latent image**. It is important for the grains to be free from structural defects such as dislocations and grain boundaries as these interfere with the deposition of the Ag atoms on the surface of the grains. However, the formation of the latent image is dependent on the presence of point defects.

AgBr has the NaCl or rock-salt crystal structure. However, unlike the alkali halides, which contain mainly Schottky defects, AgBr has been shown to contain mostly Frenkel defects, in the form of interstitial Ag^+ ions. For a grain to possess a latent image it need only have as few as four Ag atoms in a cluster on the surface. The formation of the clusters of Ag atoms is a complex process that is still not fully understood. However, it is thought to take place in several stages. The first stage is when light strikes one of the AgBr crystals and an electron is promoted from the valence band to the conduction band. The band gap of AgBr is 2.7 eV, so the light absorbed is visible from the extreme blue end of the spectrum. This electron eventually neutralizes one of the interstitial silver ions (Ag_i^+):



In the next stages this Ag atom speck has to grow into a cluster of atoms on the surface of the crystal. A possible sequence of events for this is





Notice that only the odd numbered clusters seem to interact with the electrons.

In reality the process is even more complex than this because emulsions made from pure AgBr are not sensitive enough and so they also contain **sensitizers** such as sulphur or organic dyes, which absorb light of longer wavelength than AgBr and so extend the spectral range. The sensitizers form traps for the photoelectrons on the surfaces of the grains; these electrons then transfer from an excited energy level of the sensitizer to the conduction band of AgBr.

The film containing the latent image is then treated with various chemicals to produce a lasting negative. First of all it is developed: a reducing agent such as an alkaline solution of hydroquinone is used to reduce the AgBr crystals to Ag. The clusters of Ag atoms act as a catalyst to this reduction process, and all the grains with a latent image are reduced to Ag. The process is rate controlled, so the grains that have not reacted with the light are unaffected by the developer unless the film is developed for a very long time, when eventually they will be reduced and a fogged picture results. The final stage in producing a negative is to dissolve out the remaining light-sensitive AgBr. This is done using 'hypo' – sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$), which forms a water-soluble complex with Ag^+ ions.

5.6 COLOUR CENTRES

During early research in Germany it was noticed that if crystals of the alkali halides were exposed to X-rays they became brightly coloured. The colour was thought to be associated with a defect known then as a **Farbenzentre** (colour centre), now abbreviated to **F-centre**. Since then it has been found that many forms of high-energy radiation (UV, X-rays, neutrons) will cause F-centres to form. The colour produced by the F-centres is always characteristic of the host crystal, so for instance NaCl becomes deep yellowy-orange, KCl, violet and KBr, blue-green.

Subsequently it was found that F-centres can also be produced by heating a crystal in the vapour of an alkali metal; this gives a clue to the nature of these defects. The excess alkali metal atoms diffuse into the crystal and settle on cation sites; at the same time an equivalent number of anion site vacancies are created and ionization gives an alkali metal

cation with an electron trapped at the anion vacancy (Figure 5.16). In fact, it does not even matter which alkali metal is used; if NaCl is heated with potassium the colour of the F-centre does not change because it is characteristic of the electron trapped at the anion vacancy in the host halide. Work with electron spin resonance (ESR) techniques has confirmed that F-centres are indeed unpaired electrons trapped at vacant lattice (anion) sites.

The trapped electron provides a classic example of an 'electron in a box'. A series of energy levels are available for the electron, and the energy required to transfer from one level to another falls in the visible part of the electromagnetic spectrum, hence the colour of the F-centre. There is an interesting natural example of this phenomenon: the mineral fluorite, CaF_2 , is found in Derbyshire as 'Blue John' and its beautiful blue-purple coloration is due to the presence of F-centres.

Many other colour centres have now been characterized in alkali halide crystals. The **H-centre** is formed by heating (for instance) NaCl in Cl_2 gas. In this case a $[\text{Cl}_2]^-$ ion is formed and occupies a single anion site (Figure 5.16b). F-centres and H-centres are perfectly complementary; if they meet they cancel one another out!

Another interesting natural example of colour centres lies in the colour of smoky quartz and amethyst. These semiprecious stones are basically crystals of silica (SiO_2) with some impurity present. In the case of smoky quartz the silica contains a little Al impurity. The Al substitutes for the Si in the lattice and the electrical neutrality is maintained by H^+ present in the same amount as Al. The colour centre arises when ionizing radiation interacts with an $[\text{AlO}_4]^{5-}$ group, liberating an electron which is then trapped by H^+ :



The $[\text{AlO}_4]^{4-}$ group is now electron-deficient and can be considered to have a 'hole' trapped at its centre. This group is the colour centre,

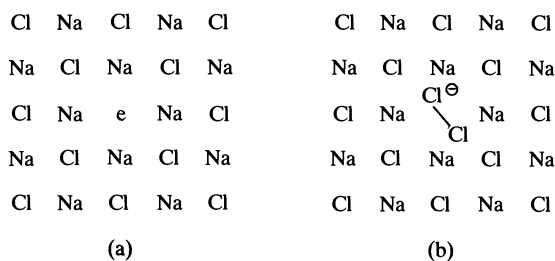


Figure 5.16 (a) The F-centre, an electron trapped on an anion vacancy. (b) H-centre.

absorbing light and producing the smoky colour. In crystals of amethyst the impurity present is Fe^{3+} , and on irradiation $[\text{FeO}_4]^{4-}$ colour centres are produced which absorb light to give the characteristic purple coloration.

5.7 NON-STOICHIOMETRIC COMPOUNDS

5.7.1 Introduction

Previous sections in this chapter have shown that it is possible to *introduce* defects into a perfect crystal by adding an impurity. Such an addition causes point defects of one sort or another to form but they no longer occur in complementary pairs. Such impurity-induced defects are said to be **extrinsic**. We have also noted that when assessing what defects have been created in a crystal, it is important to remember that the overall charge on the crystal must always be zero.

Colour centres are formed if a crystal of NaCl is heated in sodium vapour; sodium is taken into the crystal, and the formula becomes Na_{1+x}Cl . The sodium atoms occupy cation sites, creating an equivalent number of anion vacancies; they subsequently ionize to form a sodium cation with an electron trapped at the anion vacancy. The solid so formed is a **non-stoichiometric compound** because the ratio of the atomic components is no longer the simple integer that we have come to expect for well-characterized compounds. A careful analysis of many substances, particularly inorganic solids, shows that it is common for the atomic ratios to be non-integral: uranium dioxide, for instance, can range in composition from $\text{UO}_{1.65}$ to $\text{UO}_{2.25}$, certainly not the perfect UO_2 that we might expect! There are many other examples, some of which are discussed here in some detail.

What kind of compounds are likely to be non-stoichiometric? 'Normal' covalent compounds are assumed to have a fixed composition where the atoms are usually held together by strong covalent bonds formed by the pairing of two electrons. Breaking these bonds usually takes quite a lot of energy, and so under normal circumstances a particular compound does not show a wide range of composition; this is true for most molecular organic compounds for instance. Ionic compounds also are usually stoichiometric, because to remove or add ions requires a considerable amount of energy. We have seen, however, that it is possible to make ionic crystals non-stoichiometric by doping them with an impurity, as with the example of Na added to NaCl. There is also another mechanism whereby ionic crystals can become non-stoichiometric: if the crystal contains an element with a variable valency, a change in the number of ions of that element can be compensated by changes in ion charge; this maintains the charge balance but alters the stoichiometry. Elements with a variable

valency mostly occur in the transition elements, the lanthanides and the actinides.

In summary, non-stoichiometric compounds can have formulae that do not have simple integer ratios of atoms; they also usually exhibit a range of composition. They can be made by introducing impurities into a system, but are frequently a consequence of the ability of the metal to exhibit variable valency. Table 5.5 lists a few non-stoichiometric compounds together with their composition ranges.

Until recently, defects both in stoichiometric and non-stoichiometric crystals were treated entirely from the point of view that point defects are randomly distributed. However, isolated point defects are not scattered at random in non-stoichiometric compounds but are often dispersed throughout the structure in some kind of regular pattern. In the next sections we try to explore the relationship between stoichiometry and structure.

It is difficult to determine the structure of compounds containing defects and it is only very recently that much of our knowledge has been formed. X-ray diffraction is the usual method for the determination of the structure of a crystal; however, this method yields the *average* structure for a crystal. For pure, relatively defect-free structures this is a good representation but for non-stoichiometric and defect structures it avoids precisely the information that one wants to know. For this kind of structure

Table 5.5 Approximate composition ranges for some non-stoichiometric compounds

<i>Compound</i>		<i>Composition range*</i>
TiO _x	[$\approx$ TiO]	$0.65 < x < 1.25$
	[$\approx$ TiO ₂]	$1.998 < x < 2.000$
VO _x	[$\approx$ VO]	$0.79 < x < 1.29$
Mn _x O	[$\approx$ MnO]	$0.848 < x < 1.000$
Fe _x O	[$\approx$ FeO]	$0.833 < x < 0.957$
Co _x O	[$\approx$ CoO]	$0.988 < x < 1.000$
Ni _x O	[$\approx$ NiO]	$0.999 < x < 1.000$
CeO _x	[$\approx$ Ce ₂ O ₃]	$1.50 < x < 1.52$
ZrO _x	[$\approx$ ZrO ₂]	$1.700 < x < 2.004$
UO _x	[$\approx$ UO ₂]	$1.65 < x < 2.25$
Li _x V ₂ O ₅		$0.2 < x < 0.33$
Li _x WO ₃		$0 < x < 0.50$
TiS _x	[$\approx$ TiS]	$0.971 < x < 1.064$
Nb _x S	[$\approx$ NbS]	$0.92 < x < 1.00$
Y _x Se	[$\approx$ YSe]	$1.00 < x < 1.33$
V _x Te ₂	[$\approx$ VTe ₂]	$1.03 < x < 1.14$

* Note that all composition ranges are temperature-dependent and the figures here are intended only as a guide.

determination, a technique that is sensitive to *local* structure is needed, and such techniques are very scarce. Structures are often elucidated from a variety of sources of evidence: X-ray and neutron diffraction, density measurements, spectroscopy (when applicable) and more recently high-resolution electron microscopy (HREM) and Extended X-ray Absorption Fine Structure (EXAFS); magnetic measurements have also proved useful in the case of FeO. Probably HREM has done most to clarify the understanding of defect structures, as it is capable under favourable circumstances of giving information on an atomic scale by 'direct lattice imaging'.

Non-stoichiometric compounds are of potential use to industry because their electronic, optical, magnetic and mechanical properties can be modified by changing the proportions of the atomic constituents. This is widely exploited and researched by the electronics and other industries.

5.7.2 Non-stoichiometry in wustite

Ferrous oxide is known as **wustite (FeO)**, and it has the NaCl (rock salt) crystal structure. Accurate chemical analysis shows that it is non-stoichiometric: it is always deficient in iron. The FeO phase diagram (Figure 5.17) shows that the compositional range of wustite increases with temperature and that stoichiometric FeO is not included in the range of stability. Below 570°C wustite disproportionates to α -iron and Fe₃O₄.

There are two ways in which an iron deficiency could be accommodated by a defect structure: there could either be iron vacancies giving a formula Fe_{1-x}O, or alternatively there could be an excess of oxygen in interstitial positions, with the formula, FeO_{1+x}. A comparison of the theoretical and measured densities of the crystal distinguishes between the alternatives. The easiest method of measuring the density of a crystal is the flotation method. Liquids of differing densities (that dissolve in one another) are mixed together until a mixture is found that will just suspend the crystal, so that it neither floats nor sinks. The density of that liquid mixture must then be the same as that of the crystal, and it can be found by weighing an accurately measured volume.

The *theoretical* density of a crystal can be obtained from the volume of the unit cell and the mass of the unit cell contents. The results of an X-ray diffraction structure determination gives both of these data, as the unit cell dimensions are accurately measured and the type and number of formula units in the unit cell are also determined. An example of this type of calculation for FeO follows. A particular crystal of FeO was found to have a unit cell dimension of 430.1 pm, a measured density of $5.728 \times 10^3 \text{ kg m}^{-3}$ and an iron to oxygen ratio of 0.945. The unit cell volume (which is a cube) is thus $(430.1 \text{ pm})^3 = 7.956 \times 10^7 (\text{pm})^3 = 7.956 \times 10^{-29} \text{ m}^3$.

There are four formula units of FeO in a perfect unit cell with the

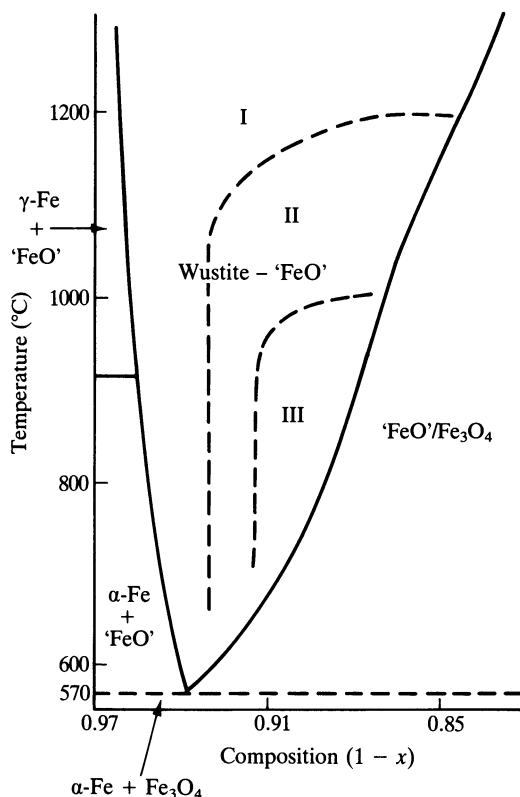


Figure 5.17 Phase diagram of the FeO system. I, II and III together comprise the wustite region.

rocksalt structure. The mass of these four units can be calculated from their relative atomic masses: Fe, 55.85 and O, 16.00. One mole of FeO weighs $(55.85 + 16.00) \text{ g} = 0.07185 \text{ kg}$, four moles weigh $(4 \times 0.07185) \text{ kg}$, and four formula units weigh $(4 \times 0.07185)/N_A \text{ kg} = 4.773 \times 10^{-25} \text{ kg}$, where **Avogadro's number** (N_A) = $6.022 \times 10^{23} \text{ mol}^{-1}$.

The sample under consideration has an Fe:O ratio of 0.945. Assume, in the first instance, that it has iron vacancies. The unit cell contents in this case will be $(4 \times 0.945) = 3.78 \text{ Fe}$ and 4 O. The mass of the contents will be $[(3.78 \times 55.85) + (4 \times 16.00)]/(N_A \times 10^3) \text{ kg}$. Dividing by the volume of the unit cell, we get a value of $5.742 \times 10^3 \text{ kg m}^{-3}$ for the density. If instead the sample possesses interstitial oxygens, the ratio of oxygens to iron in the unit cell will be given by $1/0.945 = 1.058$. The unit cell in this case will contain 4 Fe and $(4 \times 1.058) \text{ O} = 4.232 \text{ O}$. The mass of this unit cell is given by $[(4 \times 55.85) + (4.232 \times 16.00)]/(N_A \times 10^3) \text{ kg}$, giving a density of $6.076 \times 10^3 \text{ kg m}^{-3}$. Comparing the two sets of cal-

Table 5.6 Experimental and theoretical densities (10^3 kg m^{-3}) for FeO

<i>O:Fe ratio</i>	<i>Fe:O ratio</i>	<i>Lattice parameter (pm)</i>	<i>Observed density</i>	<i>Theoretical density</i>	
				<i>Interstitial O</i>	<i>Fe vacancies</i>
1.058	0.945	430.1	5.728	6.076	5.742
1.075	0.930	429.2	5.658	6.136	5.706
1.087	0.920	428.5	5.624	6.181	5.687
1.099	0.910	428.2	5.613	6.210	5.652

culations with the experimentally measured density of $5.728 \times 10^3 \text{ kg m}^{-3}$, it is clear that this sample contains iron vacancies and that the formula should be written as $\text{Fe}_{0.945}\text{O}$. A table of densities is drawn up for FeO in Table 5.6.

It is found to be characteristic of most non-stoichiometric compounds that their unit cell size varies smoothly with composition but the symmetry is unchanged. This is known as **Vegard's law**.

Summarizing, non-stoichiometric compounds are found to exist over a range of composition and throughout that range the unit cell length varies smoothly with no change of symmetry. It is possible to determine whether the non-stoichiometry is accommodated by vacancy or interstitial defects using density measurements.

Electronic defects in FeO

The discussion of the defects in FeO has so far been only structural. Now we turn our attention to the balancing of the charges within the crystal. In principle the compensation for the iron deficiency can be made either by oxidation of some Fe(II) ions or by reduction of some oxide anions. It is energetically more favourable to oxidize Fe(II). For each Fe^{2+} vacancy, two Fe^{2+} cations must be oxidized to Fe^{3+} . In the overwhelming majority of cases, defect creation involves changes in the cation oxidation state. In the case of metal excess in simple compounds, we would usually expect to find that neighbouring cation(s) would be reduced.

In a later section we will look at some general cases of non-stoichiometry in simple oxides, but before we do that we will complete the FeO story with a look at its detailed structure.

The structure of FeO

FeO has the NaCl structure with Fe^{2+} ions in octahedral sites. The iron deficiency manifests itself as cation vacancies, and the electronic compensation made for this is that for every Fe^{2+} ion vacancy there are two neighbouring Fe^{3+} ions. We might reasonably expect that the Fe^{2+} , Fe^{3+}

and the cation vacancies are randomly distributed over the octahedral sites in the *ccp* O^{2-} array in wustite. Structural studies (X-ray, neutron and magnetic) have shown that this is not the case and that some of the Fe^{3+} ions are in *tetrahedral* sites.

Although the structure of wustite is still under debate, it appears that it contains various types of **defect cluster** and that these new structures are distributed throughout the crystal. A defect cluster is a region of the crystal where the defects form an ordered structure. One possibility is known as the **Koch–Cohen cluster** and part of it is shown in Figure 5.18. It bears a strong resemblance to the structure of Fe_3O_4 , the next highest oxide of iron. We can think of wustite as fragments of Fe_3O_4 intergrown in the rock-salt structure of FeO. (The crystal structure of Fe_3O_4 is discussed in a different context in Chapter 9).

At the centre of the Koch-Cohen cluster is a modified FeO unit cell (drawn in bold in Figure 5.18). This contains four tetrahedrally coordinated Fe^{3+} ions in the tetrahedral holes; furthermore, the octahedrally coordinated iron sites at the centre of this unit cell, and at the midpoints of its edges, are vacant. The other octahedrally coordinated iron sites in the cluster are occupied, but they may contain either Fe(II) or Fe(III) ions.

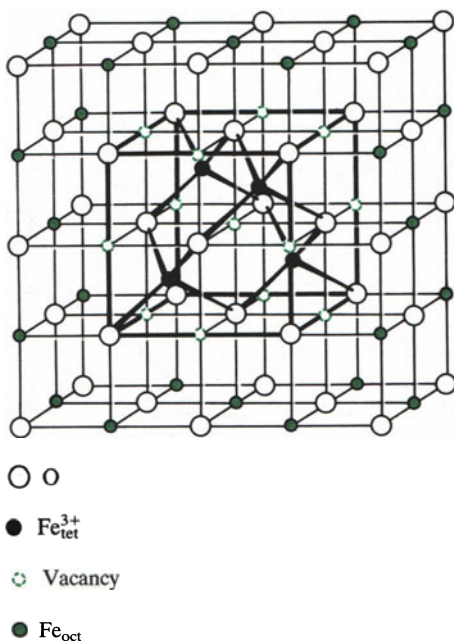


Figure 5.18 The Koch–Cohen cluster shown with the front and back planes cut away for clarity. The central section with the four tetrahedrally coordinated Fe^{3+} ions is picked out in bold.

We therefore designate them simply as Fe_{oct} . The front and back planes have been cut away from the diagram in Figure 5.18 to make the central section more visible.

It is instructive to consider the composition of a cluster such as the one shown in Figure 5.18 in some detail. Clusters such as this are often referred to by the ratio of cation vacancies to interstitial Fe^{3+} in tetrahedral holes, in this case 13:4. The complete cluster, allowing for the back and front faces which are not illustrated here, contains eight NaCl-type unit cells, and thus 32 oxide ions. A cluster with no defects would also contain 32 iron cations on the octahedral sites. Taking into account the 13 octahedral vacancies, there must be 19 Fe_{oct} ions and the four interstitial $\text{Fe}_{\text{tet}}^{3+}$ ions making 23 iron cations in all. The overall formula for the cluster is thus $\text{Fe}_{23}\text{O}_{32}$, almost Fe_3O_4 !

Having determined the atomic contents of the cluster, we now turn our attention to the charges. There are 32 oxide ions, so to balance them the Fe cations overall must have 64 positive charges. Twelve are accounted for by the four Fe^{3+} ions in tetrahedral positions, leaving 52 to find from the remaining 19 Fe_{oct} cations. This accounting is difficult to do by inspection. Suppose that there are $x\text{Fe}^{2+}$ ions and $y\text{Fe}^{3+}$ ions in octahedral sites; we know that

$$x + y = 19. \quad (5.26)$$

We also know that their total charges must equal 52, so

$$2x + 3y = 52 \quad (5.27)$$

giving two simultaneous equations. Solving gives $y = 14$ and $x = 5$.

The octahedral sites surrounding the central (bold) unit cell are thus occupied by five Fe^{2+} ions and by 14 Fe^{3+} ions. By injecting such clusters throughout the FeO structure, the non-stoichiometric structure is built up. The exact formula of the compound (the value of x in Fe_{1-x}O) will depend on the average separation of the randomly injected clusters. In the oxygen-rich limit when the whole structure is composed of these clusters there is a new ordered structure of formula $\text{Fe}_{23}\text{O}_{32}$ which is based on the structure of the parent compound. This new structure has its own unit cell, larger than that of the parent compound and of lower symmetry: the new structure is referred to as a **superstructure** or **superlattice** of the parent.

5.7.3 Uranium dioxide

Above 1127°C a single oxygen-rich non-stoichiometric phase of UO_2 is found with formula UO_{2+x} , ranging from UO_2 to $\text{UO}_{2.25}$. Unlike FeO, where a metal-deficient oxide was achieved through cation vacancies, in this example the metal deficiency arises from interstitial anions.

$\text{UO}_{2.25}$ corresponds to U_4O_9 , which is a well-characterized oxide of uranium known at low temperature. UO_2 has the fluorite structure (Figure 5.19). The unit cell in Figure 5.19 contains four formula units of UO_2 . (There are four uranium ions contained within the cell boundaries; the eight oxide ions come from: $(8 \times \frac{1}{8}) = 1$ at the corners, $(6 \times \frac{1}{2}) = 3$ at the face centres, $(12 \times \frac{1}{4}) = 3$ at the cell edges, and one at the cell body centre.)

As more oxygen is taken into UO_2 , the extra oxide ions go into interstitial positions. The most obvious site available is in the middle of one of the octants with no metal atom. Neutron diffraction shows that an interstitial oxide anion does not sit exactly in the centre of an octant but is displaced sideways; this has the effect of moving two other oxide ions from their lattice positions by a very small amount, leaving two vacant lattice positions. This is illustrated in Figure 5.19; in Figure 5.19a three vacant octants are picked out in colour and in Figure 5.19b the positions

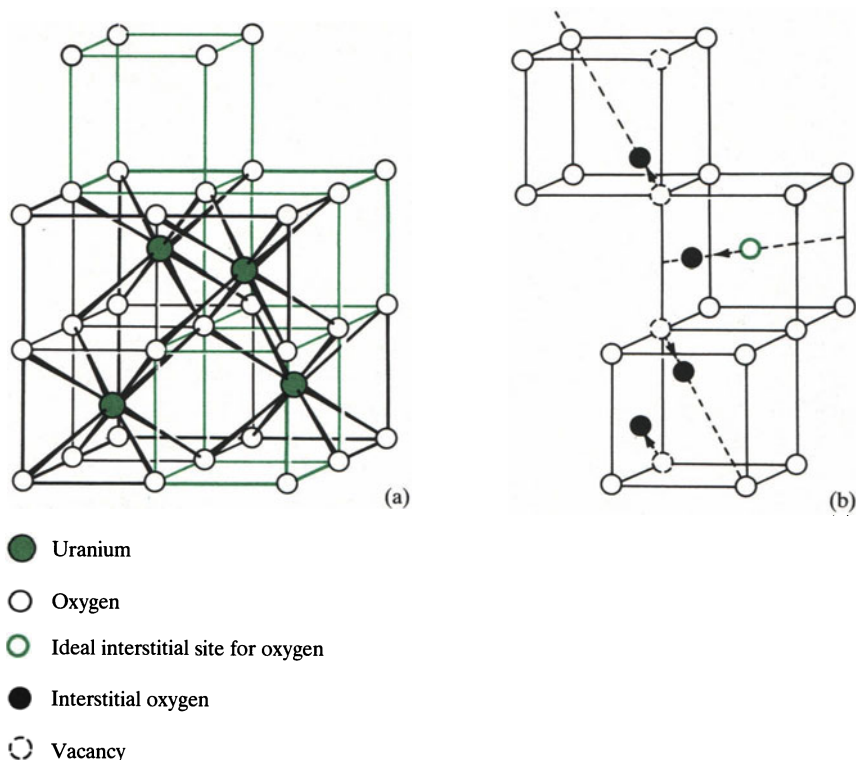


Figure 5.19 (a) The fluorite structure of UO_2 with a unit cell marked in bold and the defect cluster position in colour. (b) Interstitial defect cluster in UO_{2+x} . Uranium positions (not shown) are in the centre of every other cube.

of the one additional interstitial oxide and the two displaced oxides with their vacancies are shown. The movement of the ions from 'ideal' positions is shown by small arrows: the movement of the interstitial oxide from the centre of an octant is along the direction of a diagonal of one of the cube faces, whereas the movement of the oxide ions on lattice positions is along cube diagonals.

The atomic composition of the unit cell in Figure 5.19a when modified by the defect structure is U_4O_9 ; the loss of the displaced lattice oxygen at the centre of the top face is balanced by the gain of that at the centre of the bottom face. The net oxygen gain is just the single new interstitial in the central octant of Figure 5.19b. U_4O_9 is found to be the oxygen-rich limit for the UO_{2+x} non-stoichiometric structure. We can think of UO_{2+x} , therefore, as containing **microdomains** of the U_4O_9 structure within that of UO_2 . The electronic compensation for the extra interstitial oxide ions will most likely be the oxidation of neighbouring U(IV) atoms to either U(V) or U(VI).

This account of the UO_2 structure is actually a slightly simplified version of the truth. There are two different (but similar) positions that the interstitial oxides can take within the structure, and when both of these are ordered throughout the structure we find a very large unit cell for U_4O_9 based on $4 \times 4 \times 4$ fluorite unit cells (with a volume of 64 times that of the UO_2 unit cell). However, the discussion above illustrates the basic principles of what is happening.

5.7.4 The titanium monoxide structure

Titanium and oxygen form non-stoichiometric phases which exist over a range of composition centred about the stoichiometric 1:1 value, from $\text{TiO}_{0.65}$ to $\text{TiO}_{1.25}$. We shall look at what happens in the upper range from $\text{TiO}_{1.00}$ to $\text{TiO}_{1.25}$.

At the stoichiometric composition of $\text{TiO}_{1.00}$ the crystal structure is based on a NaCl structure with vacancies in both the metal and the oxygen sublattices; one-sixth of the titaniums and one-sixth of the oxygens are missing. Above 900°C these vacancies are randomly distributed but below this temperature they are ordered as shown in Figure 5.20.

In Figure 5.20a we show a layer through a NaCl-type structure. Every third vertical diagonal plane has been picked out by a dashed line. In the $\text{TiO}_{1.00}$ structure every other atom along the dashed lines is missing (Figure 5.20b). If we consider that in these first two diagrams we are looking at the structure along the y -axis, and that this layer is the top of the unit cells, $b = 0$, then the layer below this and parallel to it will be the central horizontal plane of the unit cell at $b = \frac{1}{2}$. This is drawn in Figure 5.20c, and again we notice that every other atom along every third diagonal plane is missing. This is true throughout the structure. In the

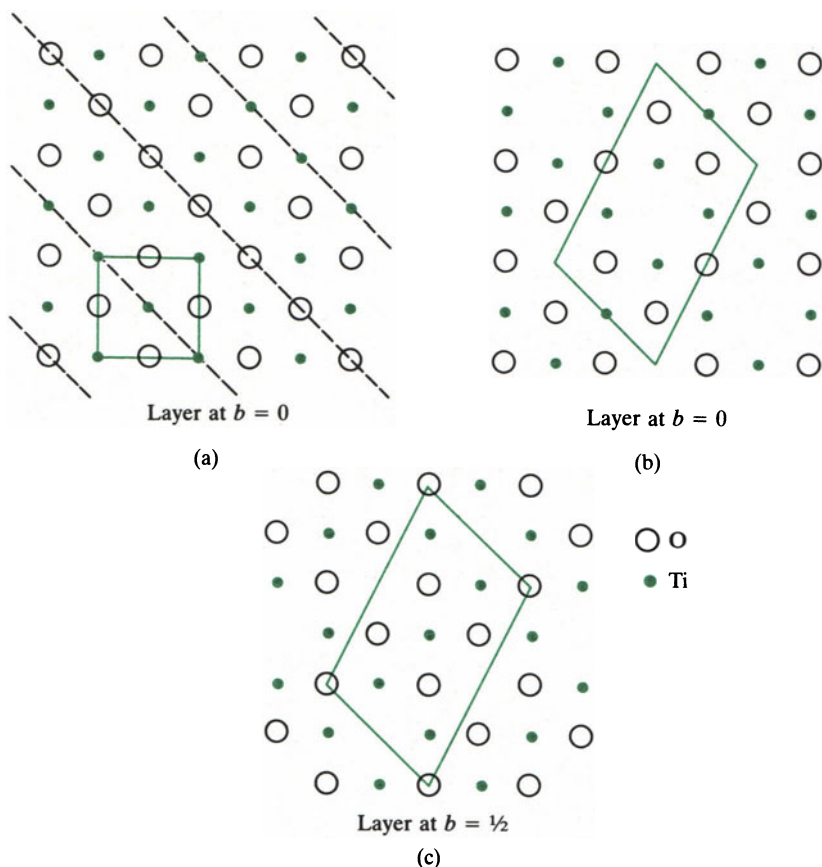


Figure 5.20 Layers parallel to the horizontal planes of Figure 1.30. (a) The hypothetical TiO structure of the NaCl type shown in Figure 1.30; the line of intersection of every third vertical diagonal plane is marked by a dashed coloured line. (b) The same plane in the observed structure of TiO; every alternate atom is removed along the diagonal lines in (a). (c) The plane directly beneath the layer in (b); again, every alternate atom is removed along the cuts made by the planes whose intersection lines are shown in (a). In (b) and (c) the cross-section of a monoclinic unit cell is indicated.

figure the unit cell of a perfect NaCl-type structure is marked on Figure 5.20a whereas the boundaries of the new unit cell, taking the ordered defects into account, are marked on Figure 5.20b and c. The new unit cell of the superlattice is **monoclinic** (see Chapter 1) because one of the angles (β) is not equal to 90° . This structure is unusual in that it is stoichiometric but contains vacancies on both the anion and cation sublattices.

As noted in Chapter 4, unusually for a transition metal monoxide, $\text{TiO}_{1.00}$ shows metallic conductivity. The existence of the vacant sites

within the TiO structure is thought to permit sufficient contraction of the lattice such that the $3d$ orbitals on titanium overlap, thus broadening the conduction band and allowing electronic conduction.

When titanium monoxide has the limiting formula $\text{TiO}_{1.25}$, it has a different defect structure, still based on the NaCl structure, but with all the oxygens present, and one in every five titaniums missing (Figure 5.21). The pattern of the titanium vacancies is shown in Figure 5.22 which shows a layer of the type in Figure 5.20 but with the oxygens omitted; only titaniums are marked. Drawing horizontal lines through the titaniums will show that every fifth one is missing; again we see that the ordering of the defects has produced a superlattice. Where samples of titanium oxide have formulae which lie between the two limits discussed here, $\text{TiO}_{1.00}$ and $\text{TiO}_{1.25}$, the structure seems to consist of portions of the $\text{TiO}_{1.00}$ and $\text{TiO}_{1.25}$ structures intergrown. Although most texts refer to the structure as $\text{TiO}_{1.25}$, as we have here, on the definitions that we have used previously when discussing 'FeO' it is more correctly written as $\text{Ti}_{0.8}\text{O}$ (Ti_{1-x}O), as this indicates that the structure contains titanium vacancies rather than interstitial oxygens.

5.8 PLANAR DEFECTS

In the introduction to this chapter we mentioned that crystals often contain **extended defects** as well as point defects. The simplest *linear*

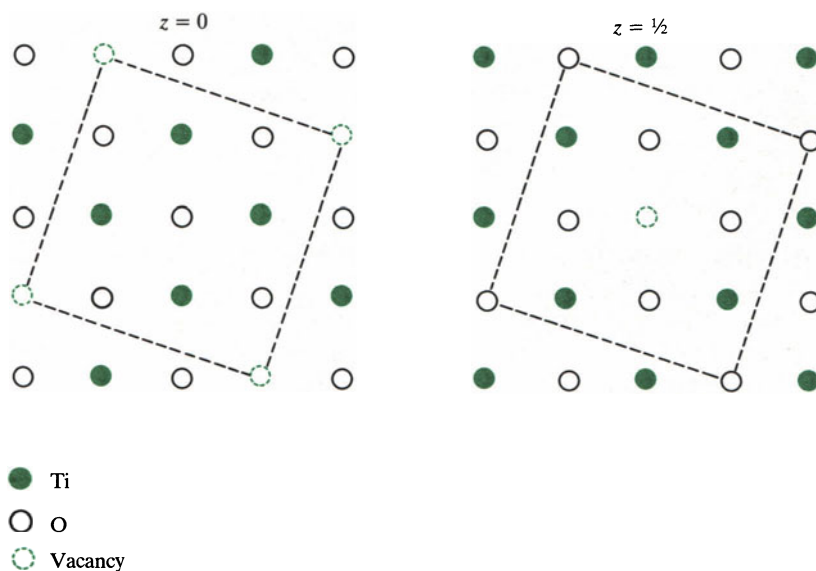


Figure 5.21 The structure of $\text{TiO}_{1.25}$ showing both O and Ti positions.

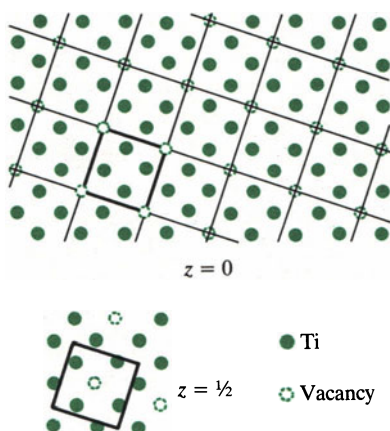


Figure 5.22 Successive Ti layers in the structure of $\text{TiO}_{1.25}$.

defect is a **dislocation** where there is a fault in the arrangement of the atoms in a line through the crystal lattice. There are many different types of *planar* defects, most of which we are not able to discuss here either for reasons of space or of complexity, such as **grain boundaries**, which are of more relevance to materials scientists, and **chemical twinning**, which can contain unit cells mirrored about the twin plane through the crystal. However, we shall look briefly at two forms of planar defect which are relevant to the kind of structural discussions in this book: (1) **crystallographic shear planes**, where the oxygen vacancies effectively collect together in a plane which runs through the crystal, and (2) **intergrowth structures**, where two different but related structures alternate throughout the crystal.

5.8.1 Crystallographic shear planes

Non-stoichiometric compounds are found for the higher oxides of tungsten, molybdenum and titanium. WO_{3-x} , MoO_{3-x} and TiO_{2-x} , respectively. The reaction of these systems to the presence of point defects is entirely different from what has been discussed previously; in fact the point defects are eliminated by a process known as **crystallographic shear (CS)**.

In these systems, a series of closely related compounds with very similar formulae and structure exists. The formulae of these compounds all obey a general formula, which for the molybdenum and tungsten oxides can be $\text{Mo}_n\text{O}_{3n-1}$, $\text{Mo}_n\text{O}_{3n-2}$, $\text{W}_n\text{O}_{3n-1}$ and $\text{W}_n\text{O}_{3n-2}$ and for titanium dioxide is $\text{Ti}_n\text{O}_{2n-1}$; n can vary taking values of four and above. The resulting series of oxides is known as a **homologous series** (like the alkanes in organic chemistry). The first seven members of the molybdenum

trioxide series are Mo_4O_{11} , Mo_5O_{14} , Mo_6O_{17} , Mo_7O_{20} , Mo_8O_{23} , Mo_9O_{26} , $\text{Mo}_{10}\text{O}_{29}$ and $\text{Mo}_{11}\text{O}_{32}$.

In these compounds we find regions of corner-linked octahedra separated from each other by thin regions of a different structure known as the crystallographic shear planes. The different members of a homologous series are determined by the fixed spacing between the CS planes. The structure of a shear plane is quite difficult to understand and these structures are usually depicted by the linking of octahedra as described in Chapter 1.

WO_3 has several polymorphs, but above 900°C the WO_3 structure is that of ReO_3 , (Figure 5.23; ignore the bold squares for the time being). (The structures of the other polymorphs are distortions of the ReO_3 structure.) ReO_3 is made up of $[\text{ReO}_6]$ octahedra that are linked together via their corners; each corner of an octahedron is shared with another. Figure 5.23a shows part of one layer of the octahedra in the structure. Notice that, within the layer, any octahedron is linked to four others; it is also linked, via its upper and lower corners, to octahedra in the layers above and below. Part of the ReO_3 structure is drawn in Figure 5.24; note that every oxygen atom is shared between two metal atoms. As six oxygens surround each Re the overall formula is ReO_3 .

The non-stoichiometry in WO_{3-x} is achieved by some of the octahedra in this structure changing from corner-sharing to edge-sharing. Look now at the octahedra marked in bold in Figure 5.23a. The edge-sharing corresponds to shearing the structure so that the chains of bold octahedra

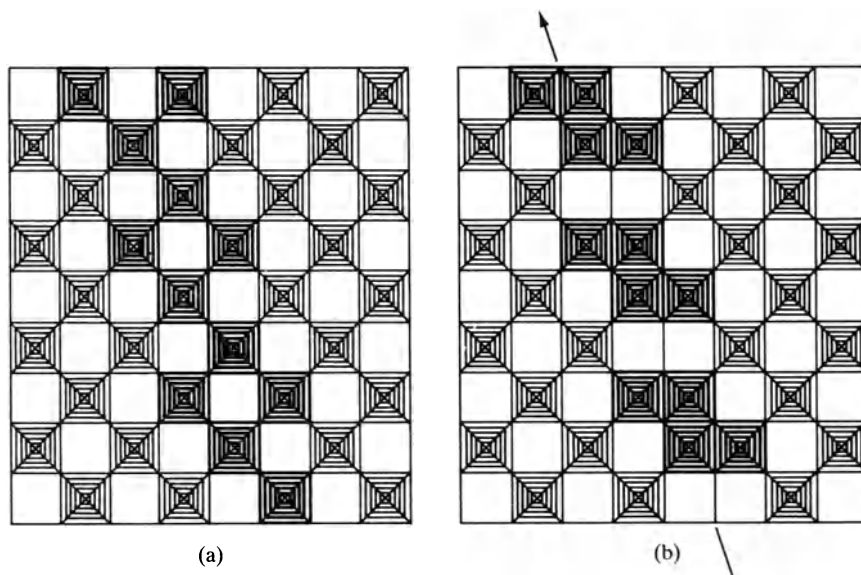


Figure 5.23 Formation of shear structure.

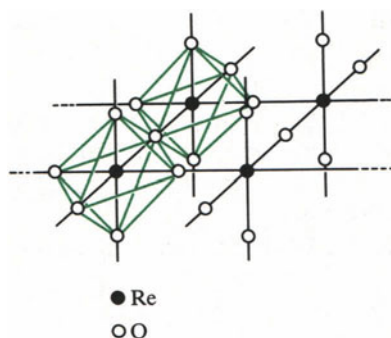


Figure 5.24 Part of the ReO_3 structure showing the linking of octahedra through the corners.

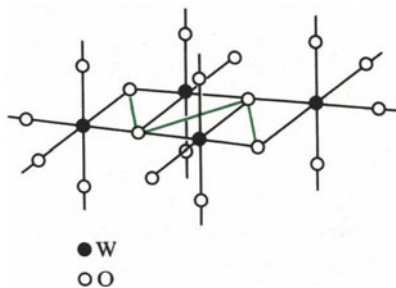
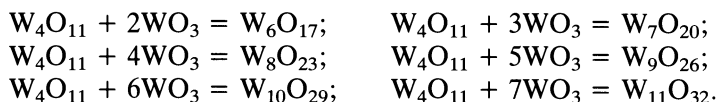


Figure 5.25 Group of four $[\text{WO}_6]$ octahedra sharing edges (marked in colour) formed by the creation of shear planes in $\text{W}_n\text{O}_{3n-1}$.

are displaced to the positions in Figure 5.23b. This shearing occurs at regular intervals in the structure and is interspersed with slabs of the 'ReO₃' structure (corner-linked $[\text{WO}_6]$ octahedra). It creates groups of four octahedra which share edges. The direction of maximum density of the edge-sharing groups is called the crystallographic shear plane and is indicated by an arrow in Figure 5.23b.

In order to see how crystallographic shear alters the stoichiometry of WO_3 , we need to find the stoichiometry of one of the groups of four octahedra that are linked together by sharing edges; one of these groups is shown in Figure 5.25. The group in this figure consists of four W atoms and 18O atoms. Fourteen of the oxygen atoms are linked out to other octahedra (these bonds are indicated), so are each shared by two W atoms, while the remaining four oxygens are only involved in the edge-sharing within the group. The overall stoichiometry is given by $[4\text{W} + (14 \times \frac{1}{2})\text{O} + 4\text{O}]$, giving W_4O_{11} .

Clearly, if groups of four octahedra with stoichiometry W_4O_{11} are interspersed throughout a perfect WO_3 structure, then the amount of oxygen in the structure is reduced and we can write the formula as WO_{3-x} . The effect of introducing the groups of four in an ordered way can be quantified. If the structure sheared in such a way that the entire structure was composed of these groups, the formula would become W_4O_{11} . If there is one $[WO_6]$ octahedron for each group of four then the overall formula becomes $[W_4O_{11} + WO_3] = W_5O_{14}$. Clearly we can extend this process to any number of $[WO_6]$ octahedra regularly interspersed between the groups:



The basic formula of the group of four W_4O_{11} can be written as W_nO_{3n-1} where $n = 4$. This formula also holds for all the other formulae that are listed above. So we have produced the general formula for the homologous series simply by introducing set ratios of the edge-sharing groups in amongst the $[WO_6]$ octahedra.

The shear planes are found to repeat throughout a particular structure in a regular and ordered fashion, so any particular sample of WO_{3-x} will have a specific formula corresponding to one of those listed above. The different members of the homologous series are determined by the fixed spacing between the CS planes. An example of one of the structures is shown in Figure 5.26. A unit cell has been marked so that the ratio of $[WO_6]$ octahedra to the groups of four is clear. Within the marked unit cell there is one group of four and seven octahedra giving the overall formula $W_4O_{11} + 7WO_3 = W_{11}O_{32}$.

Members of the Mo_nO_{3n-1} series have the same structure as their W_nO_{3n-1} analogue, even though unreduced MoO_3 does not have the ReO_3 structure, but a layer structure.

If the structures shear in such a way that groups of six octahedra share edges regularly throughout the structure, then homologous series with the general formula M_nO_{3n-2} are formed.

The homologous series for oxygen-deficient TiO_2 is given by the formula Ti_nO_{2n-1} . In this case the octahedra along the CS planes are joined to each other by sharing faces, whereas in the unreduced parts of the TiO_2 structure the octahedra share edges as in rutile.

5.8.2 Planar intergrowths

As this is rather a complex area we will only look at one example here, that of intergrowths in the **tungsten bronzes**. The term *bronze* is applied to metallic oxides that have a deep colour, metallic lustre and are either

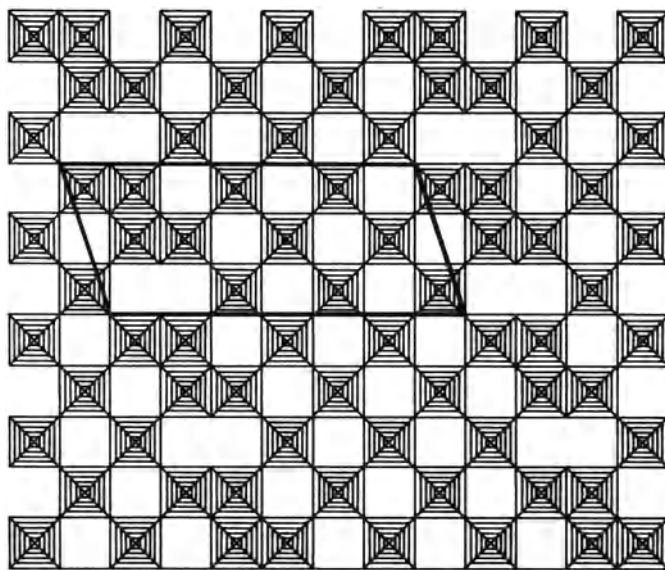


Figure 5.26 A member of the W_nO_{3n-1} homologous series with the projection of a unit cell marked.

metallic conductors or semiconductors. The sodium-tungsten bronzes, Na_xWO_3 , have colours that range from yellow to red and deep purple, depending on the value of x .

We have already seen that WO_3 has the rhenium oxide (ReO_3) structure, with $[WO_6]$ octahedra joined through the corners. This is illustrated in Figures 5.23a and 5.24. The structure contains a three-dimensional network of channels throughout the structure and it has been found that alkali metals can be incorporated into the structure in these channels. The resultant crystal structure depends on the proportion of alkali metal in the particular compound. The structures are based on three main types: *cubic* phases where the alkali metal occupies the centre of the unit cell (similar to perovskite; Chapters 1 and 10) and *tetragonal* and *hexagonal* phases. The basic structures of two of these are illustrated in Figure 5.27. The electronic conductivity properties of the bronzes are due to the fact that charge compensation has to be made for the presence of M^+ ions in the structure. This is achieved by the change in oxidation state of some of the tungsten atoms from VI to V (such processes are discussed in more detail in section 5.10).

The hexagonal bronze structure illustrated is formed when potassium reacts with WO_3 (K needs a bigger site) and the composition lies in the range $K_{0.19}WO_3$ to $K_{0.33}WO_3$. If the proportion of potassium in the compound is less than this the structure is found to consist of WO_3

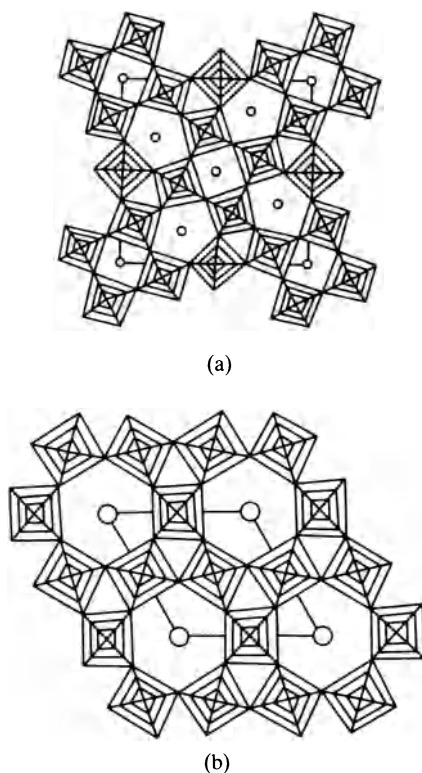


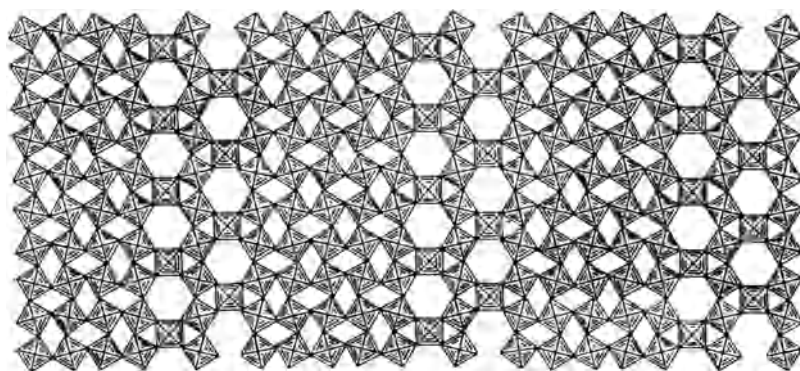
Figure 5.27 (a) The tetragonal tungsten bronze structure, and (b) the hexagonal tungsten bronze structure. The shaded squares represent WO_6 octahedra, which are linked to form pentagonal, square and hexagonal tunnels. These are able to contain a variable population of metal atoms, shown as open circles.

intergrown with the hexagonal structure in a regular fashion. The layers of hexagonal structure can be either one or two tunnels wide (Figure 5.28). Similar structures are observed for tungsten bronzes containing metals other than potassium, such as Rb, Cs, Ba, Sn and Pb. A high-resolution electron micrograph of the barium-tungsten bronze clearly shows its preferred single tunnel structure (Figure 5.29). In other samples the separation of the tunnels increases as the concentration of barium decreases.

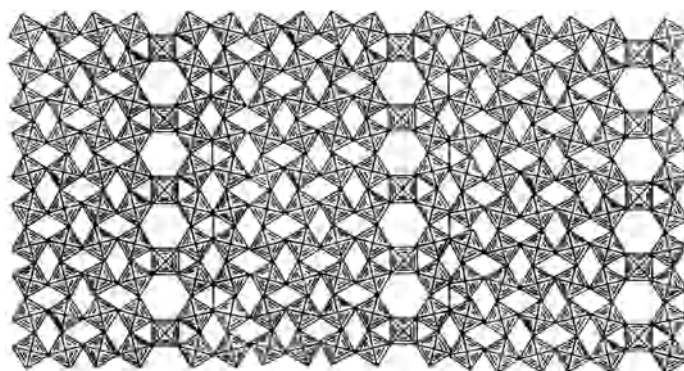
5.9 THREE-DIMENSIONAL DEFECTS

5.9.1 Block structures

In oxygen-deficient Nb_2O_5 and in mixed oxides of Nb and Ti, and Nb and W, the crystallographic shear planes occur in two sets at right angles to



(a)



(b)

Figure 5.28 The idealized structures of two intergrowth tungsten bronze phases, (a) containing double rows of hexagonal tunnels, and (b) containing single rows of tunnels. The tungsten trioxide matrix is shown as shaded squares and the hexagonal tunnels are shown empty, although in the known intergrowth tungsten bronzes the tunnels contain variable amounts of metal atoms.

each other. The intervening regions of perfect structure now change from infinite sheets to infinite columns or blocks. These structures are known as **double shear** or **block structures** and are characterized by the cross-sectional size of the blocks. The block size is expressed as the number of octahedra sharing vertices. As well as having phases built of blocks of one size, the complexity can be increased by having blocks of two or even three different sizes arranged in an ordered fashion! The block size(s) determines the overall stoichiometry of the solid. An example of a crystal showing two different block sizes is shown in Figure 5.30.

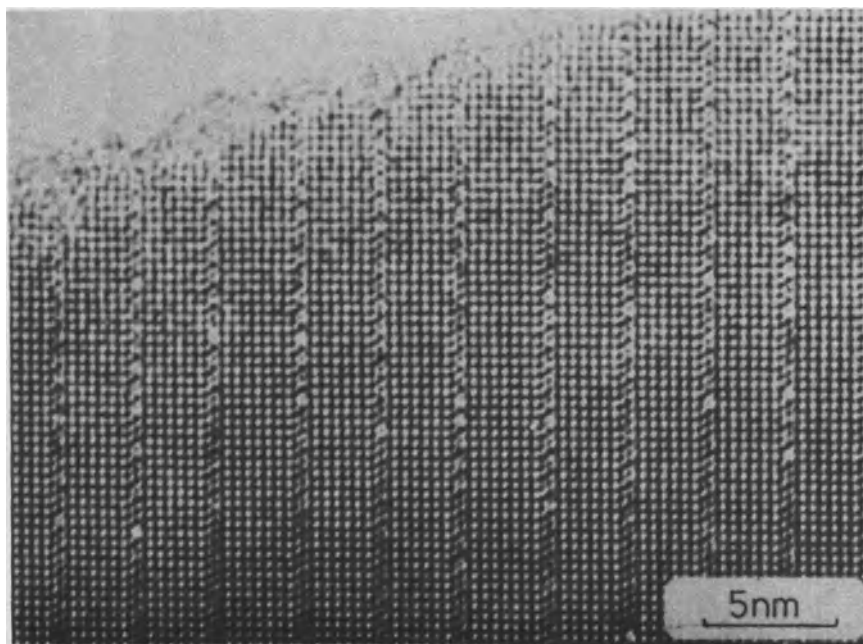


Figure 5.29 Electron micrograph of the intergrowth tungsten bronze phase Ba_xWO_3 , showing the single rows of tunnels clearly. Each black spot on the image represents a tungsten atom, and many of the hexagonal tunnels seem to be empty or only partly filled with barium.

5.9.2 Pentagonal columns

Three-dimensional faults also occur in the so-called **pentagonal column (PC) structures**. These structures contain the basic repeating unit shown in Figure 5.31a which consists of a pentagonal ring of five $[\text{MO}_6]$ octahedra. When these stack on top of one another a pentagonal column is formed that contains chains of alternating M and O atoms. These pentagonal columns can fit inside a ReO_3 type of structure in an ordered way, and depending on the spacing a homologous series is formed. One example is shown in Figure 5.31b for the compound Mo_5O_{14} . This type of structure is also found in the tetragonal tungsten bronzes.

5.9.3 Infinitely adaptive structures

In section 5.9.1 we saw that the mixed oxides of niobium and tungsten could have a range of different compositions made by fitting together rectangular columns or blocks. The closely related $\text{Ta}_2\text{O}_5\text{--WO}_3$ system

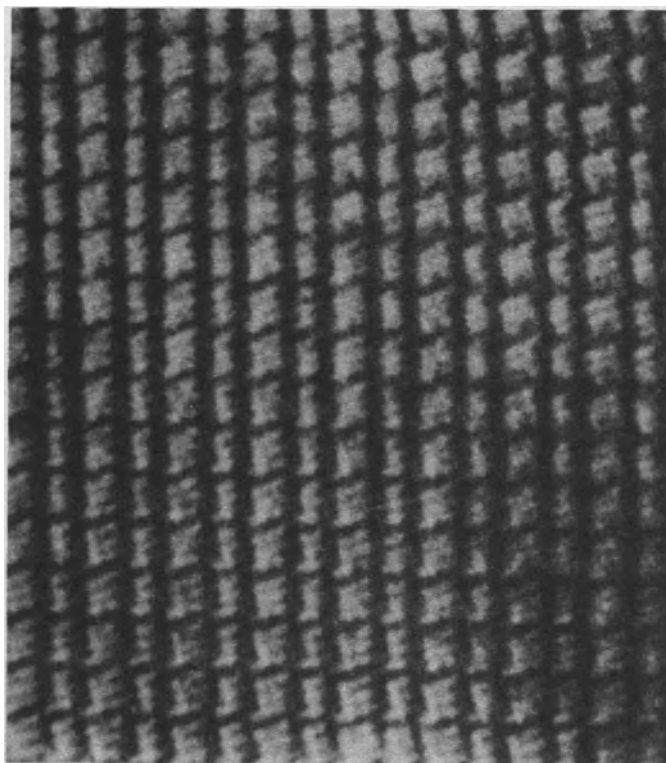


Figure 5.30 High-resolution electron micrograph of the $W_4Nb_{26}O_{77}$ structure showing strings of (4×4) and (3×4) blocks. CS planes between the blocks show as darker contrast. (Photograph by courtesy of Dr J.L. Hutchison.)

does something even more unusual! A large number of compounds form, but they are built up by fitting together pentagonal columns (PCs). The idealized structures of two of these compounds are shown in Figure 5.32: the structures have a wave-like skeleton of PCs. As the composition varies, so the wavelength of the backbone changes, giving rise to a huge number of possible ordered structures, known as **infinitely adaptive compounds**.

5.10 ELECTRONIC PROPERTIES OF NON-STOICHIOMETRIC OXIDES

Earlier we considered the structure of non-stoichiometric FeO in some detail. If we apply the same principle to other binary oxides we can define four types of compound.

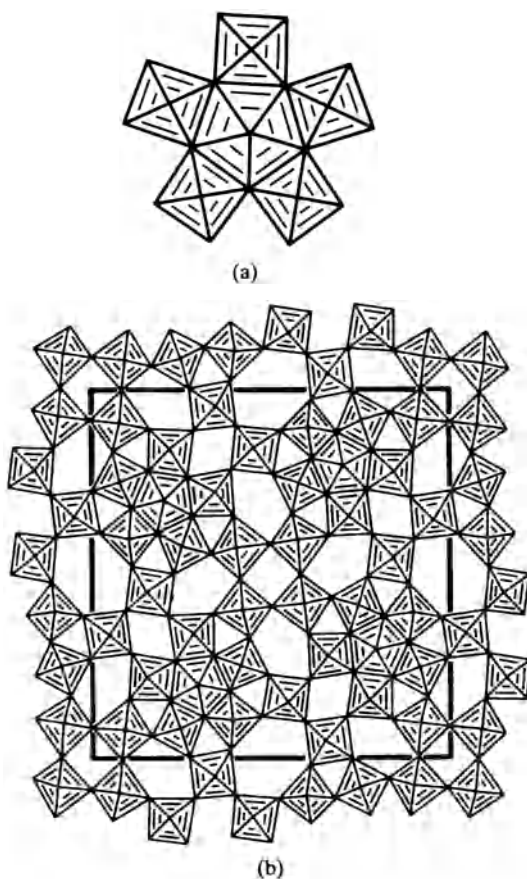


Figure 5.31 (a) A pentagonal column, and (b) the structure of Mo_5O_{14} .

Metal excess: type A – anion vacancies present, formula MO_{1-x}
 type B – interstitial cations, formula M_{1+x}O
 Metal deficiency: type C – interstitial anions, formula MO_{1+x}
 type D – cation vacancies, formula M_{1-x}O

Figure 5.33 illustrates some of the structural possibilities for simple oxides with A, B, C and D type non-stoichiometry, assuming that they have the NaCl structure.

We looked in some detail earlier at the structure of FeO ; this falls into the **type D** category. (Other compounds falling into the type D category are MnO , CoO and NiO .)

Type A oxides compensate for metal excess with **anion vacancies**. In order to maintain the overall neutrality of the crystal two electrons have to be introduced for each anion vacancy. These can be trapped at a

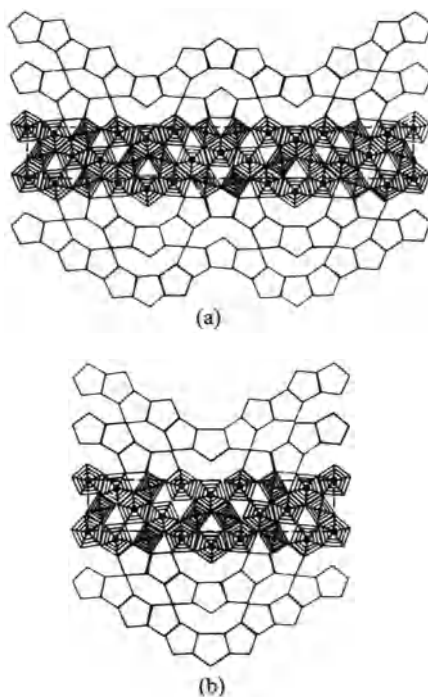


Figure 5.32 The idealized structures of (a) $\text{Ta}_{22}\text{W}_4\text{O}_{67}$ and (b) $\text{Ta}_{30}\text{W}_2\text{O}_{81}$. These phases are built from pentagonal columns, shown as shaded pentagons, and octahedra, shown as shaded squares. The wavelength of the chains of pentagonal columns varies with composition in such a way that *any* given anion to cation ratio can be accommodated by an ordered structure.

vacant anion site (Figure 5.33a). However, it is an extremely energetic process to introduce electrons into the crystal and so we are more likely to find them associated with the metal cations (Figure 5.33b), which we can describe as reducing those cations from M^{2+} to M^+ .

Type B oxides have a metal excess which is incorporated into the lattice in **interstitial** positions. This is shown in Figure 5.33a as an interstitial atom, but it is more likely that the situation in Figure 5.33b will hold, where the interstitial atom has ionized and the two electrons so released are now associated with two neighbouring ions, reducing them from M^{2+} to M^+ . Cadmium oxide (CdO) has this type of structure. Zinc(II) oxide also is type B, but has the wurtzite structure.

Type C oxides compensate for the lack of metal with **interstitial anions**. The charge balance is maintained by the creation of two M^{3+} ions for each interstitial anion, each of which we can think of as M^{2+} associated with a positive hole.

Before considering the conductivity of these non-stoichiometric oxides

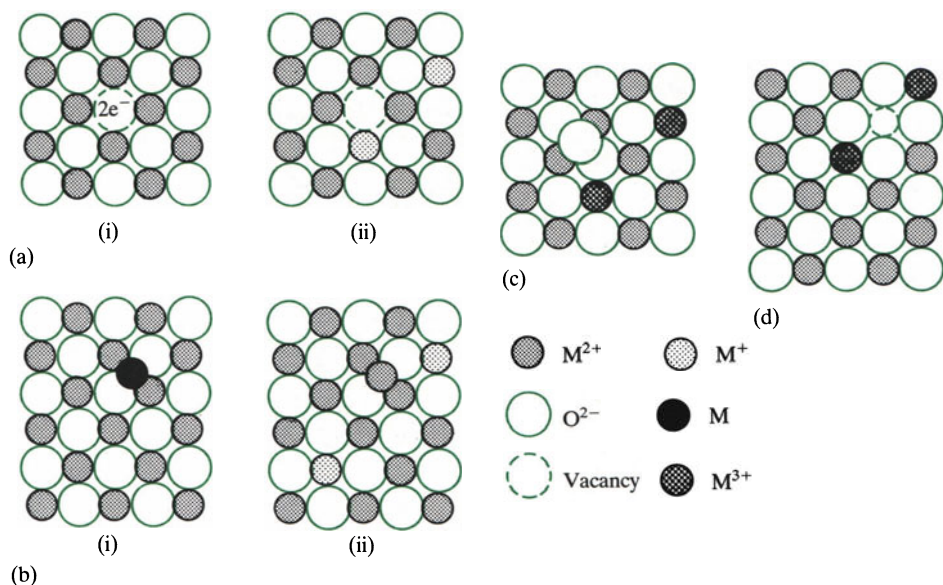


Figure 5.33 Structural possibilities for binary oxides. (a) Type A oxides: metal excess/anion vacancies. (i) This shows the two electrons that maintain charge neutrality, localized at the vacancy. (ii) The electrons are associated with the normal cations making them into M^+ . (b) Type B oxides: metal excess/interstitials. (i) This shows an interstitial *atom*, whereas in (ii) the atom has ionized to M^{2+} , and the two liberated electrons are now associated with two normal cations, reducing them to M^+ . (c) Type C oxides: metal deficiency/interstitial anions. The charge compensation for an interstitial anion is by way of two M^{3+} ions. (d) Type D oxides: metal deficiency/cation vacancies. The cation vacancy is compensated by two M^{3+} cations.

it is probably helpful to recap what we know about the structure and properties of the stoichiometric binary oxides of the first row transition elements. A summary of the properties of binary oxides is given in Table 5.7.

We discussed the conductivity of the stoichiometric oxides in Chapter 4 and saw that their conductivity is dependent on two competing effects: on the one hand the d orbitals overlap to give a band – the bigger the overlap the greater the band width – and electrons in the band are delocalized over the whole structure; on the other hand, interelectronic repulsion tends to keep electrons localized on individual atoms. TiO and VO behave as metallic conductors and must therefore have good overlap of the d orbitals producing a d electron band. This overlap arises partly because Ti and V are early in the transition series (the d orbitals have not suffered the contraction, due to increased nuclear charge, seen later in the series) and partly because of the unusual crystal structure where one-

Table 5.7 Properties of the first row transition element monoxides

<i>Element</i>	<i>Ca</i>	<i>Sc</i>	<i>Ti</i>	<i>V</i>	<i>Cr</i>	<i>Mn</i>	<i>Fe</i>	<i>Co</i>	<i>Ni</i>	<i>Cu</i>	<i>Zn</i>
Structure of stoichiometric oxide MO	NaCl structure	Does not exist	Defect NaCl structure $\frac{1}{6}$ vacancies	Defect NaCl structure	Does not exist	NaCl structure	(NaCl structure)*	NaCl structure	NaCl structure	PtS structure	Wurtzite structure (NaCl at high pressure)
Defect structure			Ti _{1-δ} O Ti vacancies (inter-growths of TiO _{1.00} and TiO _{1.25} structures)	Similar to TiO		Mn _{1-δ} O Mn vacancies	Fe _{1-δ} O Fe vacancies in defect clusters	Co _{1-δ} O Co vacancies	Ni _{1-δ} O Ni vacancies		Zn _{1+δ} O interstitial Zn
Conductivity of stoichiometric compound			Metallic	Metallic <120 K		Insulator	(Insulator)*	Insulator	Insulator		Insulator
Conductivity of non-stoichiometric compound			Metallic	Metallic		<i>p</i> -type hopping semi-conductor	<i>p</i> -type	<i>p</i> -type	<i>p</i> -type		<i>n</i> -type
Magnetism (Chapter 9)			Diamagnetic	Diamagnetic		Paramagnetic $\mu = 5.5 \mu_B$ (antiferromagnetic when cooled, $T_N = 122$ K)	Paramagnetic (antiferromagnetic when cooled, $T_N = 198$ K)	Antiferromagnetic ($T_N = 292$ K)	Antiferromagnetic (paramagnetic when heated, $T_N = 530$ K)		

* Exactly stoichiometric FeO is never found.

sixth of the titaniums and oxygens (VO is similar) are missing from an NaCl-type structure which allows contraction of the structure and thus better d orbital overlap.

Further along the series, stoichiometric MnO, FeO, CoO and NiO are insulators. This situation is not easily described by band theory because the d orbitals are now too contracted to overlap much (typical band widths are 1 eV) and the overlap is not sufficient to overcome the localizing influence of interelectronic repulsions. (It is this localization of the d electrons on the atoms that gives rise to the magnetic properties of these compounds that are discussed in Chapter 9.)

Returning to the non-stoichiometric oxides, in the excess metal monoxides of types A and B, we saw that extra electrons have to compensate for the excess metal in the structure. Figure 5.33 shows that these could be associated either with an anion vacancy or alternatively with metal cations within the structure. Although we have described this association as reducing neighbouring cations, this association can be quite weak, and these electrons can be free to move through the lattice; they are not necessarily strongly bound to particular atoms. Thermal energy is often sufficient to make these electrons move and so conductivity increases with temperature. We associate semiconductivity with such behaviour (metallic conductivity decreases with temperature).

In Chapter 4 we discussed semiconductivity in terms of band theory. An intrinsic semiconductor has an empty conduction band lying close above the filled valence band. Electrons can be promoted into this conduction band by heating, leaving positive holes in the valence band. The current is carried by both the electrons in the conduction band and by the positive holes in the valence band. Semiconductors such as silicon can also be doped with impurities to enhance their conductivity. For instance, if a small amount of phosphorus is incorporated into the lattice the extra electrons form impurity levels near the empty conduction band and are easily excited into it. The current is now carried by the electrons in the conduction band and the semiconductor is known as ***n*-type** (*n* for negative). Correspondingly, doping with gallium increases the conductivity by creating positive holes in the valence band and such semiconductors are called ***p*-type** (*p* for positive).

Compounds of type A and B would produce *n*-type semiconductors because the conduction is produced by electrons. Conduction in these non-stoichiometric oxides is not easily described by band theory, for the reasons given earlier for their stoichiometric counterparts: the interelectronic repulsions have localized the electrons on the atoms. So it is easier to think of the conduction electrons (or holes) localized or trapped at atoms or defects in the crystal rather than delocalized in bands throughout the solid. Conduction then occurs by jumping or **hopping** from one site to another under the influence of an electric field. In a

perfect ionic crystal where all the cations are in the same valence state this would be an extremely energetic process. However, when two valence states, such as Ni^{2+} and Ni^{3+} , are available, as in these transition metal non-stoichiometric compounds, the electron jump between them does not take much energy. Although we cannot develop this theory here, we can note that the conduction in these so-called **hopping semiconductors** can be described by the equations of diffusion theory in much the same way as we did earlier for ionic conduction. We find that the mobility of a charge carrier (either an electron or a positive hole), μ , is an activated process and we can write

$$\mu \propto \exp(-E_a/kT), \quad (5.28)$$

where E_a is the activation energy of the hop, and is of the order of 0.1–0.5 eV. The hopping conductivity is given by the expression

$$\sigma = ne\mu, \quad (5.29)$$

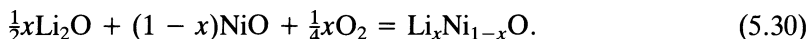
where n is the number of mobile charge carriers per unit volume and e is the electronic charge. (Notice that these equations are analogous to equations (5.8) and (5.7) in section 5.3, describing ionic mobility, μ , and ionic conductivity, σ , respectively). The density of mobile carriers, n , depends only on the composition of the crystal, and does not vary with temperature. From equation (5.28) we can see that, as for ionic conductivity, the hopping electronic conductivity increases with temperature.

In the type C and D monoxides we have shown the lack of metal as being compensated by oxidation of neighbouring cations to M^{3+} . The M^{3+} ions can be regarded as M^{2+} ions associated with a positive hole. Accordingly, if sufficient energy is available conduction can be thought to occur via the positive hole hopping to another M^{2+} ion and the electronic conductivity in these compounds will be *p*-type. MnO, CoO, NiO and FeO are materials that behave in this way. This behaviour of hopping semiconduction was described for NiO in Chapter 4 in terms of electron hopping. Regarding the charge carriers as positive holes is simply a matter of convenience and the description of a positive hole moving from Ni^{3+} to Ni^{2+} is the same as saying that an electron moves from Ni^{2+} to Ni^{3+} .

Non-stoichiometric materials can be listed which cover the whole range of electrical activity from metal to insulator. Here we have considered some metallic examples which can be described by band theory (TiO, VO) and others (such as MnO) which are better described as hopping semiconductors. Other cases, such as WO_3 and TiO_2 , fall in between these extremes and a different description again is needed. Non-stoichiometric compounds such as calcia-stabilized zirconia and β -alumina are also good ionic conductors. Indeed, stabilized zirconia exhibits both electronic and ionic conductivity though, fortunately for its industrial usefulness,

electronic conduction only occurs at low oxygen pressures. It is thus difficult to make generalizations about this complex behaviour and each case is best treated individually.

Semiconductor properties are extremely important to the modern electronics industry, which is constantly searching for new and improved materials. Much of their research is directed at extending the composition range and thus the properties of these materials. The composition range of a non-stoichiometric compound is often quite narrow (a so-called line phase), so to extend it (and thus extend the range of its properties also) the compound is doped with an impurity. To take one example: if we add Li_2O to NiO and then heat to high temperatures in the presence of oxygen, Li^+ ions become incorporated in the lattice and the resulting black material has the formula $\text{Li}_x\text{Ni}_{1-x}\text{O}$, where x lies in the range 0–0.1. The equation for the reaction (using stoichiometric NiO for simplicity) is given by:



To compensate for the presence of the Li^+ ions, Ni^{2+} ions will be oxidized to Ni^{3+} or the equivalent of a high concentration of positive holes located at Ni cations.

This process of creating electronic defects is called **valence induction** and it increases the composition range of 'NiO' tremendously. Indeed, at high Li concentrations the conductivity approaches that of a metal (although it still exhibits semiconductor behaviour in that its conductivity increases with temperature).

5.11 CONCLUSIONS

In this chapter we have tried to give some idea of the size and complexity of this subject and also its fascination, without it becoming overwhelming. The main point to emerge from our explorations is that the concept of random, isolated point defects does not explain the complex structures of non-stoichiometric compounds but that there are many different ways for defects to become either ordered or even eliminated.

FURTHER READING

Defects

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A very readable book, written for materials scientists, but with much material relevant to this book. Suitable for higher level undergraduates and postgraduates.

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Useful sections on F-centres, luminescence, phosphors and lasers.

Sodium–sulphur battery

- Sudworth, J.L. and Tilley, A.R. (1985) *The Sodium Sulfur Battery*, Chapman & Hall, London.
Very specialized text containing much industrial detail.

QUESTIONS

1. If ΔH_m° for the formation of Schottky defects in a certain MX crystal is 200 kJ mol^{-1} , calculate n_s/N and n_s per mole for the temperatures 300, 500, 700 and 900 K.
2. Table 5.8 gives the variation of defect concentration with temperature for CsI. Determine the enthalpy of formation for one Schottky defect in this crystal.

Table 5.8 Defect concentration data for CsI

$T(K)$	n_s/N
300	1.08×10^{-16}
400	1.06×10^{-12}
500	2.63×10^{-10}
600	1.04×10^{-8}
700	1.43×10^{-7}
900	4.76×10^{-6}

- If we increase the quantity of impurity (say CaCl_2) in the NaCl crystal, how will this affect the plot shown in Figure 5.8? How is the transition point in the graph affected by the purity of the crystal?
- In NaCl the cations are more mobile than the anions. What effect, if any, do you expect small amounts of the following impurities to have on the conductivity of NaCl crystals: (a) AgCl ; (b) MgCl_2 ; (c) NaBr ; (d) Na_2O ?
- Unlike fluorides, pure oxides with the fluorite structure (MO_2) show high anion conduction only at elevated temperatures, above about 2300 K. Suggest a reason for this.
- Figure 5.34 shows the fluorite structure with the tetrahedral environment of one of the anions depicted in colour. (The anion behind this tetrahedron has been omitted for clarity.) Suppose the coloured anion jumps to the octahedral hole at the body centre. Describe, and sketch, the pathway it takes in terms of the changing coordination by cations.

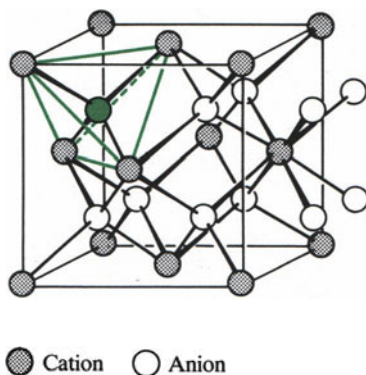


Figure 5.34 The fluorite structure, showing the coordination tetrahedron (colour) around one of the anions (also colour).

7. Make a simple estimate of the energy of defect formation in the fluorite structure. (a) Describe the coordination by nearest neighbours and next-nearest neighbours of an anion both for a normal lattice site and for an interstitial site at the centre of the unit cell shown in Figure 5.3a. (b) Use the potential energy of two ions, given by

$$E = -\frac{e^2 Z}{4\pi\epsilon_0 r}$$

$$= -(2.31 \times 10^{-28} \text{ J m}) Z/r,$$

where Z is the charge on the other ion and r is the distance between them, to estimate the energy of defect formation in fluorite; $a = 537 \text{ pm}$.

8. The zinc blende structure of $\gamma\text{-AgI}$, a low-temperature polymorph of AgI , is shown in Figure 5.35. Discuss the similarities and differences between this structure and that of $\alpha\text{-AgI}$. Why do you think that the conductivity of the Ag^+ ions is lower in $\gamma\text{-AgI}$?

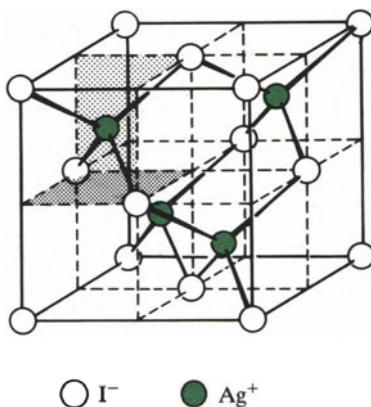


Figure 5.35 The zinc blende structure of $\gamma\text{-AgI}$.

9. The compounds in Table 5.4 mostly contain either I^- ions or ions from the heavier end of Group 6. Explain.
10. Undoped β -alumina shows a maximum conductivity and minimum activation energy when the sodium excess is around 20–30 mole %. Thereafter, further increase in the sodium content causes the conductivity to decrease. By contrast, β -alumina crystals doped with Mg^{2+} have a much higher conductivity than do undoped crystals. Explain these observations.

11. Confirm the presence of iron vacancies for a sample of wustite which has a unit cell dimension of 428.2 pm, an Fe:O ratio of 0.910 and an experimental density of $5.613 \times 10^3 \text{ kg m}^{-3}$.
12. How does the change in lattice parameter of 'FeO' with iron content corroborate the iron vacancy model and refute an oxide interstitial model?
13. How would you expect the formation of colour centres to affect the density of the crystal?
14. Figure 5.36 shows the central section of a possible defect cluster for FeO. (a) Determine the vacancy: interstitial ratio for this cluster. (b) Assuming that this section is surrounded by Fe ions and oxide ions in octahedral sites as in the Koch–Cohen cluster, determine the formula of a sample made totally of such clusters. (c) Determine the numbers of Fe^{2+} and Fe^{3+} ions in octahedral sites.

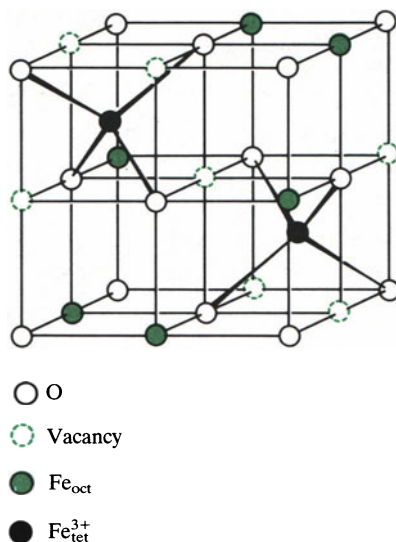


Figure 5.36 A possible cluster in Fe_{1-x}O .

15. Use Figure 5.20 to confirm that TiO is a one-sixth defective NaCl structure, by counting up the atoms in the monoclinic cell.
16. Figure 5.21 shows layers in the $\text{TiO}_{1.25}$ structure with both the Ti and O sites marked. Use this and Figure 5.22 to demonstrate that the unit cell shown has the correct stoichiometry for the crystal.
17. How would you expect charge neutrality to be maintained in $\text{TiO}_{1.25}$?

18. Take a simple case where two metal oxide octahedra wish to eliminate oxygen by sharing. How does the formula change as they (i) share a corner, (ii) share an edge, (iii) share a face?
19. Figure 5.37 shows a member of the homologous series, W_nO_{3n-1} . What formula does it correspond to?

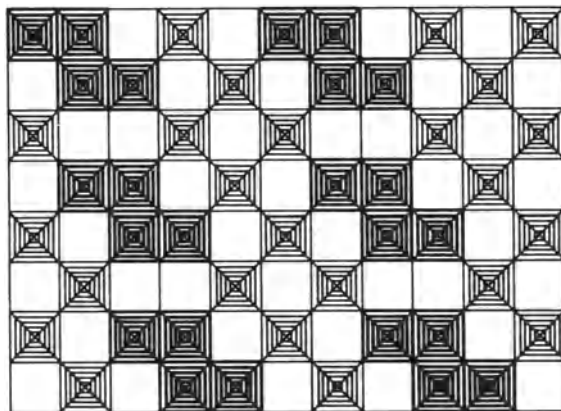


Figure 5.37 A member of the W_nO_{3n-1} homologous series.

20. ZnO is a type B (excess metal) material. What do you expect to happen to its electronic properties if it is doped with Ga_2O_3 under reducing conditions?

6.1 INTRODUCTION

There are a number of solids whose properties are not isotropic. They may, for example, conduct electrons along planes, but not between planes, or they may only conduct along chains of atoms. Such solids are known as **low-dimensional solids**. There has been recent interest in developing devices using such materials, for example in batteries, in solar cells and in photocopiers, and there has been theoretical interest because they can be treated as if they were one- or two-dimensional, and the equations for one and two dimensions are simpler than for three dimensions. Examples of these solids are found in both organic and inorganic chemistry. Much research interest has centred on organic compounds; a polymer with low density and metallic conductivity would be extremely useful technologically, for example, in switching devices, sensors and 'smart' windows. The first low-dimensional metals found were, however, inorganic. Examples are given of both organic and inorganic solids, starting with one-dimensional electronic conductors.

6.2 ONE-DIMENSIONAL SOLIDS

In Chapter 4, we took a hypothetical one-dimensional solid – a chain of hydrogen atoms. The solids studied below contain chains of atoms or molecules which can be treated in a similar manner to the hypothetical chain. In the crystals of these solids the chains are not completely isolated, but because the forces between chains are much less than those bonding the chains, the chains can be treated as one-dimensional solids. The first solid we consider is an organic polymer, polyacetylene.

6.2.1 Polyacetylene and related compounds

Most organic polymers are electrical insulators; a mouldable plastic that was a conductor would be a technological breakthrough. To be

conducting, the polymer must have electrons delocalized along the chain length. In small conjugated alkenes such as butadiene with alternate double and single bonds, the π electrons are delocalized over the molecule. If we take a very long conjugated olefin, we might expect to obtain a band of π levels, and if this band were partly occupied we would expect to have a one-dimensional conductor. Polyacetylene is just such a conjugated long chain polymer. This is formed by polymerizing ethyne (acetylene) and has two forms, *cis* and *trans* (Figure 6.1).

If polyacetylene consisted of a regular evenly spaced chain of carbon atoms, the highest occupied energy band, the π band, would be half full and polyacetylene would be an electrical conductor. In practice, polyacetylene shows only modest electrical conductivity, comparable with semiconductors such as silicon: the *cis* form has a conductivity of the order of 10^{-7} S m^{-1} and the *trans* form, 10^{-3} S m^{-1} . The crystal structure is difficult to determine accurately, but diffraction measurements indicate that there is an alternation in bond lengths of about 6 pm. This is much less than would be expected for truly alternating single and double bonds (C—C, 154 pm in ethane; C=C, 134 pm in ethene). Nonetheless this does indicate that the electrons are tending to localize in double bonds rather than be equally distributed over the whole chain. What in fact is happening is that two bands, bonding and antibonding, are forming with a band gap where non-bonding levels would be expected. There are just enough electrons to fill the lower band. This leads to a lower energy than the half-full single band (Figure 6.2). This splitting of the band is an example of **Peierls' theorem** which asserts that a one-dimensional metal is always electronically unstable with respect to a non-metallic state; there is always some way of opening an energy gap and creating a semiconductor.

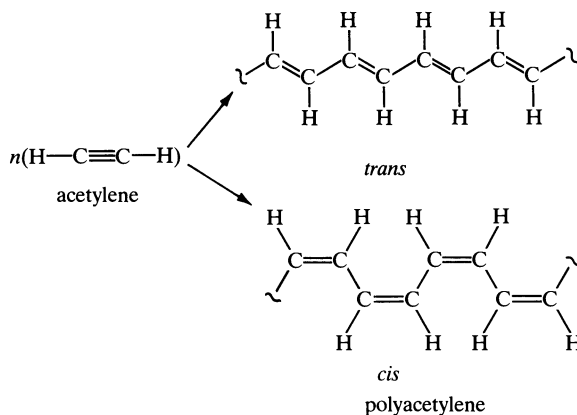


Figure 6.1 *cis*- and *trans*-polyacetylene.

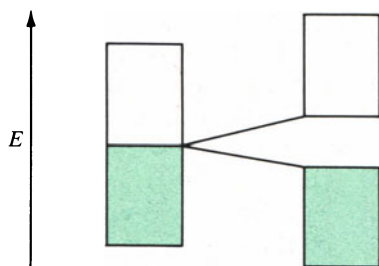


Figure 6.2 The band gap in polyacetylene produced by the alternation of long and short bonds along the chain.

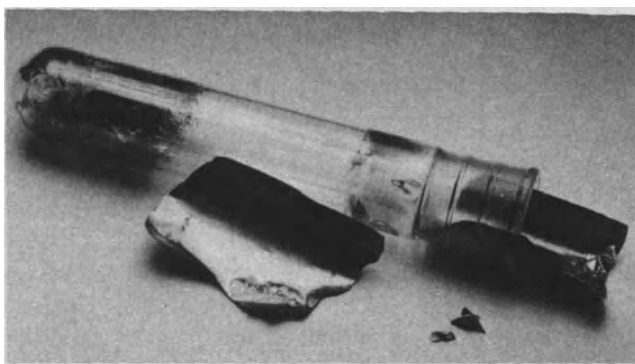


Figure 6.3 A film of polyacetylene forms on the inner surface of the reaction vessel, after ethyne gas passes over the catalyst solution of the walls. The paperthin flexible sheet of polyacetylene is then stripped from the walls prior to doping.

Thus, although a very simple bonding picture of such solids would suggest a half-filled band and metallic conductivity, the best that can be expected is a semiconducting polymer. Furthermore, there were other problems in finding useful conducting polymers. At first, attempts to make polyacetylene and similar solids resulted in short chain molecules or amorphous, unmeltable powders. Then in 1961, Hatano and co-workers in Tokyo managed to produce thin films of polyacetylene, and 10 years later Shirakawa and Ikeda made films of *cis*-polyacetylene which could be converted into the *trans* form. They achieved this by directing a stream of ethyne gas on to the surface of a Ziegler–Natta catalyst (a mixture of triethyl aluminium and titanium tetrabutoxide). To make a large film, the catalyst solution can be spread in a thin layer over the walls of a reaction vessel (Figure 6.3), and then ethyne gas allowed to enter. The polyacetylene produced in this way has a smooth shiny surface on one

side and a sponge-like structure. It can be converted to the thermodynamically more stable *trans* form by heating. The conversion is quite rapid above 370 K. After conversion, the smooth side of the film is silvery in appearance, becoming blue when the film is very thin.

A method to improve the conductivity was discovered when Shirakawa visited McDiarmid and Heeger in Pennsylvania later in the 1970s. The Americans had been working on smaller conjugated molecules to which they added an electron acceptor in order to make them conducting. It was a natural step to try this approach with polyacetylene. If an electron acceptor such as bromine is added to polyacetylene, it takes electrons from the lower π bonding band, forming $[(CH^{\delta+}Br_8^-)]_n$. The doped polyacetylene now has holes in its valence band and, like *p*-type semiconductors, its conductivity is greater than that of the undoped material. Other examples of dopants that can oxidize polyacetylene are I_2 , AsF_5 and $HClO_4$. The effect of these dopants is shown in Figure 6.4, where it can be seen that the conductivity rises from $10^{-3} S m^{-1}$ to as much as $10^5 S m^{-1}$ using only small quantities of dopant.

The conductivity of polyacetylene is also increased by dopants that are electron donors. For example, the polymer can be doped with alkali metals to give, for example, $[Li_8^+(CH)^{\delta-}]_n$. The electron donor dopants add electrons to the upper π band, making this partly full, and so producing an *n*-type semiconductor. The wide range of conductivities produced by these two forms of doping is illustrated in Figure 6.5.

Suggested uses of polyacetylene include a lightweight rechargeable battery and a photovoltaic cell. In the electrochemical cell proposed as the basis for the battery, two electrodes made of polyacetylene film are dipped into a solution of a lithium salt such as $LiAsF_6$ or $LiBF_4$ in

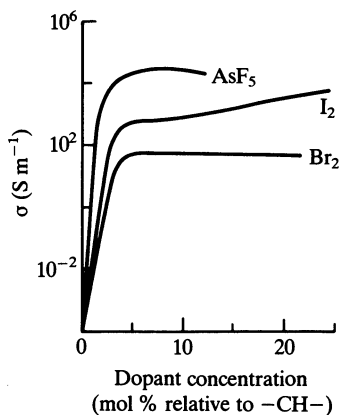


Figure 6.4 Plot showing the increase in conductivity of polyacetylene on the addition of various dopants.

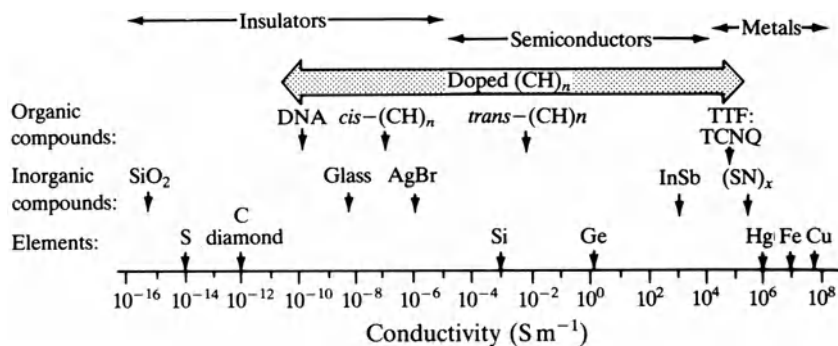
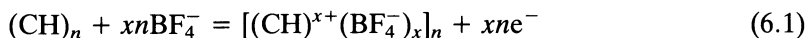


Figure 6.5 The conductivity of undoped and doped polyacetylene ((CH)_n) compared with the values for some of the better-known insulators, semiconductors and metals.

propylene carbonate. When a direct current is passed through the cell, the polyacetylene at the anode is oxidized and that at the cathode reduced. The electrode reactions are



and



The *p*-*n* junction needed for a photovoltaic cell, as described in Chapter 4, can be made by bringing together a *p*-type film and an *n*-type film of polyacetylene.

Since the development of polyacetylene, several similar polymeric materials have been prepared. Most of these are based on aromatic molecules (Figure 6.6). The conductivity of these polymers is about a hundredth of that of polyacetylene and interest has moved from possible uses as electrical conductors to uses as semiconductors. For example, poly(*p*-phenylenevinylene) has been used to make a light-emitting diode (LED; see Chapter 4) giving out red light and poly(*p*-phenylene), a blue LED. In these devices the efficiency is low if the polymers are attached directly to metal contacts. The efficiency has been increased by making a two-layer device in which the second layer is a material whose energy bands are closer to those of the metal than are those of the polymer.

6.2.2 Platinum chain compounds

Platinum chain compounds were the first one-dimensional electronic conductors found. Crystals containing chains of tetracyanoplatinate and bisoxalatoplatinate ions were prepared in the nineteenth century. The

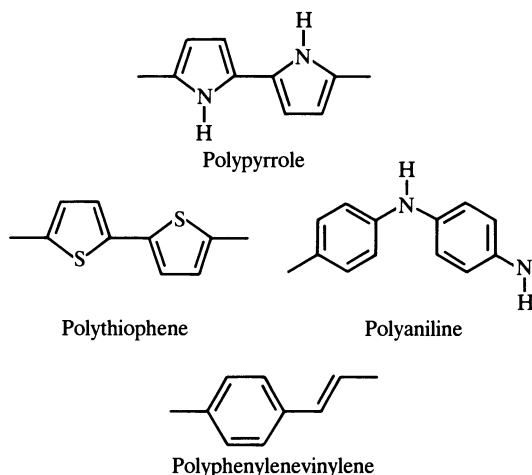


Figure 6.6 Repeating units of some conducting polymers.

compound $\text{K}_2\text{Pt}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$ is an insulator, but when it is dissolved in water and oxidized with a little bromine, copper-coloured needles of $[\text{K}_2\text{Pt}(\text{CN})_4]\text{Br}_{0.3} \cdot 3\text{H}_2\text{O}$ can be crystallized out. This salt is commonly known as KCP or KCP(Br). In the late 1960s K. Krogmann noticed that such salts had unusual conductivities and these compounds are often named after him. Such salts are unlikely to be of great commercial interest due to the weight and price of platinum. Their unusual electrical and optical properties have, however, intrigued chemists ever since their discovery.

The KCP crystals contain chains of closely spaced square-planar $[\text{Pt}(\text{CN})_4]^{2-}$ units (Figure 6.7) and the conductivity parallel to the chains is of the order of 10^4 times that perpendicular to the chains. The optical properties also resemble those of a one-dimensional metal in that light polarized parallel to the chains is reflected, giving the copper colour and metallic sheen, whereas the crystals are transparent to visible light polarized perpendicular to the chain.

The Pt–Pt separation is 289 pm along the chain; this is quite close to the Pt–Pt distance found in Pt metal (277 pm). The ligands surrounding the metal atoms ensure that the interchain separation is large (about 800 pm) so that there is no overlap of Pt orbitals at right-angles to the stacking direction. The separation of the chains can be seen in the packing diagram (Figure 6.8). The bromide ions are shown in the centre of the unit cell. These occupy only 60% of such sites and are arranged randomly among them. Water molecules and potassium ions also occupy space between the chains.

This arrangement gives us a clue to the origin of the properties of these

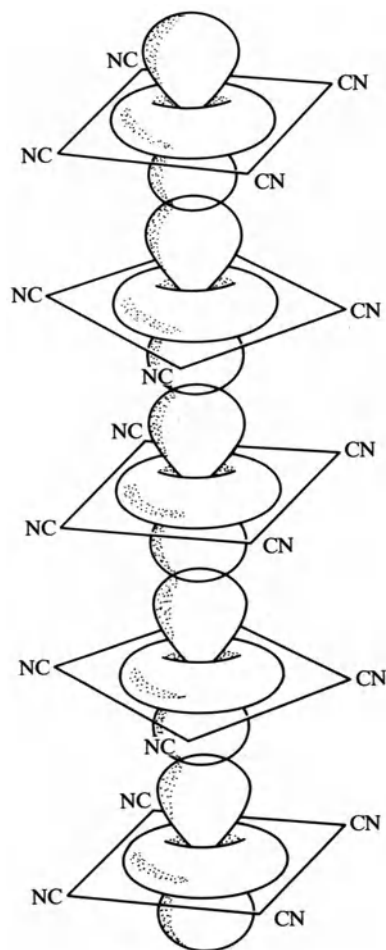


Figure 6.7 Columnar stacked structure of $[\text{Pt}(\text{CN})_4]^{x-}$ ions.

salts. The $5d$ orbitals on the Pt atoms in a chain can overlap, but there is no overlap of $5d$ orbitals on Pt atoms in different chains. If we take the chain axis to be the z -axis, then we can think of all the Pt atoms in one chain being bound together by electrons occupying orbitals formed from overlapping d_{z^2} orbitals. The overlapping $5d$ orbitals are shown in Figure 6.7. Since there are a large number of atoms in a chain, a band of orbitals delocalized over the chain is formed.

In the parent compound, $\text{K}_2\text{Pt}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$, there are just enough electrons to fill this band and so the compound is an insulator. When bromine is added, electrons are taken from the top of this band to form

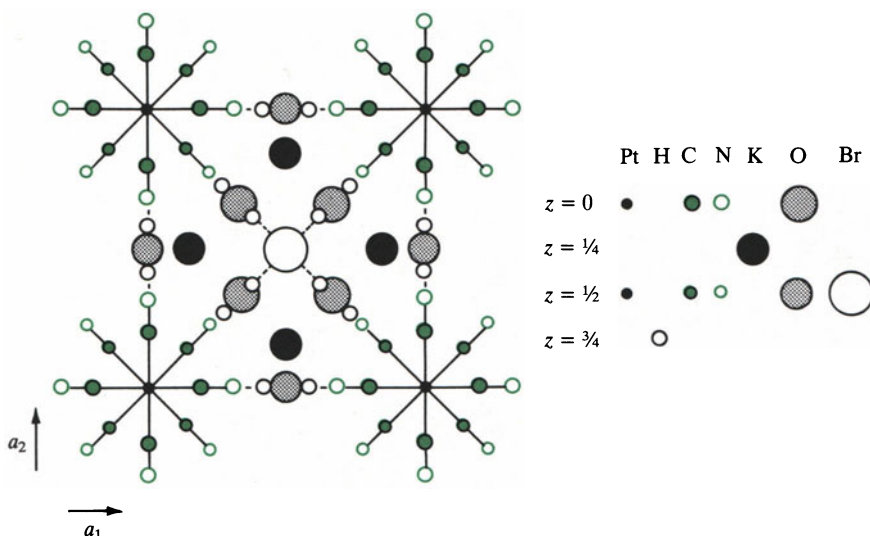


Figure 6.8 Crystal structure of KCP, showing a projection along the conducting c -axis. You are looking down a Pt chain at each corner of the unit cell: the staggering of the CN ligands can be seen.

bromide ions. There is now a partially filled band and so metallic conductivity would be expected. A closer look at the properties of KCP shows that the explanation of the conductivity is not quite that simple. KCP is a metallic conductor at room temperature, but as the temperature is lowered below 150 K the conductivity is found to drop sharply. The conductivity of metals increases as the temperature is lowered, and so it appears that a band gap is forming at low temperatures. The explanation lies with Peierls' theorem, that suggests that a one-dimensional conductor cannot be formed; there will always be a structural change that will lead to a filled band and a band gap.

The way that Peierls' theorem operates in Pt chain complexes is shown by a careful X-ray diffraction study of another Pt chain compound, $\text{Rb}_{1.67}[\text{Pt}(\text{C}_2\text{O}_4)_2] \cdot \frac{3}{2}\text{H}_2\text{O}$. (This compound also has electrons missing from the $5d$ orbitals but in this case they are compensated for by a deficiency of cations.) This crystal contains chains of Pt atoms, but the Pt–Pt separations are not all the same. In fact, three distinct Pt–Pt distances are found: 272, 283 and 302 pm; these repeat regularly throughout the crystal. In Figure 6.9, this is illustrated by showing the Pt atoms by black dots and then adding vertical lines between two atoms to represent the bond lengths (all the bond distances are exaggerated for clarity). A line drawn through the tops of all the vertical lines show a wave-like pattern rather like a sine wave. So the Pt–Pt bond distances vary periodically along the chain. As a consequence, the electron density



Figure 6.9 Periodic lattice distortion showing modulation of regular chain spacing. The vertical lines indicate the changes in bond length (exaggerated).

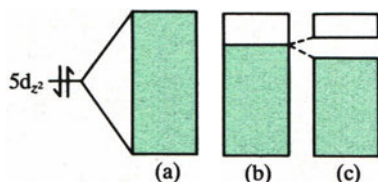


Figure 6.10 Simple band structure of a one-dimensional metallic complex. (a) Filled d band; (b) partially filled d band; (c) splitting of a partially filled band by Peierls distortion.

will vary periodically along the chain; the density will be higher between atoms that are closer together and the bonding between these atoms will be stronger. This regular variation of electron density is called a **charge density wave**. The variation in bond length is the distortion that produces a band gap (Figure 6.10), this periodically varying chain being of lower electronic energy than a regular chain and thus satisfying Peierls' theorem.

The X-ray study was done on $\text{Rb}_{1.67}[\text{Pt}(\text{C}_2\text{O}_4)_2] \cdot \frac{3}{2}\text{H}_2\text{O}$ because the bond length differences are fairly large in this salt, and because the variation in bond length coincided with the crystal lattice in a simple fashion so that it could be measured by traditional diffraction methods. A periodic variation of Pt–Pt distances also appears in KCP but this is smaller. At low temperatures, then, these Pt chain compounds will distort to produce a band gap and thus will be semiconductors. At room temperature, the electronic levels interact with lattice vibrations and the variation in bond length disappears.

Many Pt chain compounds have been made in addition to KCP. Some, like the rubidium salt mentioned above, are cation-deficient. Others have chloride or even bifluoride ions (HF_2^-) in place of bromide. Table 6.1 lists a selection of these salts and their properties. Note that the ligands attached to Pt are always composed of small atoms, typically C, N and O. Ligands with larger atoms such as S or P would not allow the Pt atoms to approach sufficiently closely to form chains. Although most work has been done on Pt, similar chain compounds are also found with other metals, particularly those with d^8 configurations which favour square planar complexes, for example iridium in oxidation state 1.

Table 6.1 Platinum chain compounds and their properties

<i>Compound</i>	<i>Abbreviation</i>	<i>Pt–Pt bond length (pm)</i>	<i>Conductivity ($S\ m^{-1}$)</i>
$K_2[Pt(CN)_4]Br_{0.3} \cdot 3H_2O$	KCP(Br)	289	30×10^3
$Rb_2[Pt(CN)_4](FHF)_{0.4}$	RbCP(FHF)	280	230×10^3
$Cs_2[Pt(CN)_4]Cl_{0.3}$	CsCP(Cl)	286	20×10^3
$K_{1.75}[Pt(CN)_4] \cdot \frac{3}{2}H_2O$	K(def)CP	296	$0.5\text{--}10 \times 10^3$
$Rb_{1.67}[Pt(C_2O_4)_2] \cdot \frac{3}{2}H_2O$	Rb–OP	$\left\{ \begin{array}{l} 272 \\ 283 \\ 302 \end{array} \right.$	0.7
$Mg_{0.82}[Pt(C_2O_4)_2] \cdot 6H_2O$	Mg–OP	285	$0.02\text{--}5 \times 10^3$

6.2.3 Other one-dimensional solids and molecular metals

Apart from polyacetylene, there are other examples of conjugated, conducting polymers as discussed in Section 6.2.1. There is, however, another class of organic one-dimensional conductors in which there are chains composed of stacks of two unsaturated cyclic molecules arranged alternately. The first one of this class discovered was TTF–TCNQ. The two molecules involved are tetrathiafulvalene (TTF) and tetracyanoquinonodimethane (TCNQ). These are shown in Figure 6.11, which also shows how they are stacked in the crystal.

The electrical conductivity of TTF–TCNQ is of the order of $10^2\ S\ m^{-1}$ at room temperature and increases with decreasing temperature until about 80 K when the conductivity, like that of KCP, drops as the temperature is lowered. TCNQ is a good electron acceptor and will, for example, accept electrons from alkali metal atoms to form ionic salts. In TTF–TCNQ the columns of each type of molecule interact to form delocalized orbitals. Some electrons from the highest energy filled band of TTF move across to partly fill a band of TCNQ, so that both types of columns have partially occupied bands. The number of electrons transferred corresponds to about 0.69 electrons per molecule. This partial transfer only occurs with molecules such as TTF whose electron donor ability is neither too small nor too large. With poor electron donors, no charge transfer occurs. With very good electron donors such as alkali metals one electron per TCNQ is transferred and the acceptor band is full. Thus $K^+(TCNQ)^-$ is an insulator. At low temperatures, TTF–TCNQ suffers a periodic distortion similar to that in KCP and so its conductivity drops.

Molecular solids such as TTF–TCNQ which have metallic conductivity are often referred to as **molecular metals** or synthetic metals. Polyacetylene, KCP and TTF–TCNQ are all described as one-dimensional electronic conductors because there is little interaction between chains in

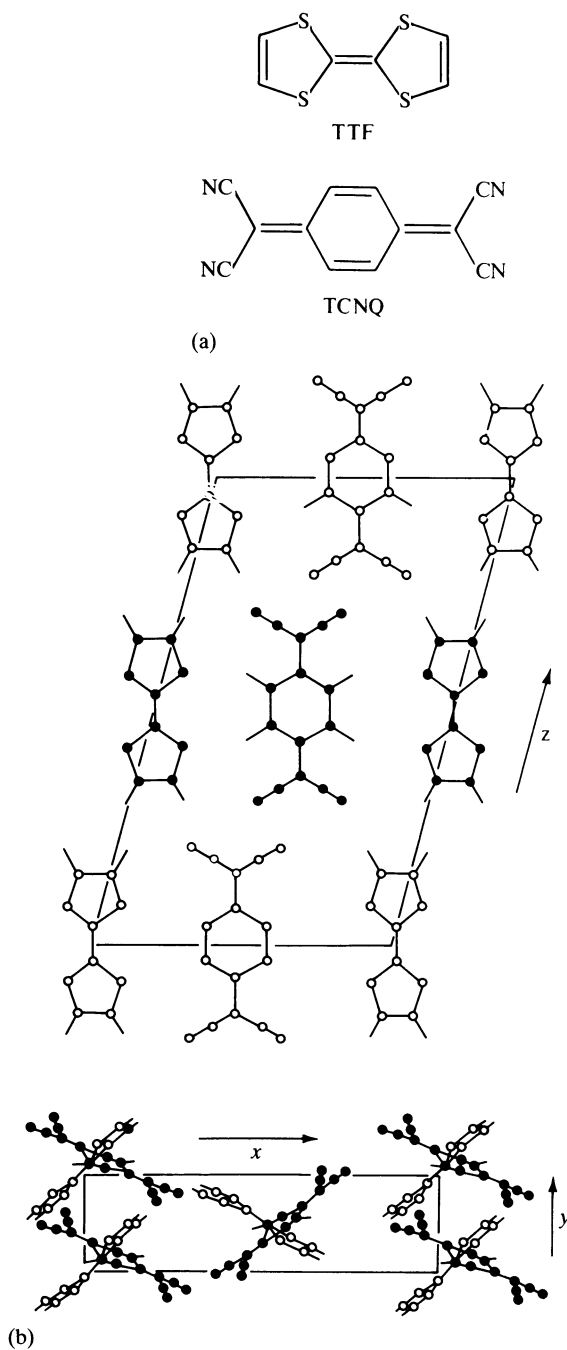


Figure 6.11 Structures of (a) TTF and TCNQ and (b) solid TTF-TCNQ showing alternate stacks of TTF and TCNQ molecules.

the crystal. There is, however, another class of molecular metals which, while appearing to resemble these solids, is less unambiguously defined as one-dimensional. For example, tetramethyl-tetraselenofulvalene (TMTSF; Figure 6.12) forms a series of salts with inorganic anions. The crystals of these salts contain stacks of TMTSF molecules and the TMTSF molecules carry a fractional charge ($0.5+$). As expected, these salts have high electronic conductivities at room temperatures. Unlike TTF–TCNQ, however, $(\text{TMTSF})_2^+(\text{ClO}_4)^-$ and other similar salts remain highly conducting at low temperatures and indeed at very low temperatures become superconducting. The reason for this seems to be that there is significant overlap between stacks so that the one-dimensional model is not as valid as for, say, TTF–TCNQ, and, in particular, Peierls' theorem no longer holds. Other materials of this type with significant interaction between chains include $(\text{SN})_x$ and $\text{Hg}_{3-x}\text{AsF}_6$, both of which become superconducting at low temperatures.

An interesting class of molecular metals are the **metallophthalocyanines**. The basic building block of these is shown in Figure 6.13. These form stacks and there are parallel stacks of counterions. When partially oxidized, the crystals of these compounds have very high electrical conductivities in the direction of the stacks which persist down to very low temperatures (1.5 K). Here the metals interact as in KCP, but the conduction electrons are also delocalized over the large unsaturated ligands and are not confined to the metal ions.

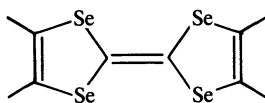


Figure 6.12 Structure of tetramethyl-tetraselenofulvalene, TMTSF.

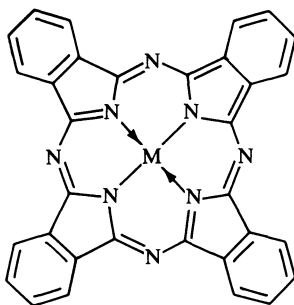


Figure 6.13 Phthalocyanine macrocycle coordinated to a metal M. The macrocycle can have hydrogen atoms or other groups attached to it.

6.3 TWO-DIMENSIONAL SOLIDS

Many solids adopt layer structures, particularly metal salts with less electronegative anions such as sulphide or iodide or with metals to the bottom right of the Periodic Table such as lead or cadmium. Such structures show that a purely ionic model is not appropriate for these solids and that there is considerable covalent or metallic bonding present. We shall be concerned here with those solids for which the layer structure produces interesting properties, particularly electronic properties. We consider an example of a layered metal sulphide which has been the subject of much research due to its potential use in batteries, but first this section takes a rather different example of a two-dimensional conductor.

6.3.1 Graphite

Graphite is a very familiar substance, with many uses. The lead in lead pencils is graphite, and finely divided forms of graphite are used to absorb gases and solutes. Its absorption properties find a wide range of applications from gas masks to decolouring food. Graphite formed by pyrolysis of oriented organic polymer fibres is the basis of carbon fibres. Graphite is also used as a support for several industrially important catalysts. Its electronic conductivity is exploited in several industrial electrolysis processes where it is used as an electrode. Crystals of graphite are, however, only good conductors in two dimensions, and it is this two-dimensional aspect that we are concerned with here.

Crystals of graphite contain layers of interlocking hexagons (Chapter 1; Figure 6.14). Figure 6.14 shows the most stable form in which the layers are stacked ABAB with the atoms in every other layer directly above each other. There is another form which also contains layers of interlocking hexagons but in which the layers are stacked ABCABC. Each carbon can be thought of as having three single bonds to neighbouring carbons. This leaves one valence electron per carbon in a p orbital at right-angles to the plane of the layer. These p orbitals combine to form delocalized orbitals which extend over the whole layer. If the layer contains n carbon atoms, then n orbitals are formed, and there are n electrons to fit in them. Thus half of the delocalized orbitals are filled. Were the orbitals to form one band, then this would explain the conductivity of graphite since there would be a half-filled band confined to the layers. The situation is close to this, but not quite as simple. The delocalized orbitals in fact form two bands, one bonding and one anti-bonding. (This is reminiscent of diamond, where as shown in Chapter 4, the s/p band splits with a gap where non-bonding orbitals would lie.) The lower band is full and the upper band empty. Graphite is a conductor because the band gap is zero, and electrons are thus readily promoted to

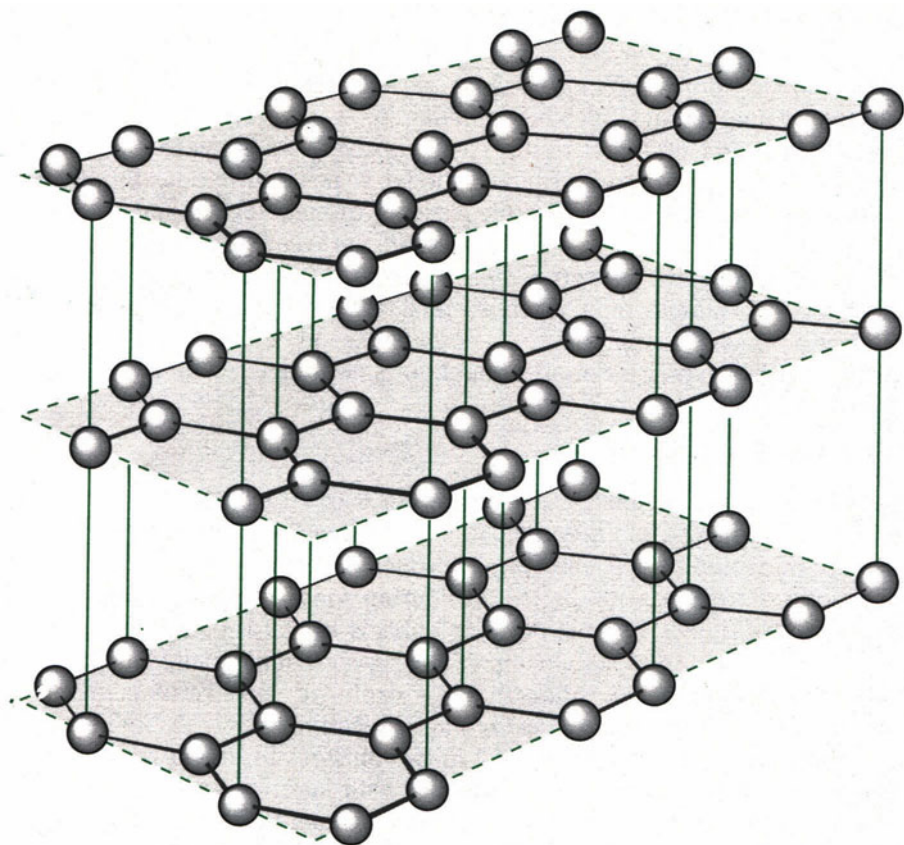


Figure 6.14 Hexagonal structure of graphite layers.

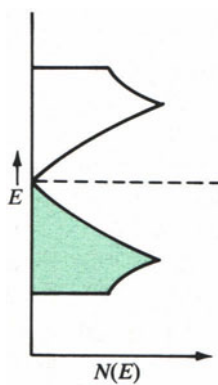


Figure 6.15 Band structure of graphite.

the upper band. The band structure for graphite is shown in Figure 6.15. Because the density of states is low at the Fermi level, the conductivity is not as high as that for a typical metal. It can, however, be increased as shown below.

6.3.2 Intercalation compounds of graphite

Because the bonding between layers in graphite is weak, it is easy to insert molecules or ions into the spaces between layers. The solids produced by reversible insertion of such guest molecules into lattices are known as **intercalation compounds**, and although originally applied to layered solids this term is now taken to include other solids with similar host–guest interactions. Since the 1960s attention has been paid to intercalation compounds as being of possible importance as catalysts and as electrodes for high-energy density batteries.

Many layered solids form intercalation compounds, but graphite is particularly interesting because it forms compounds with both electron donors and electron acceptors. Amongst electron donors, the most extensively studied are the alkali metals. The alkali metals enter graphite between the layers and produce strongly coloured solids in which the layers of carbon atoms have moved further apart. For example, potassium forms a golden compound KC_8 in which the interlayer spacing is increased by 200 pm. The potassium donates an electron to the graphite (forming K^+) and the conductivity of the graphite now increases because it has a partially full antibonding band.

The first graphite intercalation compound was made in 1841. This contained sulphate, an electron acceptor. Since then many other electron acceptor intercalation compounds have been made with, for example, NO_3^- , CrO_3 , Br_2 , FeCl_3 and AsF_5 . In these compounds the graphite layers donate electrons to the inserted molecules or ions, thus producing a partially filled bonding band. This increases the conductivity and some of these compounds have electrical conductivity approaching that of aluminium.

In graphite the current is carried through the layers by delocalized p electrons. There are very few examples of other layered solids with delocalized p electrons, but there are a number of transition metal salts with d electrons delocalized over layers, and we now discuss one of these.

6.3.3 Titanium disulphide: the lithium–titanium disulphide battery

Titanium disulphide (TiS_2) has a CdI_2 structure, as mentioned in Chapter 4. This structure was discussed in Chapter 1 (see Figure 1.41) and a view of TiS_2 is illustrated in Figure 6.16. The solid is golden-yellow and has a high electrical conductivity along the titanium layers. As shown in

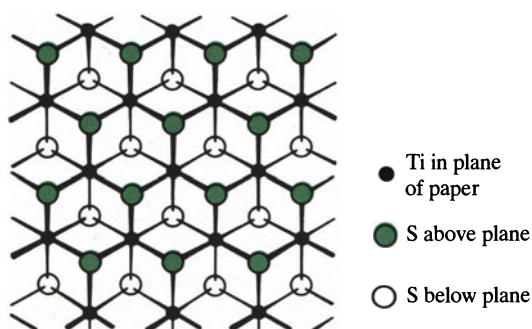


Figure 6.16 The structure of TiS_2 viewed from above.

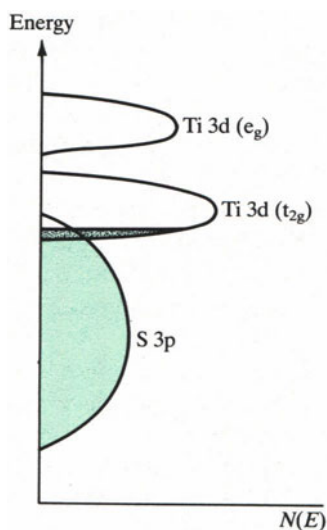


Figure 6.17 Band structure of TiS_2 .

Chapter 4, the conductivity of TiS_2 arises from a very small band gap or from a slight overlap of the S 3p valence band and Ti 3d conduction band. This situation is similar to that in graphite. The band structure is repeated here (Figure 6.17).

As in graphite, the conductivity of TiS_2 can be increased by forming intercalation compounds. These are generally formed with molecules that are electron donors in contrast to the intercalation compounds of graphite which are formed with both electron donors and electron acceptors. The electron donors can be metals such as the alkali metals or copper, or organic molecules such as amines. The electrons from the donor go into

the conduction band of TiS_2 , increasing the number of electrons able to carry current.

One possible use of the intercalation compounds is in rechargeable batteries and in the 1970s Whittingham developed a battery that operated at room temperature based on the intercalation of Li in TiS_2 . In the **lithium–titanium disulphide battery** one electrode is lithium metal and the other is TiS_2 bonded to a polymer such as teflon. The electrolyte is a lithium salt dissolved in an organic solvent. Typically, the solvent is a mixture of dimethoxyethane (DME) and tetrahydrofuran (THF). The set-up is shown schematically in Figure 6.18. When the circuit is complete, lithium metal from the lithium electrode dissolves giving solvated ions, and solvated ions in the solution are deposited in the TiS_2 . These ions intercalate into the disulphide, and the charge is balanced by electrons from the external circuit. Thus the two electrode reactions are



and



giving an overall reaction:



The intercalation compound formed has layers of a variable number of lithium ions between sulphide layers (Figure 6.19).

When the TiS_2 has completely discharged, the battery can be recharged by applying a voltage across AB. A voltage high enough to overcome the

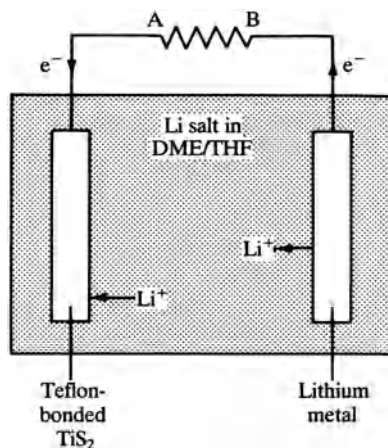


Figure 6.18 The Li– TiS_2 battery during a discharge phase.

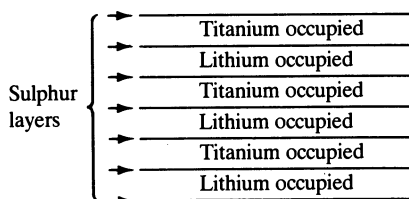


Figure 6.19 Occupation pattern of octahedral holes between close-packed layers of sulphur atoms in LiTiS_2 .

free energy of the cell reaction will cause lithium ions to return to the solvent and lithium to be deposited on the metal electrode, thus restoring the battery to its original condition. The usefulness of the Li-TiS_2 electrode depends on the electrode material being a good conductor and on the electrode reaction being reversible. Li_xTiS_2 is a particularly good electrical conductor, because not only is the electronic conductivity increased by the donation of electrons to the conduction band, but also the lithium ions themselves act as current carriers and so the compound is both an electronic and an ionic conductor. (Ionic conductors are described in Chapter 5.)

Early commercial batteries of the type shown in Figure 6.18 did not stand up to repeated recharging. When the lithium was deposited on the electrode it formed particles with a large surface area which tended to catch fire. This can be overcome by using lithium intercalated in graphite in place of lithium as the electrode. Other intercalation compounds have also been used in batteries. For example, Sony have used Li_xCoO_2 as the cathode. This compound is made not by intercalating lithium into CoO_2 but by partially removing lithium from the double oxide LiCoO_2 .

A possible way of replacing the expensive ether solvent in the battery by water has also been suggested. This is to saturate the water with lithium hydroxide, thus inhibiting the reaction of lithium with the water.

Titanium disulphide is probably the best-known example of a layered transition metal sulphide, but layered structures are also found for the disulphides of Zr, Hf, V, Nb, Ta, Mo and W. At one time there was considerable interest in these compounds because some of their intercalates were found to be superconductors at very low temperatures. It was hoped that by altering the interlayer spacing, a compound would be found that was superconducting at higher temperatures. Unfortunately, it soon transpired that altering the spacing by inserting different molecules had very little effect on the temperature at which superconductivity appeared. It was concluded that the superconductivity was confined to the layers. When high temperature superconductors were discovered, it was in a different class of compound, as will be described in Chapter 10.

FURTHER READING

Hoffmann, R. (1988) *Solids and Surfaces*, VCH Publishers, Inc. New York.
An unusual solid state chemistry book. The approach is probably more suitable for postgraduates and it concentrates on surfaces, but has sections on one- and two-dimensional solids.

Cox, P.A. (1987) *Electronic Structure and Chemistry of Solids*, Oxford University Press, Oxford.
See comments following Chapter 4. This contains a section on low-dimensional conductors.

The following two articles at an approachable level were written by researchers in one-dimensional metallic complexes.

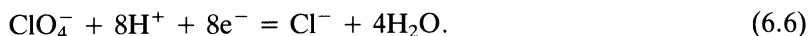
Day, P. (1983) Low-dimensional solids, *Chemistry in Britain*, April, 306.

Underhill, A.E. and Watkins, D.M. (1980) One-dimensional metallic complexes, *Chemical Society Reviews*, 429.

Bloor, D. (1983) Organic conductors, *Chemistry in Britain*, September, 725.
This article discusses low-dimensional organic conductors such as polyacetylene.

QUESTIONS

1. Which orbitals would you expect to combine to form a delocalized band in polyphenylenevinylene?
2. Would doping of polyacetylene with (a) Rb, (b) H_2SO_4 give an *n*-type or a *p*-type conductor?
3. When polyacetylene $(\text{CH})_n$ is doped with chloric (VII) acid, HClO_4 , some of the acid is used to oxidize the polyacetylene and some to provide a counter anion. The oxidation reaction for the acid is given in equation (6.6). Write a balanced equation for the overall reaction.



4. What is the oxidation state of platinum in $\text{KCP}(\text{Br})$?
5. $(\text{SN})_x$ remains a metallic conductor down to very low temperatures. Why does this suggest that there is interaction between the chains in this solid?
6. In Chapter 4 it was shown that VO_2 is only metallic above 340 K. Below this temperature, VO_2 adopts a crystal structure in which cation–cation distances in one direction are alternately 265 and 312 pm. By analogy with polyacetylene, suggest why this would lead to the solid being non-magnetic and semiconducting.
7. HMTTF-TCNQ is metallic but HMTTF-TCNQF_4 is not. Suggest a possible explanation for the difference. HMTTF = hexamethylene-tetrathiafulvalene, TCNQ = tetracyanoquinonedimethane, and TCNQF_4 = tetracyanotetrafluoroquinonedimethane.

Zeolites and related structures

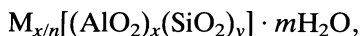
7.1 INTRODUCTION

For many years zeolites have been very useful as cation exchangers, as used in water softening, and also as molecular sieves for separating molecules of different sizes and shapes, for example in the separation of gases and as drying agents. More recently, however, research has focused on their ability to act as catalysts in a wide variety of reactions, many of them highly specific, and they are now used extensively in industry for this purpose. Approximately 40 naturally occurring zeolites have been characterized, but in the quest for new catalysts more than 130 entirely synthetic structures have been developed. Each one has been assigned a three letter designation, which we give here in parentheses.

Zeolites were first described as a mineral group by the Swedish mineralogist Baron Axel Cronstedt in 1756. They are a class of crystalline **aluminosilicates** based on rigid anionic frameworks with well-defined channels and cavities. These cavities contain exchangeable metal cations (Na^+ , K^+ , etc.) and can also hold removable and replaceable guest molecules (water in naturally occurring zeolites). It is their ability to lose water on heating that earned them their name; Cronstedt observed that on heating with a blowtorch they hissed and bubbled as though they were boiling and named them zeolites from the Greek words *zeo*, to boil and *lithos*, stone.

7.2 COMPOSITION AND STRUCTURE

The general formula for the composition of a zeolite is



where cations M of valence n neutralize the negative charges on the aluminosilicate framework.

7.2.1 Frameworks

The primary building units of zeolites are $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra (Chapter 1) linked together by **corner-sharing**, forming bent oxygen bridges (Figure 7.1). Silicon–oxygen tetrahedra are electrically neutral when connected together in a three-dimensional network as in quartz, SiO_2 . The substitution of Si(IV) by Al(III) in such a structure, however, creates an electrical imbalance, and to preserve overall electrical neutrality each $[\text{AlO}_4]$ tetrahedron needs a balancing positive charge. This is provided by exchangeable cations held electrostatically within the zeolite.

It is possible for the tetrahedra to link by sharing two, three or all four corners, thus forming a variety of different structures. The linked tetrahedra are usually illustrated by drawing a straight line to represent the oxygen bridge connecting two tetrahedral units. In this way the six linked tetrahedra in Figure 7.2a are simply represented by a hexagon (Figure 7.2b). This is known as a **6-ring**, and a tetrahedrally coordinated atom occurs at each intersection between two straight lines. Remember, however, that the oxygen bridge is not itself linear. Many different ring sizes are found in the various zeolite structures.

Many zeolite structures are based on a secondary building unit that consists of 24 silica or alumina tetrahedra linked together; here we find 4- and 6-rings linked together to form a basket-like structure called a **truncated octahedron**. This is the **sodalite unit** (or **β -cage**). Figure 7.3a shows the linked tetrahedra of the sodalite unit including the oxygen bridges, and the simplified schematic diagram is shown in Figure 7.3b. Notice that in this three-dimensional structure a tetrahedral atom is

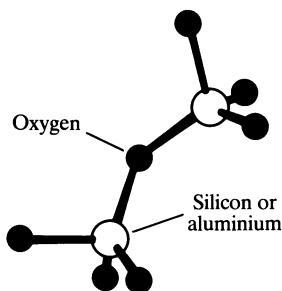
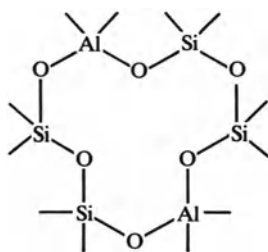
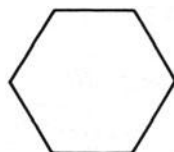


Figure 7.1 The zeolite building units. Two $\text{SiO}_4/\text{AlO}_4$ tetrahedra linked by corner-sharing.

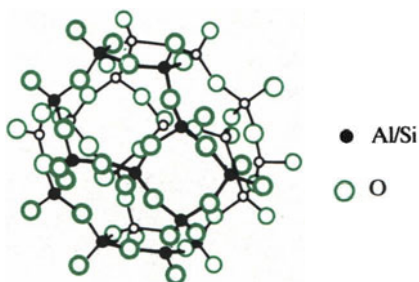


(a)

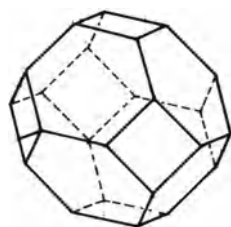


(b)

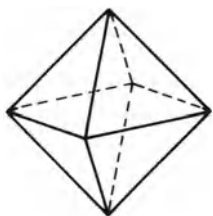
Figure 7.2 (a) 6-Ring containing two Al and four Si atoms. (b) Shorthand version of the same 6-ring.



(a)



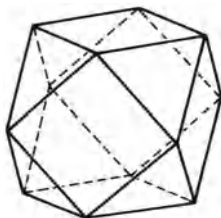
(b)



Octahedron



Truncated octahedron



Cuboctahedron



Truncated cuboctahedron

(c)

Figure 7.3 (a) The sodalite unit showing the atomic positions. (b) The truncated octahedron of linked tetrahedra which form the sodalite unit. (c) The relationship between an octahedron, a truncated octahedron, a cuboctahedron and a truncated cuboctahedron.

located at the intersection of four lines, as oxygen bridges are made by corner-sharing from all four vertices of the tetrahedron.

Several of the most important zeolite structures are based on the sodalite unit (Figure 7.4). The mineral **sodalite** (SOD) itself is composed of these units, with each 4-ring shared by two β -cages in a primitive packed array. Notice that the cavity enclosed by the eight sodalite units shown in Figure 7.4a is itself a sodalite unit (i.e. sodalite units are space-filling). This is a highly symmetrical structure and the cavities are linked together to form channels which run parallel to all three cubic crystal axes.

A synthetic zeolite, **zeolite-A** (LTA) (also called Linde A) is shown in Figure 7.4b. Here the sodalite units are again stacked in a primitive packed array, but now they are linked by oxygen bridges between the 4-rings. A three-dimensional network of linked cavities forming channels is thus formed, but now the cavities and channels are larger with an 8-ring window. The formula of zeolite-A is given by

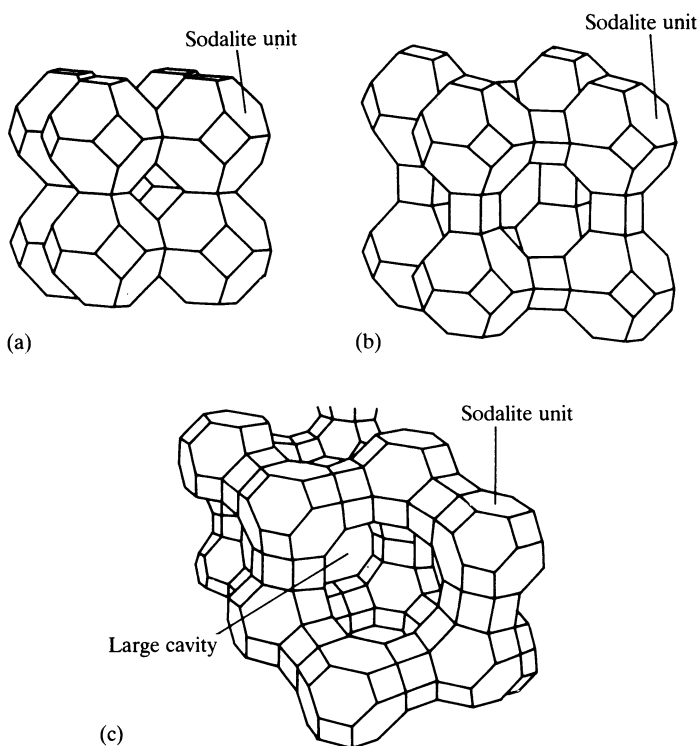


Figure 7.4 Zeolite frameworks built up from sodalite units: (a) sodalite (SOD), (b) zeolite-A (LTA), (c) faujasite (zeolites-X and -Y) (FAU).



In this fairly typical example, the Si/Al ratio is unity, and we find that in the crystal structure the Si and Al atoms strictly alternate.

The structure of **faujasite** (FAU), a naturally occurring but rather rare mineral, is shown in Figure 7.4c. The sodalite units are linked by oxygen bridges between four of the eight 6-rings in a tetrahedral array, forming hexagonal prisms. The synthetic zeolites, **zeolite-X** and **zeolite-Y** (FAU) (Linde X and Linde Y) also have this basic underlying structure. Zeolite-X structures have a Si/Al ratio between 1 and 1.5, whereas zeolite-Y structures have Si/Al ratios between 1.5 and 3. The tetrahedral array encloses a large **supercage** (also known as an **α -cage**) which is entered through a 12-ring window.

7.2.2 Si/Al ratios

We saw that zeolite-A has a Si/Al ratio of 1. Some zeolites have quite high Si/Al ratios: zeolite **ZK-4** (LTA), with the same framework structure as zeolite-A, has a ratio of 2.5. Many of the new synthetic zeolites that have been developed for catalysis are highly siliceous: **ZSM-5** (MFI) (Zeolite Socony-Mobil) can have a Si/Al ratio which lies between 20 and ∞ (the latter being virtually pure SiO_2); this far outstrips the ratio of 5.5 found in mordenite, which is the most siliceous of the naturally occurring zeolite minerals.

Clearly, changing the Si/Al ratio of a zeolite also changes its cation content; the fewer aluminium atoms there are, the fewer exchangeable cations will be present. The highly siliceous zeolites are inherently hydrophobic in character, and their affinity is for hydrocarbons.

7.2.3 Exchangeable cations

The zeolite Si/Al–O framework is rigid, but the cations are not an integral part of this framework and are often called **exchangeable cations**: they are fairly mobile and readily replaced by other cations (whence their use as cation exchange materials).

The presence and position of the cations in zeolites is important for several reasons. The cross-section of the rings and channels in the structures can be altered by changing the size or the charge (and thus the number) of the cations, and this significantly affects the size of the molecules that can be adsorbed. A change in cationic occupation also changes the charge distribution within the cavities, and thus the adsorptive behaviour and the catalytic activity. For these reasons it has become important to determine the cation positions within the framework and much research has been devoted to this in recent years.

The balancing cations in a zeolite can have more than one possible location in the structure. Figure 7.5 shows the available sites in the K^+ form of zeolite-A. Some sites occupy most of the centres of the 6-rings, while the others are in the 8-ring entrances to the β -cages. The presence of cations in these positions effectively reduces the size of the rings and cages to any guest molecules that are trying to enter. In order to alter a zeolite to allow organic molecules (for instance) to diffuse into or through the zeolite, a divalent cation could be exchanged for a univalent species,

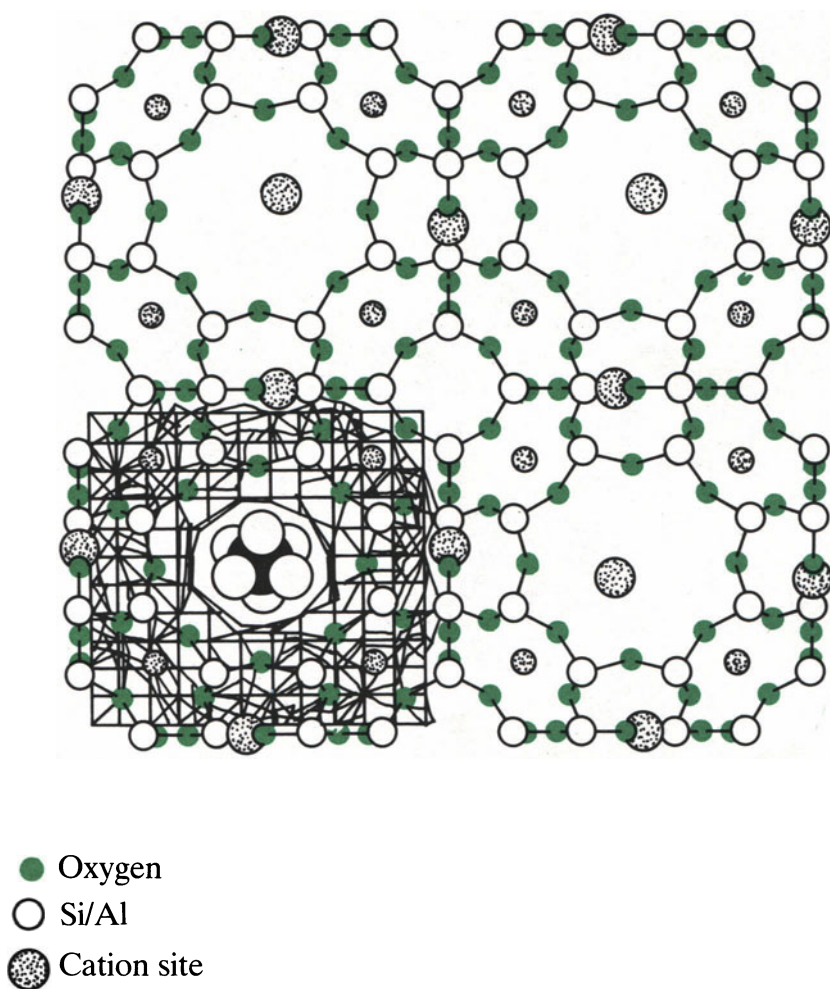


Figure 7.5 Framework and cation sites in the K^+ form of zeolite-A. In the left-hand corner a molecule of ethane is shown in the channel.

thus halving the number of cations present. The divalent cations tend to occupy the sites in the 6-rings, leaving the channels free.

Figure 7.6 shows the principal cation sites in the mineral faujasite (and thus by analogy, in zeolite-X and -Y). The principal sites are called S(I), S(I'), S(II), and S(II'). The S(I) sites are in the hexagonal prisms and are usually occupied by ions preferring higher coordination numbers. The S(I') sites are immediately adjacent in the β -cages: S(I) and S(I') are not simultaneously occupied. The S(II) sites are in the wall of the supercage and are almost all occupied. The S(II') sites are not occupied to any significant extent.

The normal crystalline zeolites contain water molecules which are coordinated to the exchangeable cations. These structures can be dehydrated by heating under vacuum, and in these circumstances the cations

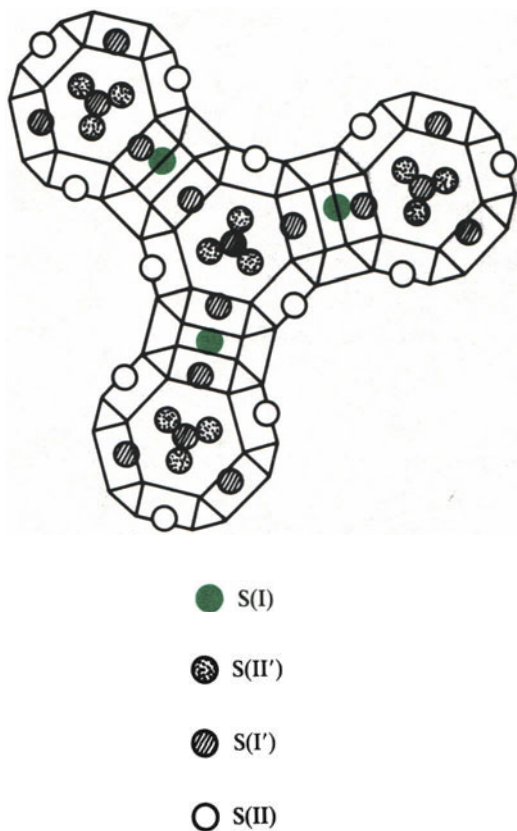


Figure 7.6 Faujasite framework (oxygen not shown) with principal cation sites. S(I') and S(II') are within the β -cages. S(I) and S(II) are in the hexagonal biprisms and the supercages, respectively.

move position at the same time, frequently settling on sites with a lower coordination number. The dehydrated zeolites are extremely good drying agents, absorbing water to get back to the preferred hydrated condition.

7.2.4 Cavities and channels

The important structural feature of zeolites, which can be exploited for various uses, is the network of linked **cavities** or **pores** forming a system of **channels** throughout the structure. These cavities are of molecular dimensions and can adsorb species small enough to gain access to them. A controlling factor in whether molecules can be adsorbed in the cavities is the size of the **window** or **pore-opening** into the channel. Hence the importance of the number of tetrahedra forming the window, i.e. the ring size.

Figure 7.4 shows how the window size can vary. A cavity in sodalite is bounded by a 4-ring with a diameter of about 260 pm: although this is a very small opening it can admit water molecules. The pore-opening in zeolite-A is 410 pm, determined by an 8-ring window; this is still considerably smaller than the diameter of the internal cavity, which measures 1140 pm in diameter. Faujasite has a 12-ring window of diameter 740 pm, leading into the α -cage of diameter 1180 pm. Values for these and other zeolites are shown in Table 7.1.

The windows to the channels thus form a three-dimensional sieve with mesh widths between about 300 and 1000 pm, hence the well-known name **molecular sieve** for these crystalline aluminosilicates. Zeolites have large internal surface areas and high sorption capacities for molecules small enough to pass through the window into the cavities. They can be used to separate mixtures such as straight-chain and branched-chain hydrocarbons.

Table 7.1 Approximate window and cavity diameters in zeolites

<i>Zeolite</i>	<i>No. of tetrahedra in ring</i>	<i>Window diameter (pm)</i>	<i>Cavity diameter (pm)</i>
Sodalite (SOD)	4	260	600
Zeolite-A (LTA)	8	410	1140
Erionite-A (ERI)	8	360 × 520	
ZSM-5 (MFI)	10	510 × 550 540 × 560	
Faujasite (FAU)	12	740	1180
Mordenite (MOR)	12	670 × 700	
	8	290 × 570	
Zeolite-L (LTL)	12	710	

The zeolites fall into three main categories. The tunnels may be parallel to (a) a single direction, so that the crystals are **fibrous**; (b) two directions arranged in planes, so that the crystals are **lamellar**; or (c) three directions, such as cubic axes, in which there is strong bonding in three directions. The most symmetrical structures have cubic symmetry. By no means do all zeolites fall neatly into this classification; some, for instance, have a dominant two-dimensional structure interlinked by smaller channels.

A typical fibrous zeolite is **edingtonite** (EDI), $\text{Ba}[(\text{AlO}_2)_2(\text{SiO}_2)_3] \cdot 4\text{H}_2\text{O}$, which has a characteristic chain formed by the regular repetition of five tetrahedra. The chains link together through oxygen atoms but the concentration of atoms within the chain gives the crystal its fibrous character (Figure 7.7).

Lamellar zeolites occur frequently in sedimentary rocks, e.g. **phillipsite** (PHI), $(\text{K/Na})_5[(\text{SiO}_2)_{11}(\text{AlO}_2)_5] \cdot 10\text{H}_2\text{O}$ (Figure 7.8), which has channels running parallel to the *a*-crystallographic axis.

In Figure 7.4b the eight sodalite units illustrated enclose a larger cavity. An alternative way of viewing the crystal structure is to consider the shape of these cavities and how they connect. The cavity has a shape known as a **truncated cuboctahedron**, a cuboctahedron with its corners missing (Figure 7.3c). Figure 7.9 shows the zeolite-A structure again, but

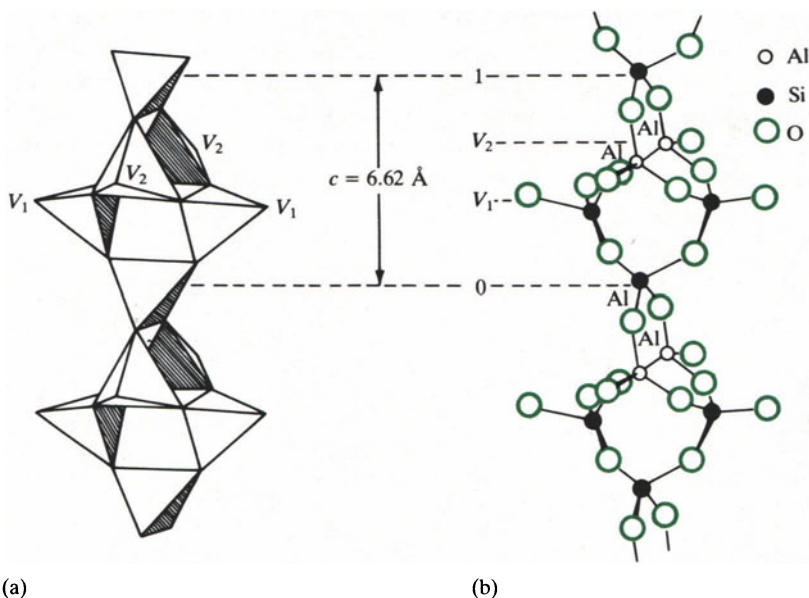


Figure 7.7 The common structural feature of the fibrous zeolites, the chain of linked tetrahedra. It is attached to neighbouring chains by the vertices V_1 and V_2 .

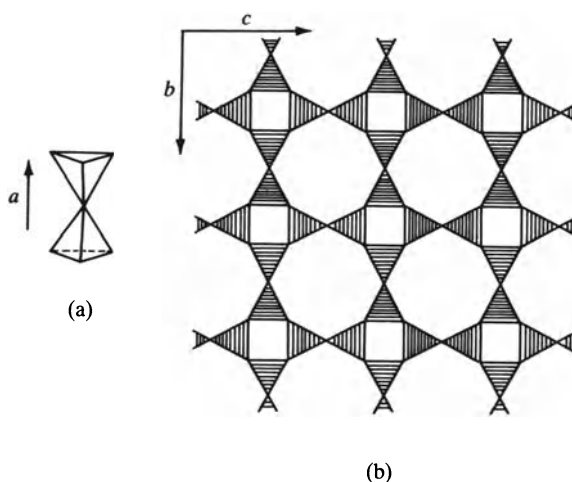


Figure 7.8 The structure of a lamellar zeolite (phillipsite). The double tetrahedral unit shown in (a) projects in the plan (b) as a single (equilateral) triangle.

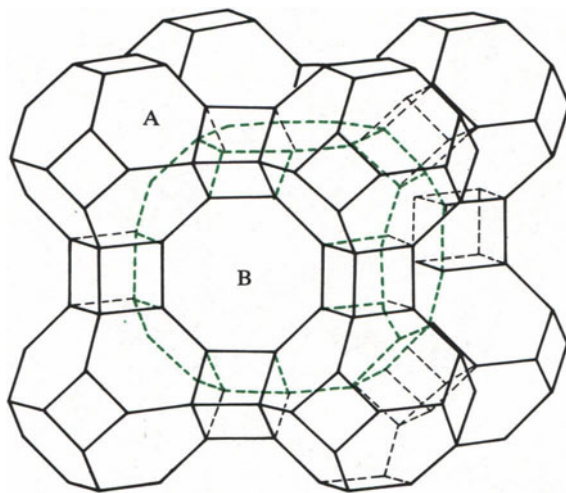


Figure 7.9 Zeolite-A (LTA) structure showing the truncated cuboctahedron shape of the supercage.

with the cavity now outlined in colour. The truncated cuboctahedra are also space-filling (each shares its octagonal face with six others), forming channels which run parallel to the three cubic axial directions through these large cavities.

In the mid-1970s some completely novel zeolite structures were

synthesized which led to significant new developments. This family of framework structures comprising the zeolites synthesized by the oil company Mobil, ZSM-5 and ZSM-11 (MEL), and silicalite (MFI) and some closely related natural zeolites, have been given the generic name **pentasil**. ZSM-5 is a catalyst now widely used in the industrial world. Its structure is generated from the pentasil unit shown in Figure 7.10 (as are the others of this group). These units link into chains, which join to make layers. Appropriate stacking of these layers gives the various pentasil structures. In ZSM-5 the layers are related by inversion and in ZSM-11 the layers are related by mirror symmetry. Both ZSM-5 and ZSM-11 are characterized by channels controlled by 10-ring windows with diameters

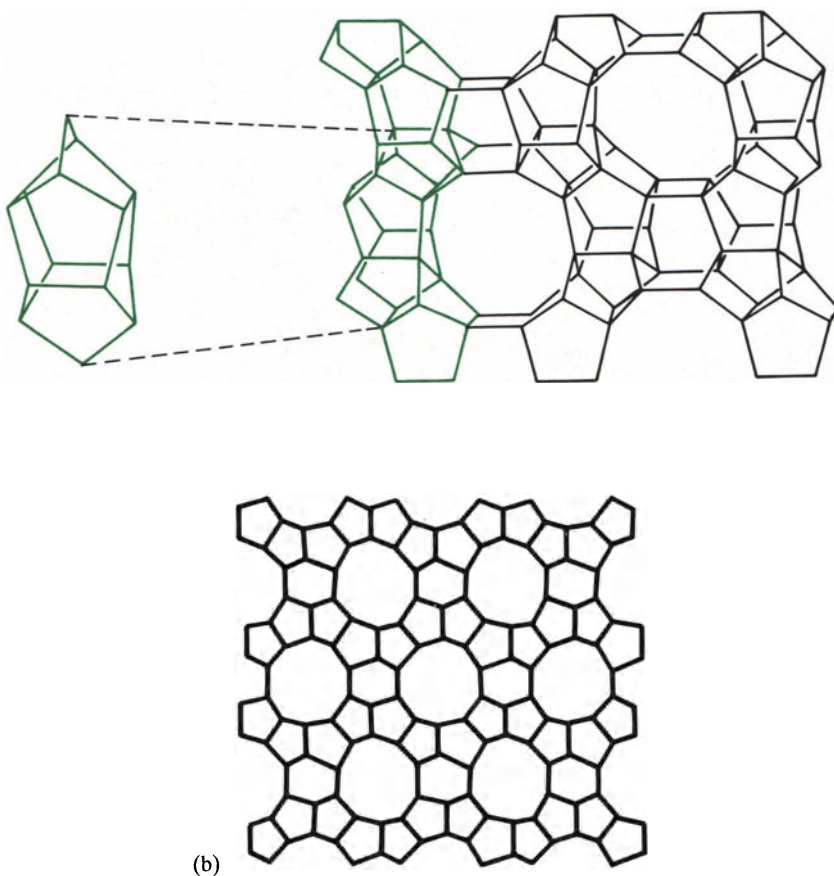


Figure 7.10 (a) A pentasil unit (in colour) together with a slice of the structure of ZSM-5, showing a linked chain of pentasil units highlighted in colour. (b) Plan of layers in ZSM-5.

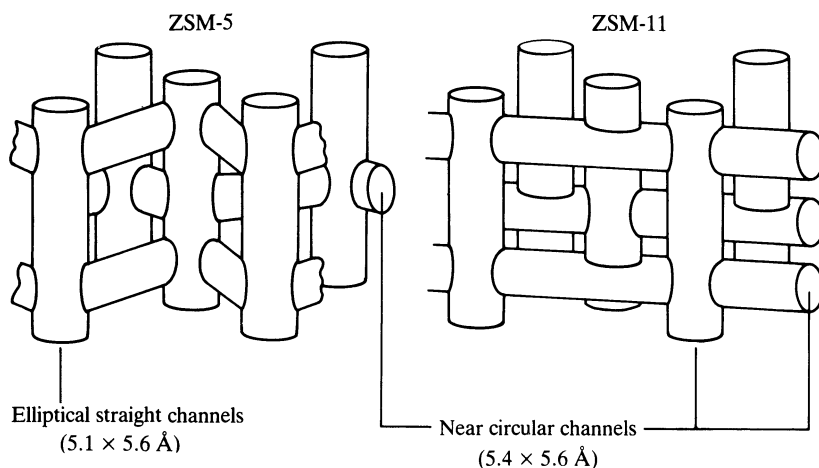


Figure 7.11 The interconnecting channel systems in (a) ZSM-5 (MFI) and (b) ZSM-11 (MEL).

of about 550 pm. The pore systems in these zeolites do not link big cavities, but they do contain intersections where larger amounts of free space are available for molecular interactions to take place. Figure 7.11a shows the pore system of ZSM-5 with nearly circular zig-zag channels intersecting with straight channels of elliptical cross-section. This contrasts with the ZSM-11 structure which just has intersecting straight channels of almost circular cross-section (Figure 7.11b).

The channel system for **mordenite** (MOR), a naturally occurring zeolite, is shown in Figure 7.12. There are two types of channels, governed by 8- and 12-ring windows, respectively, all running parallel to each other and interconnected only by smaller 5- and 6-ring systems.

7.3 PREPARATION OF ZEOLITES

Zeolites are prepared from solutions containing sodium silicates and aluminates, $[\text{Al}(\text{OH})_4]^-$, at high pH, obtained by using an alkali metal hydroxide and/or an organic base. A gel forms by a process of copolymerization of the silicate and aluminate ions. The gel is then heated gently (at 60–100°C) in a closed vessel under hydrothermal conditions, for about 2 days, producing a condensed zeolite. The product obtained is determined by the synthesis conditions: temperature, time, pH and mechanical movement are all possible variables (see Chapter 3). The presence of organic bases is useful for synthesizing silicon-rich zeolites.

The formation of novel silicon-rich synthetic zeolites has been faci-

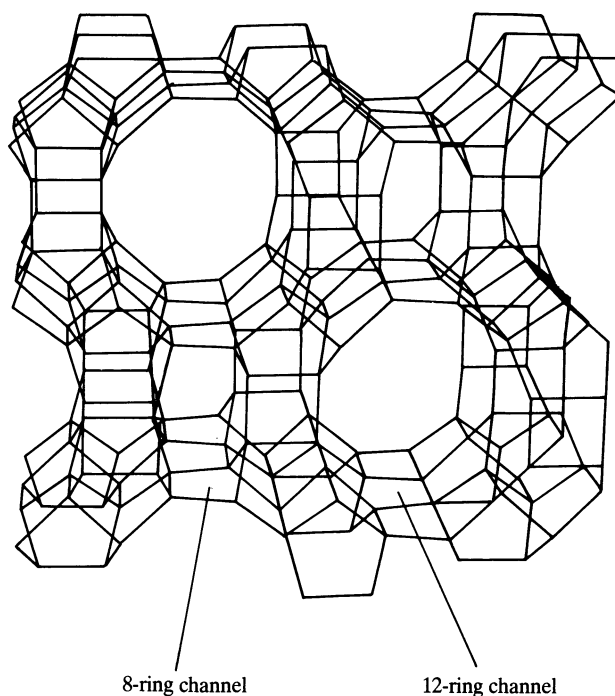


Figure 7.12 The channel structure of mordenite (MOR).

litated by the use of **templates** such as large quaternary ammonium cations instead of Na^+ . For instance, the tetramethylammonium cation, $[(\text{CH}_3)_4\text{N}]^+$, is used in the synthesis of ZK-4. The aluminosilicate framework condenses around this large cation, which can subsequently be removed by chemical or thermal decomposition. ZSM-5 is produced in a similar way using tetra-*n*-propyl ammonium. Only a limited number of large cations can fit into the zeolite framework, and this severely reduces the number of $[\text{AlO}_4]$ tetrahedra that can be present, producing a silicon-rich structure.

The preparation of silicon-rich zeolites such as zeolite-Y, can be achieved by varying the composition of the starting materials but can also be done by subsequent removal of aluminium from a synthesized aluminosilicate framework using a chemical treatment. There are several different methods available, one being extraction of the aluminium by mineral acid and another, extraction using complexing agents.

7.4 STRUCTURE DETERMINATION

The structures of the zeolite frameworks have mostly been determined by X-ray and neutron crystallographic techniques. Some of the naturally

occurring minerals were characterized in the 1930s and the synthetic zeolites have been investigated from 1956 onwards. Unfortunately, it is extremely difficult for diffraction techniques to determine a structure unequivocally: as we saw in Chapter 2 X-rays are scattered by the electron cloud surrounding a nucleus, and because Al and Si are next to each other in the Periodic Table they have very similar atomic scattering factors. The consequence of this is that Al and Si atoms are virtually indistinguishable on the basis of crystallographic data. It is possible to build up a picture of the overall shape of the framework with accurate atomic positions but not to decide which atom is Si and which is Al.

The positions of Si and Al atoms have always been assigned by applying **Loewenstein's rule** which forbids the presence of an Al–O–Al linkage in the structure. A corollary of this rule is that when the Si/Al ratio is 1, the amount of aluminium in a zeolite is maximum and the Si and Al atoms alternate throughout this structure.

When it comes to locating the cations, other problems arise. Not every cation site is completely occupied, so although the cation sites can be located, their occupancy is averaged. Furthermore, zeolites are usually microcrystalline and for successful diffraction studies larger single crystals are needed (although Rietveld powder techniques have been successfully applied, especially with neutrons). One of the techniques currently being used to elucidate zeolite structures successfully is **magic angle spinning NMR spectroscopy (MAS NMR)**. This technique eliminates the broadening of the NMR signals normally observed in solids. The line broadening is due to various anisotropic interactions, all of which contain a $(3 \cos^2\theta - 1)$ term. When $\cos\theta = (1/3)^{1/2}$, i.e. $\theta = 54^\circ 44'$, this term becomes zero. Spinning the sample about an axis inclined at this so-called **magic angle** to the direction of the magnetic field eliminates these sources of broadening, and thus improves the resolution in chemical shift of the spectra.

^{29}Si has a nuclear spin $I = \frac{1}{2}$, and so gives sharp spectral lines with no quadrupole broadening or asymmetry; the sensitivity is quite high and

^{29}Si has a natural abundance of 4.7%.

Pioneering work using MAS NMR on zeolites was carried out by E. Lippmaa and G. Engelhardt in the late 1970s. They showed that up to five peaks could be observed for the ^{29}Si spectra of various zeolites and that these corresponded to the five different Si environments that can exist. Each Si is coordinated by four oxygen atoms, but each oxygen can then be attached either to a Si or to an Al atom giving the five possibilities: $\text{Si}(\text{OAl})_4$, $\text{Si}(\text{OAl})_3(\text{OSi})$, $\text{Si}(\text{OAl})_2(\text{OSi})_2$, $\text{Si}(\text{OAl})(\text{OSi})_3$ and $\text{Si}(\text{OSi})_4$. They also showed, most importantly, that characteristic ranges of these shifts could be assigned to each coordination type. These ranges could then be used in further structural investigations of other zeolites. These ranges are shown in Figure 7.13. A MAS NMR spectrum of the zeolite analcite (ANA) is shown in Figure 7.14. Analcite has all five

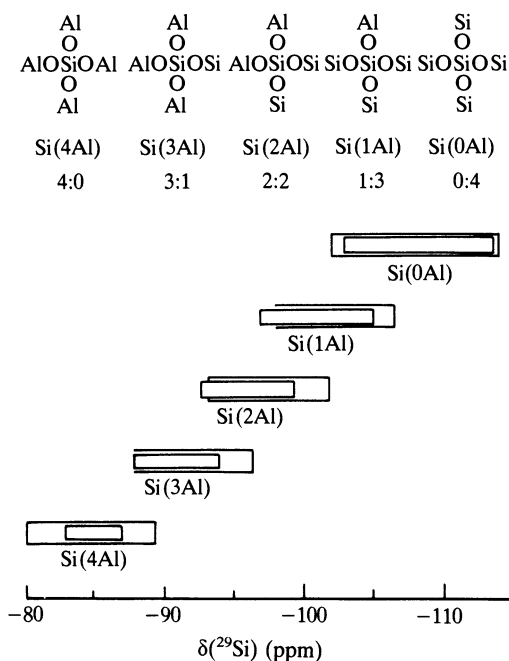


Figure 7.13 The five possible local environments of a silicon atom together with their characteristic chemical shift ranges. The inner boxes represent the ^{29}Si shift ranges suggested in the earlier literature. The outer boxes represent the extended ^{29}Si shift ranges which are more unusual.

possible environments. Even with this information it is still an extremely complicated procedure to decide where each linkage occurs in the structure. The cation positions can give useful information as they tend to be as close as possible to the negatively charged Al sites.

^{27}Al has a 100% natural abundance and a nuclear spin $I = \frac{5}{2}$, resulting in a strong resonance which is broadened and rendered asymmetric by second-order quadrupolar effects. Because Loewenstein's rule precludes Al–O–Al linkages, every tetrahedral Al environment is $\text{Al}(\text{OSi})_4$ and consequently only a single resonance is observed, although the Al chemical shifts of individual zeolites have characteristic values. However, determining the ^{27}Al MAS NMR spectrum of a zeolite can have great diagnostic value as it distinguishes between three different types of coordination: octahedrally coordinated Al, $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, is frequently trapped as a cation in the pores and gives a peak at about 0 ppm (with $[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ used as the reference), whereas tetrahedrally coordinated Al in the framework gives a peak in the range 50–65 ppm, and tetrahedral $[\text{AlCl}_4]^-$ gives a peak at about 100 ppm. Such a peak can

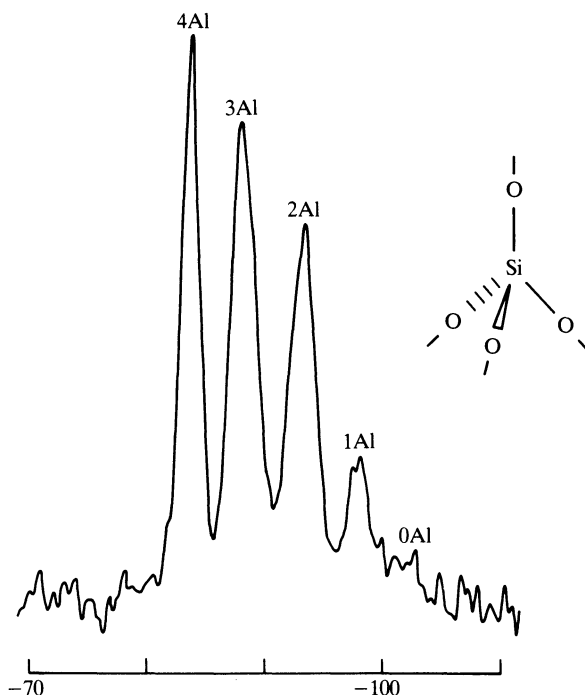


Figure 7.14 ^{29}Si MAS NMR spectrum at 79.6 MHz of the zeolite $\delta(^{29}\text{Si})$ (ppm) analcite (ANA), showing five absorptions characteristic of the five possible permutations of Si and Al atoms attached at the corners of the SiO_4 tetrahedron as indicated.

occur when a zeolite has been treated with SiCl_4 in order to increase the Si/Al ratio in the framework and should disappear with washing.

An important feature of ^{29}Si MAS NMR spectra is that measurement of the intensity of the observed peaks allows the Si/Al ratio of the framework of the sample to be calculated. This can be extremely useful when developing new zeolites for catalysis, as much research has concentrated on making highly siliceous varieties by replacing the Al in the framework. Conventional chemical analysis only gives an overall Si/Al ratio, which includes trapped octahedral Al species and $[\text{AlCl}_4]^-$ which has not been washed away. At high Si/Al ratios, ^{27}Al MAS NMR results are more sensitive and accurate and so are preferred.

High resolution electron microscopy is also used extensively for structural examination of zeolites, particularly for intergrowths and faults. Zeolite- β was investigated by HREM and shown to consist of intergrowths of two different 12-ring structures. EXAFS has been used to determine the local coordination geometry of the exchangeable cations and how this changes on reaction or dehydration.

7.5 USES OF ZEOLITES

7.5.1 Dehydrating agents

Normal crystalline zeolites contain water molecules, which are coordinated to the exchangeable cations. As we noted previously, these structures can be dehydrated by heating under vacuum; in these circumstances the cations move position, frequently settling on sites with a much lower coordination number. The dehydrated zeolites are very good drying agents, adsorbing water to get back to the preferred high coordination condition.

7.5.2 Zeolites as ion exchangers

The cations M^{n+} in a zeolite will exchange with others in a surrounding solution. In this way the Na^+ form of zeolite-A can be used as a water softener: the Na^+ ions exchange with the Ca^{2+} ions from the hard water. The water softener is reusable as it can be regenerated by running through a very pure saline solution; this is a familiar procedure to anyone who has used a dishwasher. Zeolite-A is now added to detergents as a water softener, replacing the polyphosphates which have given concern about possible ecological damage. It is possible to produce drinking water from seawater by desalinating it through a mixture of Ag and Ba zeolites. This is such an expensive process, however, that it is only useful in emergency.

Some zeolites have a strong affinity for particular cations. **Clinoptilolite** (HEU) is a naturally occurring zeolite which sequesters caesium. It can be used to recover ^{137}Cs from radioactive waste, exchanging its own Na^+ ions for Cs^+ cations. Similarly, zeolite-A can be used to recover radioactive strontium. Zeolites were heavily used in the clean-up operations after the Chernobyl and Three-Mile Island incidents.

7.5.3 Zeolites as adsorbents

Because dehydrated zeolites have very open porous structures, they have large internal surface areas and are capable of adsorbing large amounts of substances other than water. The ring size of the windows leading into the cavities determine the size of the molecules that can be adsorbed. An individual zeolite has a highly specific sieving ability that can be exploited for purification or separation. This was first noted for **chabazite** (CHA) as long ago as 1932, when it was observed that it would adsorb and retain small molecules such as formic acid and methanol, but would not adsorb benzene and larger molecules. Chabazite has been used commercially to adsorb polluting SO_2 emissions from chimneys. Similarly, the 410 pm pore-opening in zeolite-A, determined by an 8-ring (this is much smaller

than the diameter of the internal cavity, which is 1140 pm), can admit a methane molecule, but excludes a larger benzene molecule. Computer graphics are extremely useful for illustrating whether a molecule is able to pass through a pore-opening or channel (see Figure 7.5, which shows an ethane molecule in the zeolite-A supercage). The atoms are assigned their van der Waals radii for this purpose.

The zeolites that are useful as molecular sieves do not show an appreciable change in the basic framework structure on dehydration, although the cations move to positions of lower coordination. After dehydration, zeolite-A and others are remarkably stable to heating and do not decompose below about 700°C. The cavities in dehydrated zeolite-A amount to about 50% of the volume.

There are many uses of the selective sorbent properties of zeolites, of which we will describe just a few. Table 7.2 gives a brief summary of the industrial uses that are made. The zeolites are regenerated after use by heating, evacuation or flushing with pure gases.

Table 7.2 Applications of molecular sieves in industrial adsorption processes

<i>Fields of application</i>	<i>Uses</i>		
	<i>Drying</i>	<i>Purification</i>	<iseparations< i=""></iseparations<>
Refineries and petrochemical industry	Paraffins, olefins, acetylenes, reformer gas, hydrocracking gas, solvents	Sweetening* of 'liquid petrol gas' and aromatics, removal of CO ₂ from olefin-containing gases, purification of synthesis gas	Normal and branched-chain alkanes
Industrial gases	H ₂ , N ₂ , O ₂ , Ar, He, CO ₂ , natural gas	Sweetening and CO ₂ removal from natural gas, removal of hydrocarbons from air, preparation of protective gases	Aromatic compounds
Industrial furnaces	Exogas, cracking gas, reformer gas	Removal of CO ₂ and NH ₃ from exogas and from ammonia fission gas	Nitrogen and oxygen

* 'Sweetening' is the removal of sulphur-containing compounds.

It is possible to 'fine-tune' the pore-opening of a zeolite to allow the adsorption of specific molecules. As discussed earlier, one method is to change the cation. This method can be used to modify zeolite-A so as to separate branched and cyclic hydrocarbons from the straight-chain alkanes (paraffins). When Na^+ ions are replaced by Ca^{2+} ions the effective aperture increases. Once approximately one-third of the Na^+ ions have been replaced by Ca^{2+} , many straight chain alkanes can be adsorbed (Figure 7.15). However, all branched-chain, cyclic and aromatic hydrocarbons are excluded because their cross-sectional diameters are too large. This process can be useful industrially for separating the long straight-chain hydrocarbons required as the starting materials in the manufacture of biodegradable detergents. Petrol can also be upgraded by removing from it the straight-chain, low-octane-number alkane constituents which produce 'pinking' ('knocking'), small explosions which are harmful to engines.

At -196°C oxygen is freely adsorbed by zeolite-A (Ca form) whereas nitrogen is essentially excluded. The two molecules are not very different in size: O_2 has a diameter of 346 pm whereas that of N_2 is 364 pm. As the temperature rises the adsorption of N_2 increases to a maximum at about -100°C . The main reason is thought to be due to the thermal vibrations of the oxygen atoms in the window. Over a range of 80–300 K a variation of vibrational amplitude of 10–20 pm could well be expected and thus a

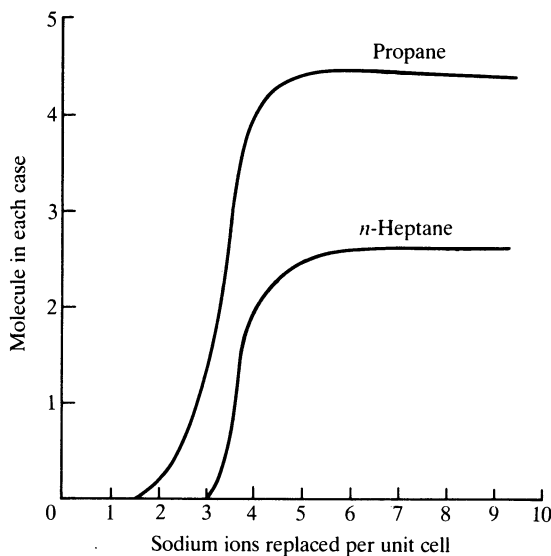


Figure 7.15 Effect of calcium exchange for sodium in zeolite-A on hydrocarbon adsorption. Replacement of four sodium ions by two calcium ions permits easy diffusion of *n*-alkanes into the zeolite channels.

variation of 30 pm in the window diameter would not be unreasonable. This would make the window just small enough at lower temperatures to exclude the N_2 molecules. Zeolite-A can be used to separate or purify these gases.

The other method used for 'fine-tuning' the pore-openings is to change the Si/Al ratio. An increase in the proportion of Si will (i) slightly decrease the unit cell size and thus the size of the cavities; (ii) decrease the number of cations, thus freeing the channels; and (iii) make the zeolite more hydrophobic (literally 'water-hating') in character. Hydrophobic zeolites can potentially be used to remove organic molecules from aqueous solution; possible uses range from the removal of toxic materials from blood, to the production of non-alcoholic beverages by the selective removal of alcohol, and to the decaffeination of coffee.

7.5.4 Zeolites as catalysts

Zeolites are very useful catalysts displaying several important properties that are not found in traditional amorphous catalysts. Amorphous catalysts have always been prepared in a highly divided state in order to give a high surface area and thus a large number of catalytic sites. The presence of the cavities in zeolites provides a very large internal surface area that can accommodate as many as 100 times more molecules than the equivalent amount of amorphous catalyst. Zeolites are also crystalline and so can be prepared with improved reproducibility: they tend not to show the varying catalytic activity of amorphous catalysts. Furthermore their molecular sieve action can be exploited to control which molecules have access to (or which molecules can depart from) the active sites. This is generally known as **shape-selective catalysis**.

The catalytic activity of decationized zeolites is attributed to the presence of acidic sites arising from the $[AlO_4]$ tetrahedral units in the framework. These acid sites may be Brønsted or Lewis in character. Zeolites as normally synthesized usually have Na^+ ions balancing the framework charges, but these can be readily exchanged for protons by direct reaction with an acid, giving surface hydroxyl groups – the **Brønsted sites**. Alternatively, if the zeolite is not stable in acid solution, it is common to form the ammonium, NH_4^+ , salt, and then heat it so that ammonia is driven off, leaving a proton. Further heating removes water from the Brønsted site, exposing a tricoordinated Al ion, which has electron-pair acceptor properties; this is identified as a **Lewis acid site**. A scheme for the formation of these sites is shown in Figure 7.16. The surfaces of zeolites can thus display either Brønsted or Lewis acid sites, or both depending on how the zeolite is prepared. Brønsted sites are converted into Lewis sites as the temperature is increased above 600°C, and water is driven off.

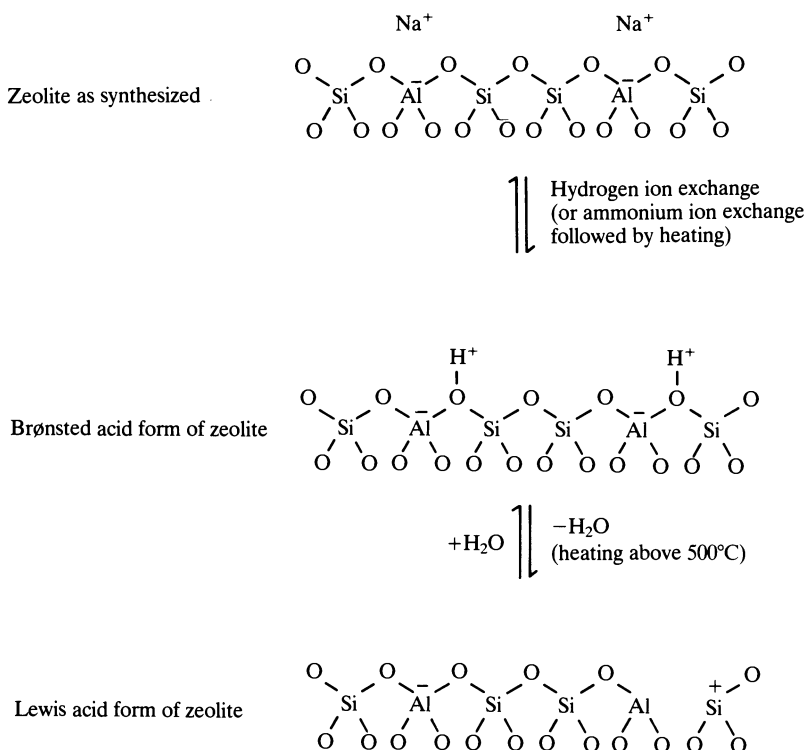
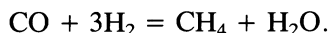


Figure 7.16 Scheme for the generation of Brønsted and Lewis acid sites in zeolites.

Not all zeolite catalysts are used in the decationized or acid form; it is also quite common to replace the Na^+ ions with lanthanide ions such as La^{3+} or Ce^{3+} . These ions now place themselves so that they can best neutralize three separated negative charges on tetrahedral Al in the framework. The separation of charges causes high electrostatic field gradients in the cavities which are sufficiently large to polarize C—H bonds or even to ionize them, enabling reaction to take place. This effect can be strengthened by a reduction in the Al content of the zeolite so that the $[\text{AlO}_4]$ tetrahedra are farther apart. If one thinks of a zeolite as a solid ionizing solvent, the difference in catalytic performance of various zeolites can be likened to the behaviour of different solvents in solution chemistry. It was a rare-earth substituted form of zeolite-X that became the first commercial zeolite catalyst for the cracking of petroleum in the 1960s. Crude petroleum is initially separated by distillation into fractions, and the heavier gas-oil fraction is cracked over a catalyst to give petrol (gasoline). A form of zeolite-Y, that has proved more stable at high temperatures, is now used. These catalysts yield $\sim 20\%$ more petrol than

earlier catalysts, and do so at lower temperatures. The annual catalyst usage for catalytic cracking is worth billions of £s, and is the single most important use of zeolites.

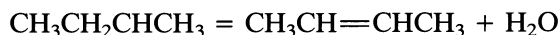
A third way of using zeolites as catalysts is to replace the Na^+ ions with other metal ions such as Ni^{2+} , Pd^{2+} or Pt^{2+} and then reduce them *in situ* so that metal atoms are deposited within the framework. The resultant material displays the properties associated with a supported metal catalyst and extremely high dispersions of the metal can be achieved. Another technique for preparing a zeolite-supported catalyst involves the physical adsorption of a volatile inorganic compound followed by thermal decomposition: $\text{Ni}(\text{CO})_4$ can be adsorbed on zeolite-X and decomposed with gentle heating to leave a dispersed phase of nearly atomic nickel in the cavities, and this has been found to be a good catalyst for the conversion of carbon monoxide to methane:



There are three types of shape-selective catalysis.

1. **Reactant-selective catalysis:** only molecules with dimensions less than a critical size can enter the pores and reach the catalytic sites, and so react there. This is illustrated diagrammatically in Figure 7.17a in which a straight-chain hydrocarbon is able to enter the pore and react but the branched-chain hydrocarbon is not.
2. **Product-selective catalysis:** only products less than a certain dimension can leave the active sites and diffuse out through the channels, as illustrated in Figure 7.17b for the preparation of xylene. A mixture of all three isomers is formed in the cavities but only the *para* form is able to escape.
3. **Transition-state-selective catalysis:** certain reactions are prevented because the transition state requires more space than is available in the cavities, as shown in Figure 7.17c for the transalkylation of dialkylbenzenes.

Reactant-selective catalysis is demonstrated in the dehydration of butanols. If butan-1-ol (*n*-butanol) and butan-2-ol (*iso*-butanol) are dehydrated either over zeolite-A or over zeolite-X (both in the Ca form) we see a difference in the products formed.



Zeolite-X has windows large enough to admit both alcohols easily, and both undergo conversion to the corresponding alkene. Over zeolite-A,

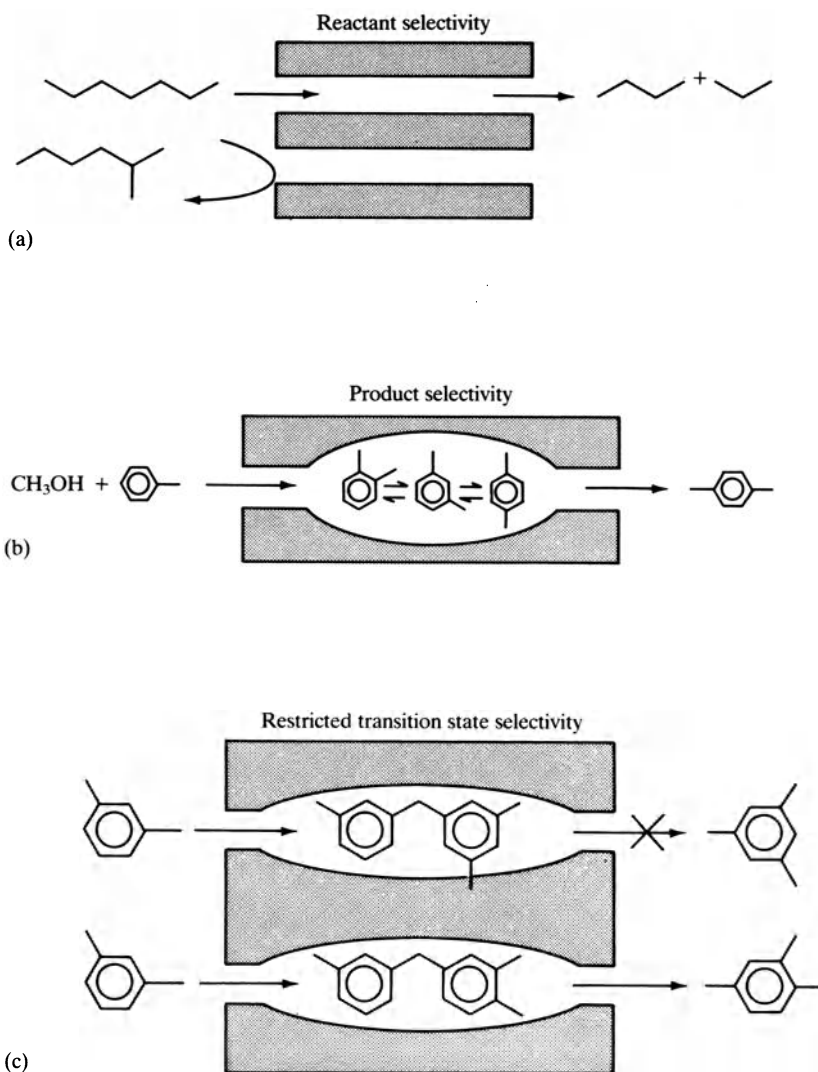


Figure 7.17 Shape-selective catalysis: (a) reactant, (b) product and (c) transition state.

however, the dehydration of the straight-chain alcohol is straightforward but virtually none of the branched-chain alcohol is converted, as it is too large to pass through the smaller windows of zeolite-A. These results are summarized in Figure 7.18. Notice that, at higher temperatures, curve d begins to rise. This is because the lattice vibrations increase with temperature, making the pore-opening slightly larger and thus beginning to admit butan-2-ol. The very slight conversion at lower temperatures is thought to take place on external sites.

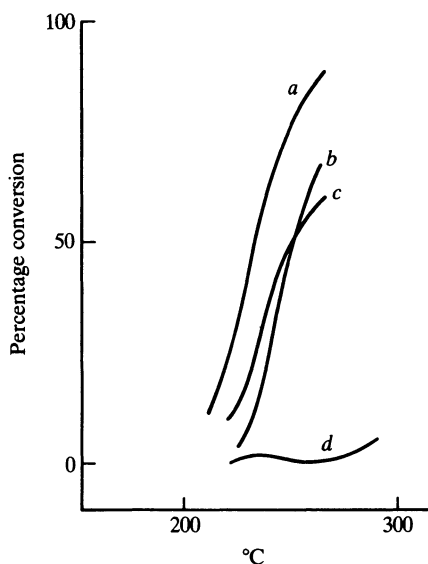
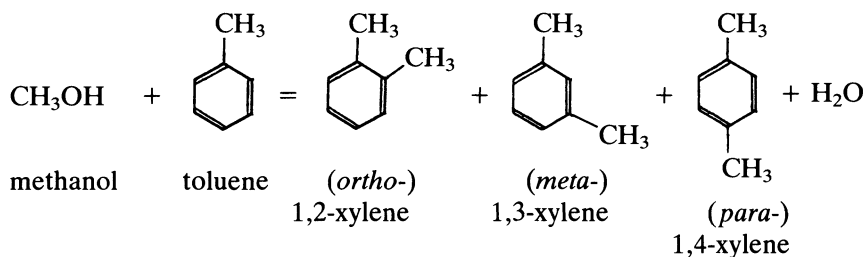


Figure 7.18 Dehydration of (a) *iso*-butanol on Ca-X, (b) *n*-butanol on Ca-X, (c) *n*-butanol on Ca-A, and (d) *iso*-butanol on Ca-A.

In the acid-catalysed transalkylation of dialkylbenzenes, one of the alkyl groups is transferred from one molecule to another. This bimolecular reaction involves a diphenylbenzene transition state. When the transition state collapses it can split to give either the 1,2,4-isomer or the 1,3,5-isomer, together with the monoalkylbenzene. When the catalyst used for this reaction is mordenite (Figure 7.17c), the transition state for the formation of the symmetrical 1,3,5-isomer is too large for the pores, and the 1,2,4-isomer is formed in almost 100% yield. (This compares with the equilibrium mixtures, in which the symmetrically substituted isomers tend to dominate.)

One of the industrial processes using ZSM-5 provides us with an example of product-selective catalysis: the production of 1,4-(*para*-)xylene. *Para*-xylene is used in the manufacture of terephthalic acid, the starting material for the production of polyester fibres such as 'Terylene'.

Xylenes are produced in the alkylation of toluene by methanol:



The selectivity of the reaction over ZSM-5 occurs because of the difference in the rates of diffusion of the different isomers through the channels. This is confirmed by the observation that selectivity increases with increasing temperature, indicating the increasing importance of diffusion limitation. The diffusion rate of *para*-xylene is approximately 1000 times faster than that of the other two isomers. The computer graphics representation in Figure 7.19 shows why *meta*- and *ortho*-xylene do not fit in the pores easily and so cannot diffuse along them. The xylenes isomerize within the pores, and so *para*-xylene diffuses out while the *ortho*- and *meta*-isomers are trapped and have more time to convert to the *para*- form before escaping. Up to 97% of selective conversion to *para*-xylene has been achieved by suitable treatment of the catalyst.

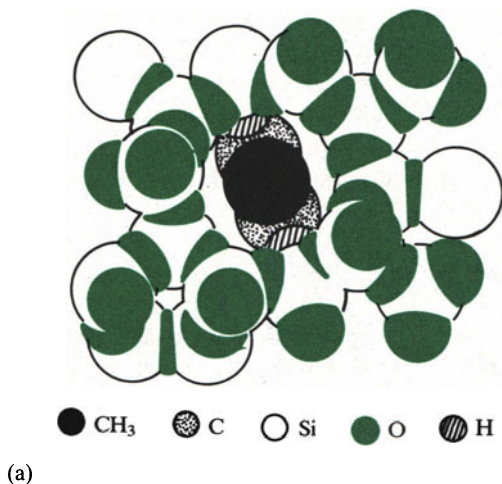
ZSM-5 is used as a catalyst in the disproportionation of toluene (a by-product of petroleum refining) to form benzene and *para*-xylene, both of which are more valuable products. ZSM-5 is also the catalyst used to convert methanol into hydrocarbons. This research received a great impetus at the end of the 1970s when oil was in short supply and prices rose sharply. Subsequently, more oil was released and prices dropped; consequently much of this research was put into abeyance, and plants were left at the pilot stage. It may prove to be an important process for those countries, such as New Zealand, with no oil reserves of their own, but which do have a supply of natural gas (CH_4). The methane is first converted to methanol, CH_3OH , which is then partially broken down into dimethyl ether and water. (Alternatively the methanol feed can be readily synthesized from carbon monoxide and hydrogen.) The conversion over ZSM-5 into hydrocarbons produces mainly branched chain and aromatic hydrocarbons in the C_9 – C_{10} range, which is ideal for high octane unleaded fuel. ZSM-5 is also used as the catalyst in the production of monoethyl benzene from benzene and ethene; it is highly selective for the mono-substituted product, which is the precursor of styrene, and does not use the harmful aluminium chloride which the old Friedel–Crafts process employed.

7.5.5 New materials

Research in zeolites has also branched out to try and prepare new materials which incorporate various molecules and ions in the cages. An early example of this is the pigment ultramarine, which is based on the sodalite structure and contains S_3^- ions trapped in the cages; these impart the beautiful blue colouration.

One area of this research has focused on depositing semiconductor materials in the zeolite cages. The resulting very small particles are called **quantum dots**. Such particles have very interesting electronic, magnetic and optical properties which are a consequence of their size rather than

p-Xylene in ZSM-5



m-Xylene in ZSM-5

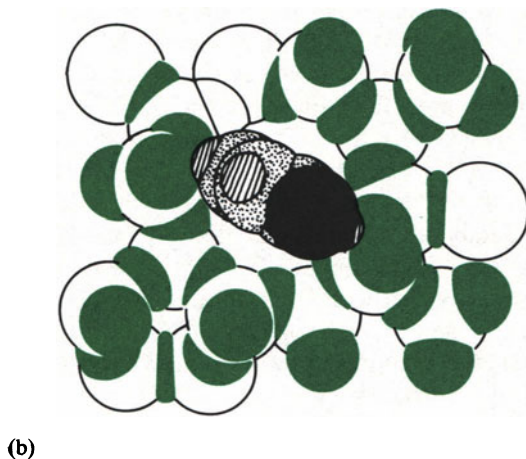


Figure 7.19 Computer graphics representations, showing how (a) *para*-xylene fits neatly in the pores of ZSM-5 whereas (b) *meta*-xylene cannot diffuse through its channels.

their chemical composition. As the pore-filling of the zeolite increases, the quantum dots become interconnected and materials are produced with properties intermediate between those of discrete particles and bulk semiconductors. One example of this is the narrow band gap semiconductor CdS, which forms discrete cubic $(\text{CdS})_4$ clusters in the sodalite cages of zeolite-A, -X and -Y.

Other guests that can be incorporated into zeolite β -cages include the alkali metals, silver and silver salts, selenium and various conducting polymers – the list is too long to explore fully here. Suffice it to say that these new materials are being investigated with respect to interesting physical properties which then have the possibility of commercial exploitation – properties such as semi-, photo- and fast-ion conductivity, luminescence, colour and quantum size effects.

7.6 OTHER FRAMEWORK STRUCTURES

Other framework structures have also been characterized which contain atoms such as aluminium and phosphorus, which are tetrahedrally coordinated by oxygen. Pure aluminium phosphate, commonly called ALPO, and its derivatives have been found to take the same structural forms as some of the zeolites, such as sodalite, faujasite, chabazite, etc., as well as some novel structures. Many of these compounds have now been discovered and there is a whole series of acronyms to denote them. The metal–aluminium phosphates can be formed with metals such as Li, Be, Mg, Mn, Fe, Co, Ni and Zn replacing some of the aluminium; these are usually designated MAPOs or MeALPOs, where M/Me stand for metal. If the compound contains silicon or silicon and a metal, partially replacing aluminium or phosphorus, then they become SAPOs and MAPSOs (or MeAPSOs or MeALPSOs!). In the same way that the replacement of Si(IV) by Al(III) in the zeolite structures leads to the formation of Brönsted acid sites, so does the replacement of Al(III) by M(II) in ALPOs; readily detachable protons are loosely bound to a framework oxygen atom near the divalent metal. Consequently there has been much interest in recent years in these compounds as possible heterogeneous catalysts which might be at least as good, if not better, than the zeolites. Indeed SAPOs have been found to be very good catalysts for the conversion of methanol to olefins.

The aluminophosphate compounds have been formed using templates, in a similar fashion to many of the zeolites. Typical templates for forming large pores are the tetra-*n*-propyl ammonium ion and tri-*n*-propylamine: one of the new channel structures formed using these is ALPO-5 shown in projection in Figure 7.20a. ALPO-5 has 12-ring windows with a diameter of about 800 pm, similar to that found in zeolite-Y. More recently extra-large-pore materials have been prepared. The first of these was an ALPO designated VPI-5 (Figure 7.20b) with 18-ring windows and a pore diameter of between 1200 and 1300 pm and others such as cloverite, a gallophosphate with a cloverleaf-shaped channel (Figure 7.21), have followed. The hope is that these large channelled structures will allow catalytic conversions to take place, using molecules which are too large to

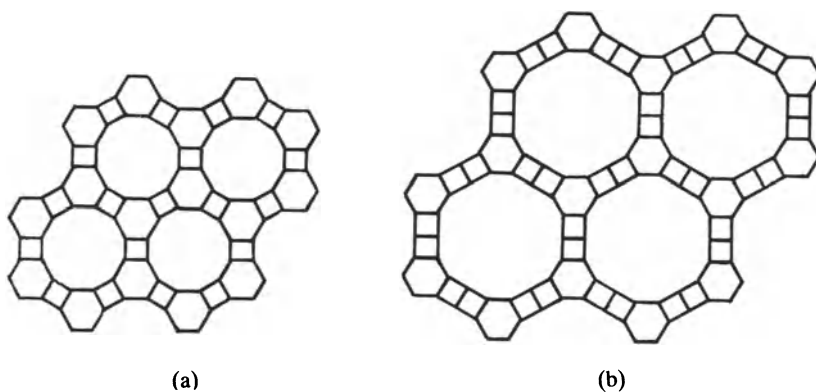


Figure 7.20 Schematic structural projection drawings of (a) ALPO-5 and (b) VPI-5.

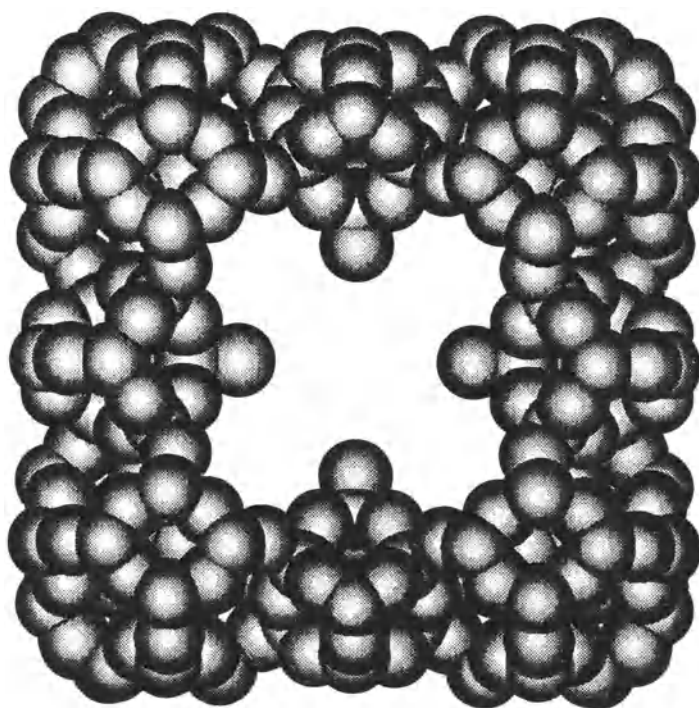


Figure 7.21 The framework of structure of the synthetic gallophosphate cloverite represented as shaded spheres of van der Waals radii. (From C.R.A. Catlow (ed.) (1992) *Modelling of Structure and Reactivity in Zeolites*, Academic Press, London. Reproduced by permission of Academic Press Ltd.)

enter the conventional zeolitic size channels; one example of this – the hydrogenation of cyclooctene using rhodium-substituted VPI-5 – has been reported.

7.7 CLAY MINERALS

Like the zeolites, the smectite clays are a class of naturally occurring aluminosilicate minerals. They are often found as components of soils and sediments, and there are some large deposits, such as the bentonite (consisting mainly of montmorillonite and beidellite) found in Cornwall, UK and Wyoming, USA. The smectite clays all have a basic layer structure which is shown in Figure 7.22; it consists of parallel layers of tetrahedral silicate $[\text{SiO}_4]$ sheets and octahedral aluminate $[\text{Al}(\text{O},\text{OH})_6]$ sheets. The silicate layers contain $[\text{SiO}_4]$ tetrahedra each linked through three corners to form an infinite layer. The aluminate layers contain a plane of octahedrally coordinated edge-linked aluminium ions, sandwiched between two inward pointing sheets of corner-linked $[\text{SiO}_4]$ tetrahedra. If there is no replacement of Si or Al, then the layers are electrically neutral, producing the mineral pyrophyllite. In the smectite clays different structures are formed because substitution of silicon and aluminium by metal ions can take place in both the tetrahedral and octahedral layers. The resulting negative charge is distributed on the oxygens of the layer surface, and any charge balance is restored by interlayer cations (usually Na^+ or Ca^{2+}); for instance, in montmorillonite approximately one-sixth of the Al^{3+} ions have been replaced by Mg^{2+} , whereas in beidellite about one-twelfth of the Si^{4+} have been replaced by Al^{3+} . The different members of the smectite group of clays are distinguished by the type and position of the cations in the framework.

The peculiar layer structure of these clays gives them cation exchange and intercalation properties that can be very useful. Molecules such as water and polar organic molecules such as glycol can easily intercalate between the layers and cause the clay to swell. Water enters the interlayer region as integral numbers of complete layers. Calcium montmorillonite usually has two layers of water molecules but the sodium form can have one, two or three water layers; this causes the interlayer spacing to increase stepwise from about 960 pm in the dehydrated clay to 1250, 1550 and 1900 pm as each successive layer of water forms.

The Na^+ and Ca^{2+} cations which make up the charge balance due to the substitution of Si and Al in the layers by other metals are usually hydrated and are located in the interlayer regions, loosely bound to the layer surfaces. They are known as **exchangeable cations**, and can be replaced easily by other cations using ion exchange methods or by protons in the form of H_3O^+ , to form an acidic clay. Such acidic clays

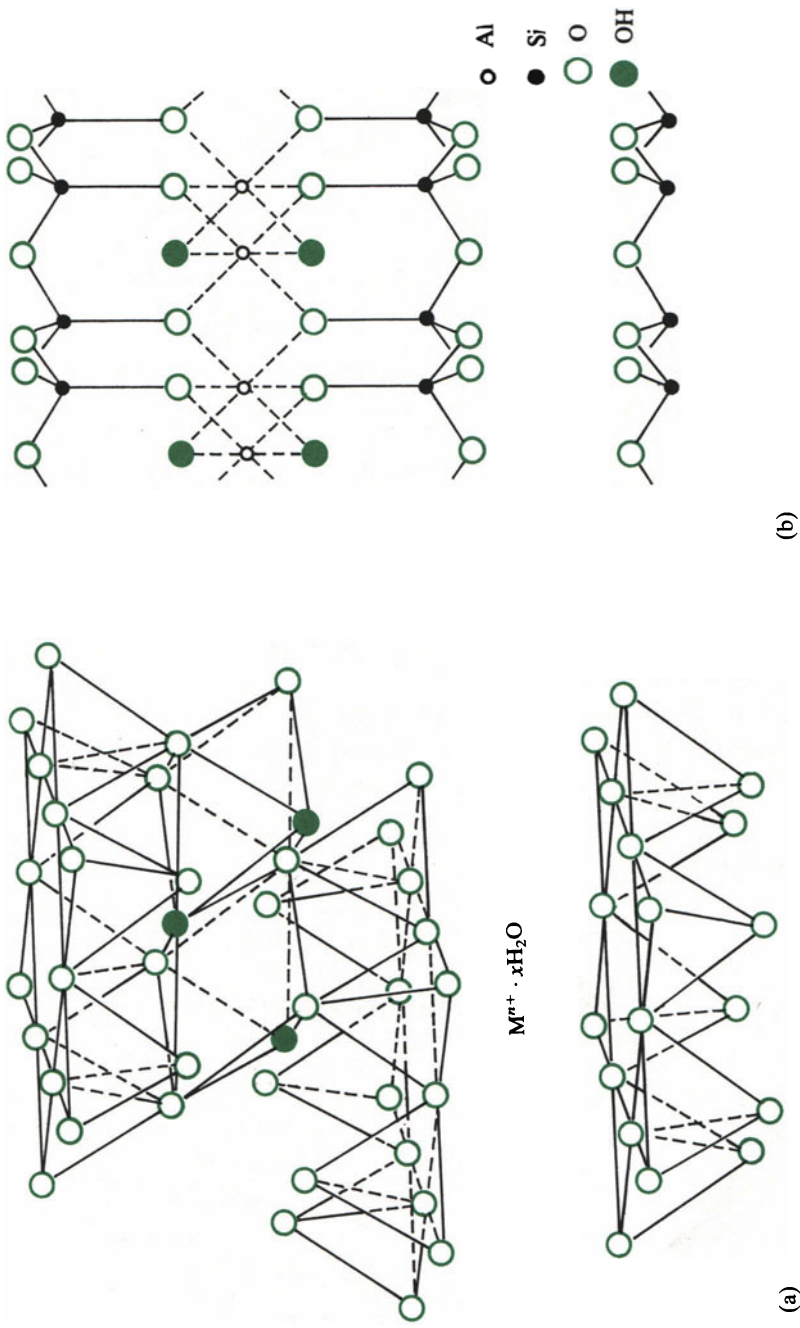


Figure 7.22 Idealized structure of the layers in a smectite clay, (a) showing only the oxygen/hydroxyl framework and (b) also showing aluminum and silicon positions.

form very useful catalysts when the reactant molecules enter the interlayer regions. For many years modified clays were used as the catalyst for petroleum cracking to produce petrol, although they have since been replaced by more thermally stable and selective zeolites. However, smectite clays can be used for the dimerization of oleic acid, the conversion of hexene to dihexyl ethers, and the formation of ethyl acetate from ethanoic acid and ethene. Recent research on clay catalysts has concentrated on the introduction of metal complexes into the interlayer region to act as the catalytic centre and also on the formation of robust molecular props to hold the interlayer regions apart – so-called **pillaring**.

One of the problems with using clays as catalysts is that at high temperatures ($>200^{\circ}\text{C}$) they start to dehydrate and the interlayer region collapses. A lot of effort has concentrated on forming temperature-stable pillars that will hold the layers apart even at high temperature and in the absence of a swelling solvent, to form a large interlayer region. The pillaring leads to a porous network between the layers analogous to the zeolite channels (Figure 7.23) and the hope is that by judicious adjustment of the size and spacings of the pillars the pore sizes can be made bigger than those of the faujasitic zeolites. Because the layers are negatively charged, the molecular props that have been used for pillaring are large cations such as tetraalkyl ammonium ions and the 'Al₁₃' Keggin ion, $[\text{Al}_{13}\text{O}_4(\text{OH})_{28}^{3+}]$ (although this is thought to form columns consisting of small clusters of alumina, Al_2O_3). Other pillars have been formed from silica and the oxides of various metals, such as iron, zirconium and tin.

7.8 POSTSCRIPT

We end this chapter with a quotation from a lecture given by Prof. J.M. Thomas. It should please those of you who are beginning to love the patterns and symmetry of crystalline solids.

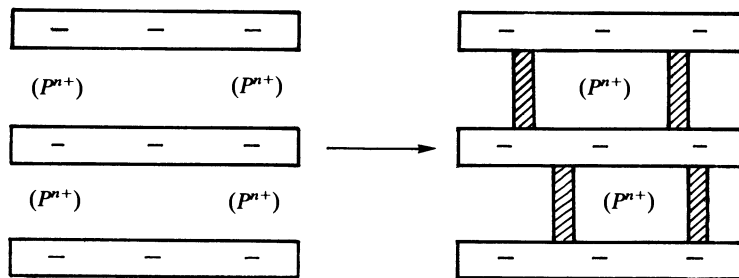


Figure 7.23 Representation of the formation of pillars in a smectite clay where P^{n+} is the pillaring cation.

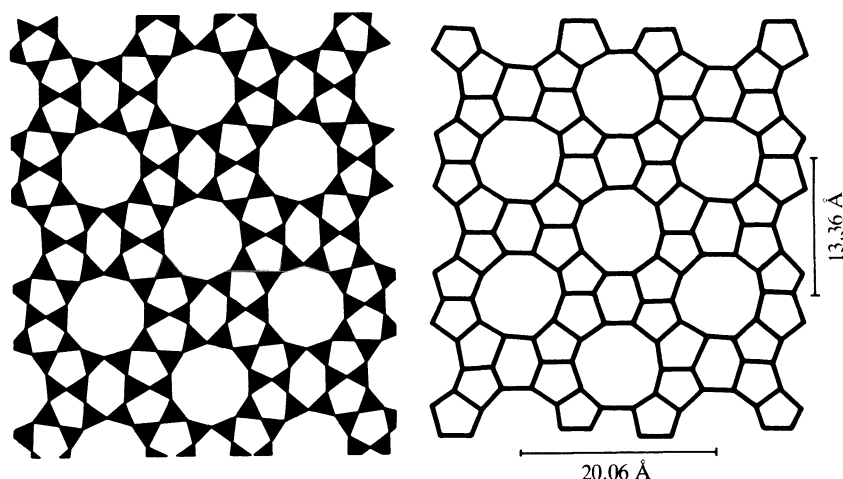


Figure 7.24 Around a central 10-membered ring in the synthetic zeolite catalyst shown schematically on the right, there are eight five-membered and two six-membered rings. In exactly the same sequence, such five- and six-membered rings circumscribe a central 10-membered ring in the pattern on the left.

... Figure 7.24 shows, on the right, a projected structure of the zeolite we have been studying, a synthetic catalyst discovered in New Jersey in 1975. Its structure was elucidated some 6 years ago. On the left, I reproduce a pattern made on the wall of a mosque in Baku in the Soviet state of Azerbaijan in 1086 AD, the year that the Domesday Book appeared by order of William the Conqueror. These two structures have exactly the same pattern.

‘There is nothing new under the sun.’

FURTHER READING

Few solid state books cover this subject. The following are specialist books and articles in the field that contain accessible material.

Breck, D.W. (1974) *Zeolite Molecular Sieves*, John Wiley, New York.

Barrer, R.M. (1982) *Hydrothermal Chemistry of Zeolites*, Academic Press, New York.

Dyer, A. (1988) *An Introduction to Zeolite Molecular Sieves*, John Wiley, New York.

Whan, D.A. (1981) Structure and catalytic activity of zeolites, *Chemistry in Britain*, 532–5.

Fyfe, C.A., Thomas, J.M., Klinowski, J. and Gobbi, G.C. (1983) Magic-angle-spinning NMR spectroscopy and the structure of zeolites, *Angewandte Chemie (International English Edition)*, **22**, 259–336.

Ramdas, S., Thomas, J.M., Betteridge, P.W., Cheetham, A.K. and Davies, E.K.

- Modelling the chemistry of zeolites by computer graphics (1984) *Angewandte Chemie (International English Edition)*, **23**, 671–9.
- Csicsery, S.M. (1985) Shape selective catalysis in zeolites, *Chemistry in Britain*, 473–7.
- Kerr, G.T. (1989) Synthetic zeolites, *Scientific American*, July, 82–7.
- Catlow, C.R.A. (ed) (1992) *Modelling of Structure and Reactivity in Zeolites*, Academic Press, London.
- Thomas, J.M. (1992) Solid acid catalysts, *Scientific American*, April, 82–8.
- Ozin, G.A., Kuperman, A. and Stein, A. (1989) Advanced zeolite materials science, *Angewandte Chemie (International English Edition)*, **28**, 359–76.

QUESTIONS

1. Figure 7.25 shows the ^{29}Si MAS NMR spectrum of faujasite. Use this figure to determine which Si environments are most likely to be present.

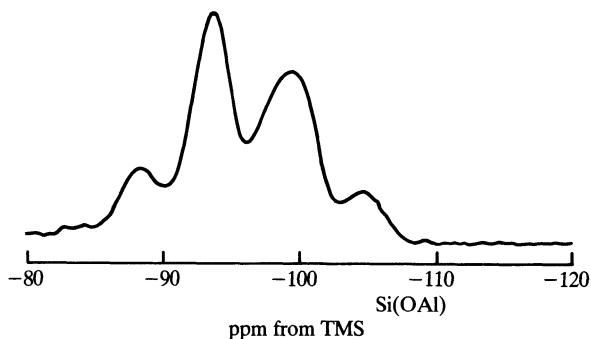


Figure 7.25 ^{29}Si MAS NMR spectrum at 79.6 MHz of faujasite of Si/Al = 2.61 (zeolite-Y).

2. Figure 7.26 shows the ^{29}Si spectrum of the same sample of faujasite as Figure 7.25, but after treatment with SiCl_4 and washing with water. What has happened to it?
3. A sample of faujasite was treated with SiCl_4 and four ^{27}Al MAS NMR spectra were taken at various stages afterwards (Figure 7.27). Describe carefully what has happened during the process.
4. Zeolite-A has a single peak in the ^{29}Si MAS NMR spectrum at 89 ppm and has a Si/Al ratio of 1. Comment on these observations.
5. Zeolite-A (Ca form), when loaded with platinum, has been found to be a good catalyst for the oxidation of hydrocarbon mixtures. How-

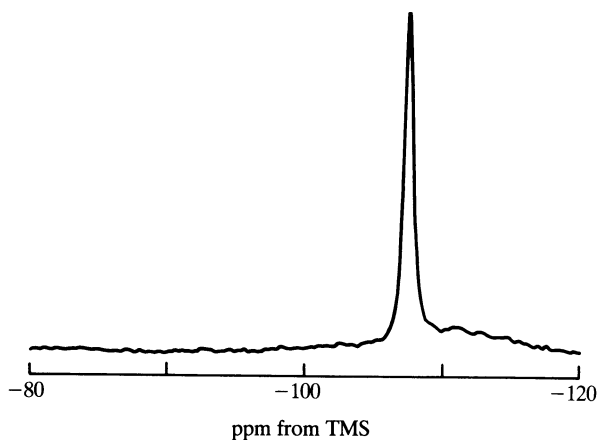


Figure 7.26 ^{29}Si MAS NMR spectrum at 79.6 MHz of faujasite of $\text{Si}/\text{Al} = 2.61$ after successive dealumination with SiCl_4 and washings.

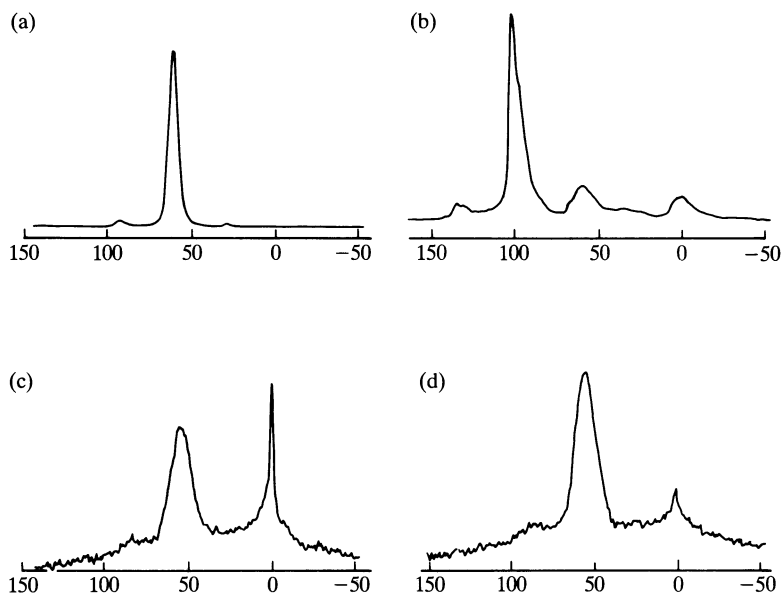


Figure 7.27 ^{27}Al MAS NMR spectra at 104.2 MHz obtained on zeolite-Y samples at various stages of the SiCl_4 dealumination procedure. (a) Starting faujasite sample. (b) Intact sample after reaction with SiCl_4 before washing. (c) Sample (b) after washing with distilled water. (d) After several washings.

ever, if the mixture contains branched-chain hydrocarbons, these do not react. Suggest a possible reason.

6. Both ethene and propene can diffuse into the channels of a particular mordenite catalyst used for hydrogenation. Explain why only ethane is produced.
7. Explain why, when 3-methyl pentane and *n*-hexane are cracked over zeolite-A (Ca form) to produce smaller hydrocarbons, the percentage conversion for 3-methyl pentane is less than 1% whereas that for *n*-hexane is 9.2%.
8. When toluene is alkylated by methanol with a ZSM-5 catalyst, increase in the crystallite size from 0.5 to 3 μm approximately doubles the amount of *para*-xylene produced. Suggest a possible explanation.
9. The infrared stretching frequency of the hydroxyl associated with the Brønsted sites in decationized zeolites, falls in the range 3600–3660 cm^{-1} . As the Si/Al ratio in the framework increases, this frequency tends to decrease. What does this suggest about the acidity of the highly siliceous zeolites?

8.1 INTRODUCTION

Perhaps the most well-known example of solid state optical devices is the **laser** and, with the advent of video- and compact discs and laser printers, lasers are becoming almost commonplace. Of interest to the solid state chemist are two types of laser, typified by the **ruby laser** and the **gallium arsenide laser**. Because laser light is more easily modulated than light from other sources, it is increasingly used for sending information; light travelling along optical fibres replaces electrons travelling along wires in, for example, telecommunications. To transmit light over long distances the optical fibres must have particular absorption and refraction properties and the development of suitable substances has become an important area of research.

Applications of solid state optical properties were known and commercially important before lasers were developed and we also consider examples of these. **Light-emitting diodes (LEDs)** are used for displays on digital watches and scientific instruments. The mechanism by which light is produced in LEDs is similar to that in the gallium arsenide (GaAs) laser. Another important group of solids are the light-emitting solids known as **phosphors** which are used on television screens and fluorescent light tubes.

Broadly speaking, there are two situations that have to be considered in explaining devices such as those we have mentioned. In the first, which is relevant to the ruby laser and to phosphors for fluorescent lights, the light is emitted by an impurity ion in a host lattice. We are concerned here with what is essentially an atomic spectrum modified by the lattice. In the second case, which applies to LEDs and the gallium arsenide laser, the optical properties of the delocalized electrons in the bulk solid are important. We shall start with the first case and take atomic spectra as our starting point.

8.2 THE INTERACTION OF LIGHT WITH ATOMS

When an atom absorbs a photon of light of the correct wavelength it undergoes a transition to a higher energy level. To a first approximation in many cases, we can think of one electron in the atom absorbing the photon and being excited. The electron will only absorb the photon if the photon's energy matches that of the energy difference between the initial and final electronic energy level, and if certain rules, known as **selection rules**, are obeyed. In light atoms the electron cannot change its spin and its orbital angular momentum must change by one unit; in terms of quantum numbers $\Delta s = 0$, $\Delta l = \pm 1$. (One way of thinking about this is that the photon has zero spin and one unit of angular momentum. Conservation of spin and angular momentum then produces these rules.) For a sodium atom, for example, the $3s$ electron can absorb one photon and go to the $3p$ level (there is no restriction on changes of the principal quantum number). The $3s$ electron will not, however, go to the $3d$ or $4s$ level. Figure 8.1 illustrates allowed and forbidden transitions.

However, the spin and orbital angular momenta are not entirely independent and coupling between them allows forbidden transitions to occur; however, the probability of an electron absorbing a photon and

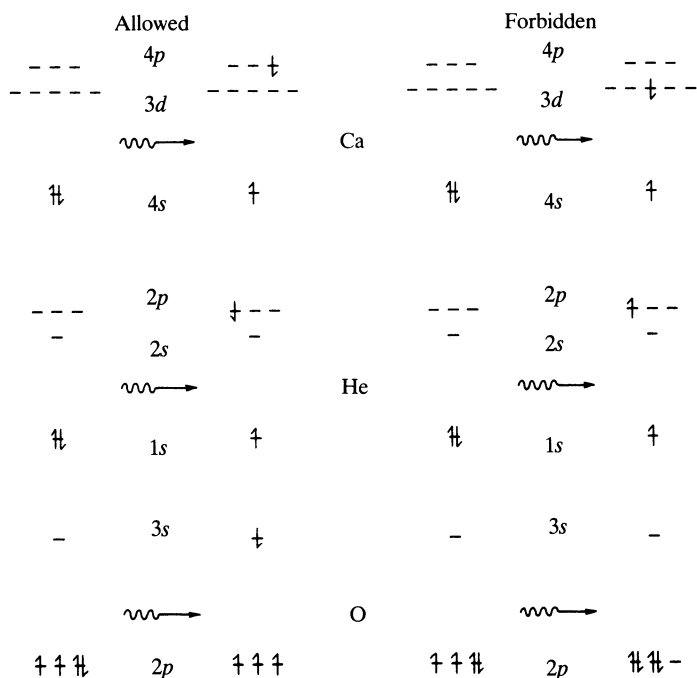


Figure 8.1 Allowed and forbidden atomic transitions.

being excited to a forbidden level is much smaller than the probability of it being excited to an allowed level. Consequently spectral lines corresponding to forbidden transitions are less intense than those corresponding to allowed transitions.

An electron that has been excited to a higher energy level will sooner or later return to the ground state. It can do this in several ways. The electron may simply emit a photon of the correct wavelength at random some time after it has been excited. This is known as **spontaneous emission**. Alternatively, a second photon may come along and instead of being absorbed may induce the electron to emit. This is known as **induced** or **stimulated emission** and plays an important role in the action of lasers. The emitted photon in this case is in phase with and travelling in the same direction as the photon inducing the emission; the resulting beam of light is said to be coherent. Finally, the atom may collide with another atom, losing energy in the process, or give energy to its surroundings in the form of vibrational energy. These are examples of non-radiative transitions. Spontaneous and stimulated emission obey the same selection rules as absorption. Non-radiative transitions have different rules. In a crystal (or of course a molecule), the atomic energy levels and selection rules are modified. Let us take as an example an ion with one d electron outside a closed shell (Ti^{3+} for example). This will help us understand the ruby laser.

In the free ion the five $3d$ orbitals all have the same energy. In a crystal these levels are split; for example, if the ion occupied an octahedral hole, the $3d$ levels would be split into a lower, triply degenerate (t_{2g}) level and a higher, doubly degenerate (e_g) level (Figure 8.2). An electronic transition between these levels is now possible. In the free ion a transition from one d level to another involves zero energy change, and so would not be observed even if it were allowed. In the crystal, the transition involves a change in energy, but is still forbidden by the selection rules. Lines corresponding to such transitions can, however, be observed, albeit with low intensity, because the crystal vibrations mix different electronic energy levels. Thus the $3d$ levels may be mixed with the $4p$ giving a small fraction of 'allowedness' to the transition. Figure 8.3 shows an absorption band due to a transition from t_{2g} to e_g for the ion Ti^{3+} which has one d electron. (This band is in fact two closely spaced bands as the excited state is distorted from a true octahedron and the e_g level is further split into two.) The role played by a similar forbidden transition in the operation of the ruby laser is described below.

8.2.1 The ruby laser

Ruby is corundum (one form of Al_2O_3) with 0.04–0.5% Cr^{3+} ions as an impurity replacing aluminium ions. The aluminium ions, and hence the

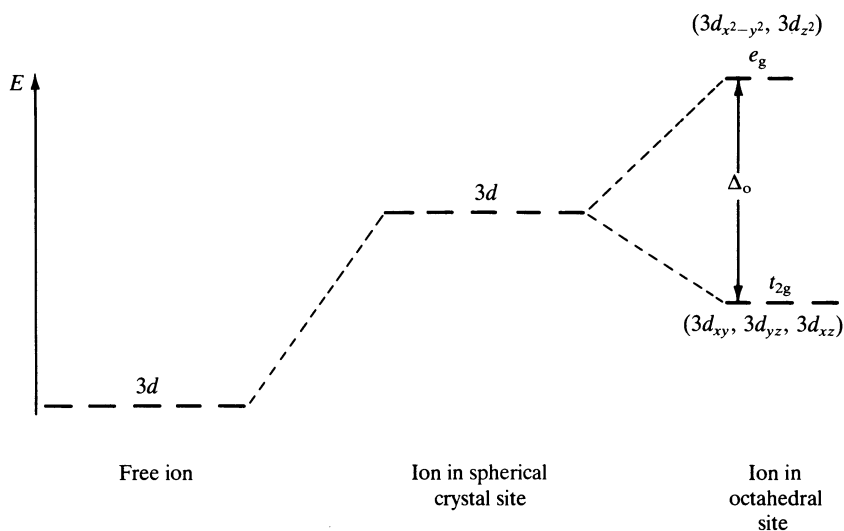


Figure 8.2 Splitting of d levels in an octahedral site in a crystal.

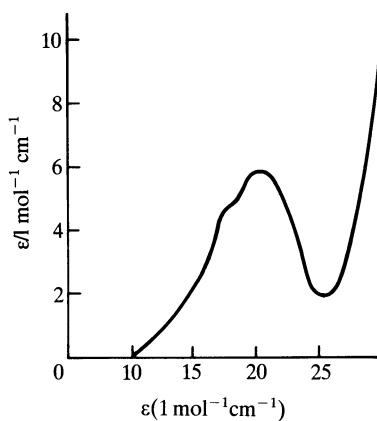


Figure 8.3 The t_{2g} to e_g transition of Ti^{3+} . The band is in fact two overlapping bands. This is due to a further splitting of the e_g levels.

chromium ions, occupy distorted octahedral sites. As discussed above, therefore the $3d$ levels of the chromium ion will be split. Cr^{3+} has three $3d$ electrons and, in the ground state, these occupy separate orbitals with parallel spins. When light is absorbed, one of these electrons can undergo a transition to a higher energy $3d$ level; this is similar to the transition discussed in the previous section, but with three electrons it is necessary to consider changes in the electron repulsion as well as changes in orbital

energies. Including electron repulsion changes gives two transitions corresponding to the jump from the lower to the higher $3d$ level.

Having absorbed light and undergone one of these transitions, the chromium ion could now simply emit radiation of the same wavelength and return to the ground state. However, in ruby there is a fast, radiationless transition in which the excited electron loses some of its energy and the crystal gains vibrational energy. The chromium ion is left in a state in which it can only return to the ground state by a transition in which an electron changes its spin. Such a transition is doubly forbidden since it still breaks the rule that forbids $3d \rightarrow 3d$ and is even less likely to occur than the original absorption process. The states involved are shown schematically in Figure 8.4. The ions absorb light and go to states 3 and 4. They then undergo a radiationless transition to state 2. Because the probability of spontaneous emission for state 2 is low, and there is no convenient non-radiative route to the ground state, a considerable population of state 2 can build up. When eventually (about 5 ms later) some ions in state 2 return to the ground state, the first few spontaneously emitted photons interact with other ions in state 2 and induce these to emit. The resulting photons will be in phase and travelling in the same direction as the spontaneously emitted photons and will induce further emission as they travel through the ruby. The ruby is in a reflecting cavity so that the photons are reflected back into the crystal when they reach the edge. The reflected photons induce further emission and by this means an appreciable beam of coherent light is built up. The mirror on one end can then be removed and a pulse of light emitted. The name **laser** is a reflection of this build up of intensity. It is an acronym standing for Light

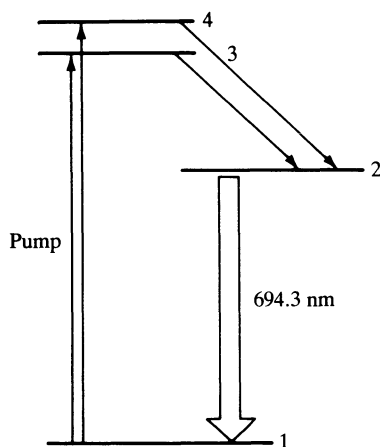


Figure 8.4 The states of the Cr^{3+} ion involved in the ruby laser transition.

Amplification by Stimulated Emission of Radiation. (Similar devices producing coherent beams of microwave radiation are known as masers.) A typical arrangement for a pulsed ruby laser is shown in Figure 8.5. A high-intensity flash lamp excites the Cr^{3+} ions from level 1 to levels 3 and 4. The lamp can lie alongside the crystalline rod of ruby or be wrapped around it. At one end of the reflective cavity surrounding the ruby crystal is a Q switch, which switches from being reflective to transmitting the laser light and can be as simple as a rotating segmented mirror, but is usually a more complex device.

Ruby was the first material for lasers but there are now several other crystals that are employed. The crystals used need to contain an impurity with an energy level such that return to the ground state is only possible by a forbidden transition in the infrared, visible or near ultraviolet. It must also be possible to populate this level via an allowed (or at least less forbidden) transition. Research has tended to concentrate on transition metal ions and lanthanide ions in various hosts since these ions have suitable transitions of the right wavelength. Some examples are given in Table 8.1 with the wavelength of the laser emission.

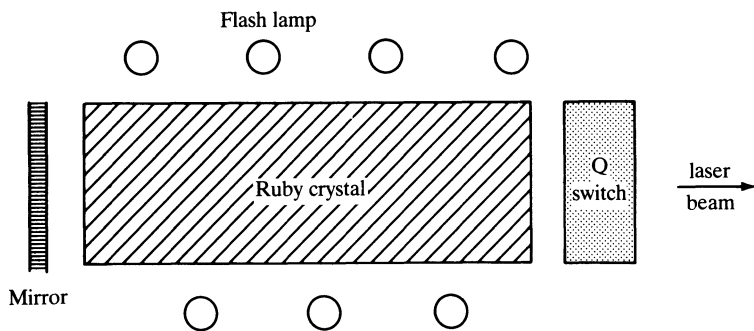


Figure 8.5 Sketch of a ruby laser.

Table 8.1

<i>Ion</i>	<i>Host</i>	<i>Wavelength emitted (nm)</i>
Nd^{3+}	Fluorite (CaF_2)	1046
Sm^{3+}	Fluorite	708.5
Ho^{3+}	Fluorite	2090
Nd^{3+}	Calcium tungstate (CaWO_4)	1060

8.2.2 Phosphors in fluorescent lights

Phosphors are solids which absorb energy and re-emit it as light. As in the lasers we have just described the emitter is usually an impurity ion in a host lattice. However, for the uses to which phosphors are put it is not necessary to produce intense, coherent beams of light, and the emitting process is spontaneous rather than induced. There are many applications of phosphors, for example television pictures are produced by phosphors that are bombarded with an electron beam (cathode rays). In terms of tonnage produced, one of the most important applications is fluorescent light tubes.

Fluorescent lights produce radiation in the ultraviolet (254 nm) by passing an electric discharge through a low pressure of mercury vapour. The tube is coated inside with a white powder which absorbs the ultraviolet light and emits visible radiation. For a good fluorescent light the efficiency of the conversion should be high and the emitted light should be such that the appearance of everyday objects viewed by it should resemble as closely as possible their appearance in daylight. Most phosphors for fluorescent lights have been based on alkaline earth halophosphates such as $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$. As in lasers, the usual dopants are transition metal or lanthanide ions, but more than one impurity ion is needed to approximate the whole visible spectrum. Not all the impurity ions need to be capable of absorbing the exciting radiation, however, as the host lattice can act to transmit the energy from one site to another. For example, in a phosphor doped with Mn^{2+} and Sb^{3+} ions, the ultraviolet radiation from the mercury lamp is only absorbed by the antimony (Sb^{3+}) ions. The excited antimony ion drops down to a lower excited state via a non-radiative transition. Emission from this lower state produces a broad band in the blue region of the visible spectrum. Some of the energy absorbed by the antimony travels through the host crystal and is absorbed by the manganese ions. The excited Mn^{2+} ions emit yellow light and return to the ground state. The two emission bands together produce something close to daylight. Phosphors have been introduced which are more efficient and give a closer approximation to daylight. A good approximation is, for example, given by a combination of blue from barium magnesium aluminate doped with divalent europium (Eu^{2+}), green from an aluminate doped with cerium (Ce^{3+}) and terbium (Tb^{3+}) ions, and red from yttrium oxide doped with trivalent europium (Eu^{3+}).

In these phosphors and in the ruby laser, light was absorbed and emitted by electrons localized on an impurity site, but in other optical devices the radiation is emitted by delocalized electrons. In the next section, therefore, we shall consider the absorption and emission of radiation in solids with delocalized electrons, in particular in semiconductors.

8.3 ABSORPTION AND EMISSION OF RADIATION IN SEMICONDUCTORS

Radiation falling on a semiconductor will be absorbed by electrons in delocalized bands, in particular those near the top of the valence band, causing these electrons to be promoted to the conduction band. Because there are many closely packed levels in an energy band, the absorption spectrum is not a series of lines as in atomic spectra, but a broad peak with a sharp threshold close to the band gap energy. The absorption spectrum of GaAs, for example, is shown in Figure 8.6.

Transitions to some levels in the conduction band are more likely than transitions to others. This is because transitions between valence band and conduction band levels, like those between atomic energy levels, are governed by selection rules. The spin selection rule still holds; when promoted to the conduction band the electron does not change its spin. Orbital angular momentum rules are not appropriate for energy bands, however, and so the rule governing change in the quantum number, l , is replaced by a restriction on the wave vector, $\mathbf{k}$. As seen in Chapter 4, the energy levels in a band are characterized by the wave vector, the momentum of the electron wave being given by $\mathbf{k}\hbar$. The momentum of a photon with wavelength in the infrared, visible or ultraviolet is very small compared to that of the electron in the band. Conservation of momentum therefore produces the selection rule for transitions between bands. An electron cannot change its wave vector when it absorbs or emits radiation. Thus an electron in the valence band with wave vector, $\mathbf{k}_i$, can only undergo allowed transitions to levels in the conduction band which also have wave vector, $\mathbf{k}_i$. In some solids, for example GaAs, the level at the top of the valence band and that at the bottom of the conduction band

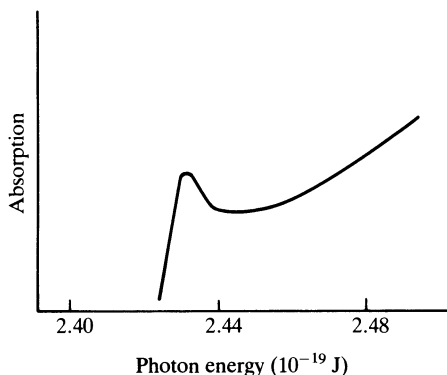


Figure 8.6 Absorption spectrum of GaAs.

have the same wave vector. There is then an allowed transition at the band gap energy. Such solids are said to have a **direct band gap**.

For other semiconductors, for example silicon, the direct transition from the top of the valence band to the bottom of the conduction band is forbidden. These solids are said to have an **indirect band gap**. Illustrations of band structures for solids with direct and indirect band gaps are given in Figure 8.7. Note that in these diagrams the energy for a band in one direction is plotted against the wave number, k . Similar diagrams were given in Chapter 4 for the free electron model but more accurate calculations show that curves of this type adopt many shapes and do not necessarily resemble those predicted by the free electron model.

The simple free electron model might suggest that the lowest energy orbital in any band is that with $k = 0$. Figure 8.8, however, illustrates two combinations of orbitals that will have $k = 0$ for a chain because all the atomic orbitals are combined in phase. The combination of p orbitals is obviously antibonding and so would be expected to have the highest energy in its band; the combination of s orbitals is bonding and would have the lowest energy in its band. If the p band lay below the s band, a transition between these levels would be allowed and would correspond to a direct transition across the band gap. In real solids the highest and lowest levels in bands will contain contributions from different types of atomic orbital and it becomes difficult to predict whether a band gap will be direct or indirect. One consequence of an indirect band gap is that an electron in the bottom level of the conduction band has only a small

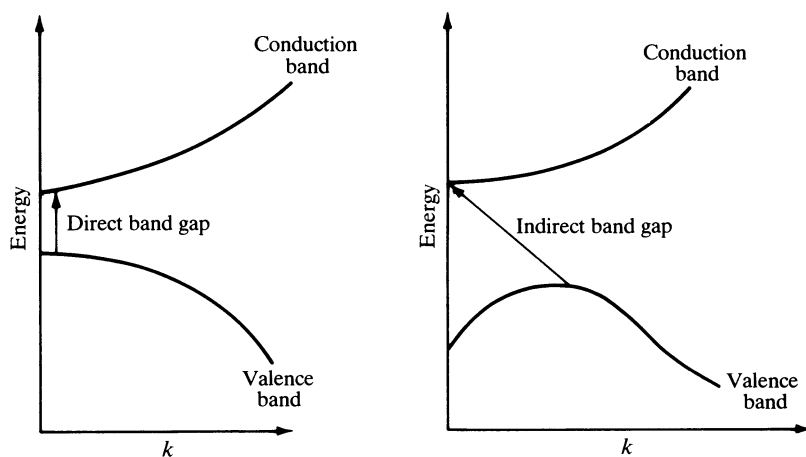


Figure 8.7 Sketch of energy bands for (a) a solid with a direct band gap and (b) a solid with an indirect band gap. Note that in this diagram the horizontal axis is k , not the density of states. In this representation a band is shown as a line going from 0 to the maximum value of k occurring for that band.

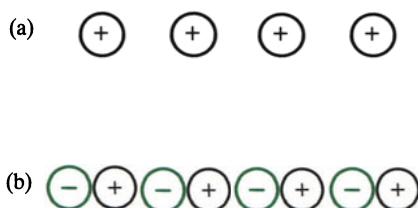


Figure 8.8 A row of (a) s orbitals and (b) p orbitals, both with $k = 0$.

probability of emitting a photon and returning to the top of the valence band. This is of importance when selecting materials for some of the applications we are going to consider.

Transitions across the band gap are also responsible for the appearance of many solids. Because a solid is very concentrated, the probability that a photon whose energy corresponds to an allowed transition is absorbed is very high. Many such photons will therefore be absorbed at or near the surface of the solid. These photons will then be re-emitted in random directions so that some will be reflected back towards the source of radiation and some will travel further into the solid. Those travelling into the solid stand a very good chance of being re-absorbed and then re-emitted, again in random directions. The net effect is that the radiation does not penetrate the solid but is reflected by its surface. If the surface is sufficiently regular, then solids which reflect visible radiation appear shiny. Thus silicon, whose band gap is at the lower end of the visible region and has allowed transitions covering most of the visible wavelengths, appears shiny and metallic. Many metals have strong transitions between the conduction band and a higher energy band which lead to their characteristic metallic sheen. Some metals such as tungsten and zinc have a band gap in the infrared and transitions in the visible are not so strong. These metals appear relatively dull. Gold and copper have strong absorption bands due to excitation of d band electrons to the s/p conduction band. In these elements the d band is full and lies some way below the Fermi level (Figure 8.9). The reflectivity peaks in the yellow part of the spectrum and blue and green light are less strongly absorbed; hence the metals appear golden. Very thin films of gold appear green because the yellow and red light is absorbed and only the blue and green transmitted. Insulators typically have band gaps in the ultraviolet and, unless there is a localized transition in the visible, appear colourless. The devices which we consider involving band gap transitions are, however, concerned with emission of light rather than absorption or reflection, the electrons being initially excited by electrical energy.

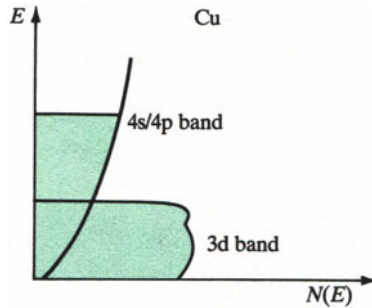


Figure 8.9 Band structure of copper.

8.3.1 Light-emitting diodes

Light-emitting diodes (LEDs) are effectively the reverse of photovoltaic cells (Chapter 4). In photovoltaic cells light is used to produce an electrical voltage; in LEDs a voltage is applied across a p - n junction to produce light. Figure 8.10 shows a p - n junction in a semiconductor such as GaAs.

The band structure shown is for the junction in the dark and with no electric field applied. Now suppose that an electrical field is applied so that the n -type is made negative relative to the p -type. Electrons will then flow from the n -type to the p -type. An electron in the conduction band moving to the p -type side can drop down into one of the vacancies in the valence band on the p -type side, emitting a photon in the process. This is more likely to happen if the transition is allowed, so that semiconductors with direct band gaps are usually used in such devices. To use the LED as

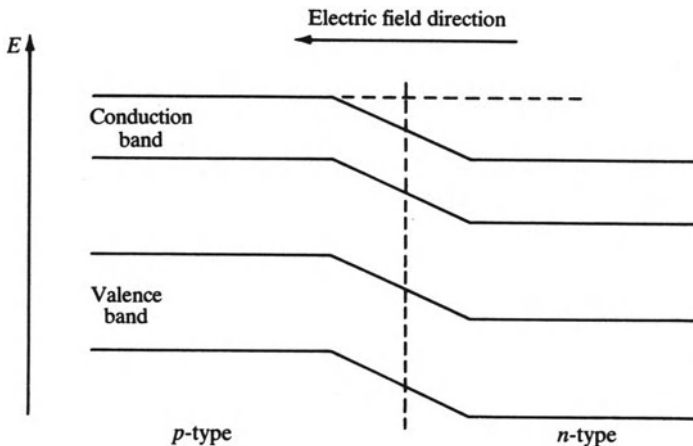


Figure 8.10 Energy bands near the junction in a p - n junction.

a display, for example, it is then wired so that an electric field is applied across the parts making up the required letters or numbers. Different colours can be produced by using semiconductors of differing band gap. GaP produces red light, but by mixing in various proportions of aluminium to form $\text{Ga}_{1-x}\text{Al}_x\text{P}$, green or orange light can be produced. Gallium nitride gives a blue light.

It should be noted that semiconductors with indirect band gaps are used for LEDs, but in these cases impurity levels play an important role. Thus GaP is used although it has an indirect band gap. Silicon, however, is not suitable because there is a non-radiative transition available to electrons at the bottom of the conduction band and these electrons donate thermal energy to the crystal lattice rather than emitting light when they return to the valence band.

When the electric field causes conduction electrons to move across the p - n junction, the resulting situation is one in which the population in the conduction band is greater than the thermal equilibrium population. An excess of electrons in an excited state is an essential feature of lasers and there are several semiconductor lasers based on the p - n junction. The best known of these is the GaAs laser.

8.3.2 The gallium arsenide laser

The GaAs laser actually contains a layer of GaAs sandwiched between layers of p - and n -type gallium aluminium arsenide ($\text{Ga}_{1-x}\text{Al}_x\text{As}$). The band gap of gallium aluminium arsenide is larger than that of GaAs (Figure 8.11).

An electric field applied across the p - n junction as in LEDs produces an excess of electrons in the conduction band of the GaAs. These electrons do not drift across into the gallium aluminium arsenide layer, however, because the bottom of the conduction band in this layer is higher in energy and the electrons would thus need to gain energy in order to move across. The excess conduction band electrons are therefore constrained to remain within the GaAs layer. Eventually one of these electrons drops down into the valence band, emitting a photon as it does so. This photon induces other conduction band electrons to return to the valence band and thus a coherent beam of light begins to build up. As in the ruby laser the initial burst of photons is reflected back by mirrors placed at the ends and induces more emission. Eventually a beam of infrared radiation is emitted. Several such lasers have been developed, most of them based on III-V compounds (that is compounds of In, Ga and/or Al with As, P or Sb). It is possible to manufacture materials with band gaps over the range 400–1300 nm by carefully controlling the ratios of the different elements.

Infrared semiconductor lasers are used, amongst many other things, for

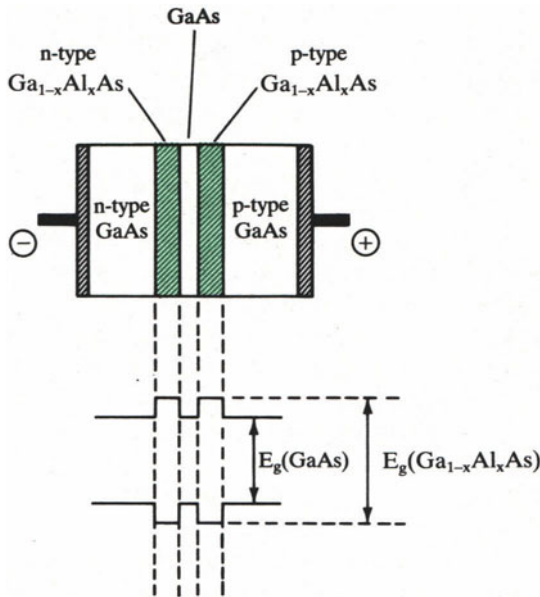


Figure 8.11 The arrangement of the different semiconductor regions in a GaAs laser. The band gap profile is shown below.

reading compact discs. A compact disc consists of a plastic disc coated with a highly reflective aluminium film and protected against mechanical damage by a layer of polymer. The original sound recording is split up into a number of frequency channels and the frequency of each channel given as a binary code (that is a series of 0s and 1s). This is converted to a series of pits in tracks on the disc, spaced approximately $1.6\mu\text{m}$ apart. A laser is focused on the disc and reflected onto a photodetector. The pits cause some of the light to be scattered thus reducing the intensity of the reflected beam. The signal read by the photodetector is read as 1 when there is a high intensity of light and as 0 when the intensity is reduced by scattering. The binary code is thus recovered and can be converted back to sound or pictures.

Lasers such as that shown in Figure 8.11 have their frequency determined by the band gap of the semiconductor used. A more recent development uses the thickness of very thin semiconductor layers to determine the wavelength of the laser.

8.3.3 The quantum cascade laser

If a very thin (less than about 40nm) layer of semiconductor is formed between two layers of a semiconductor with a larger band gap, the

One use of infrared solid state lasers such as the gallium arsenide and the quantum cascade laser is to transmit information via optical fibres. These are the subject of the next section.

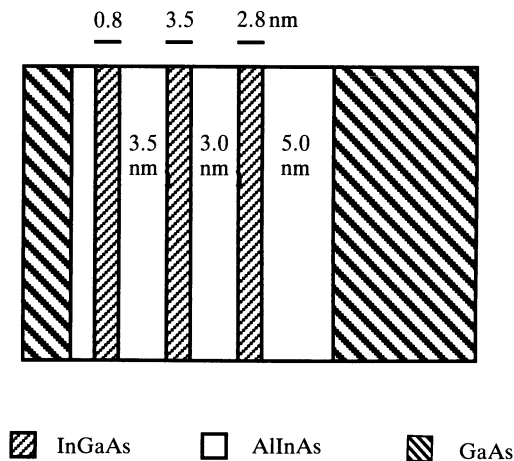


Figure 8.12 An active region of the quantum cascade laser.

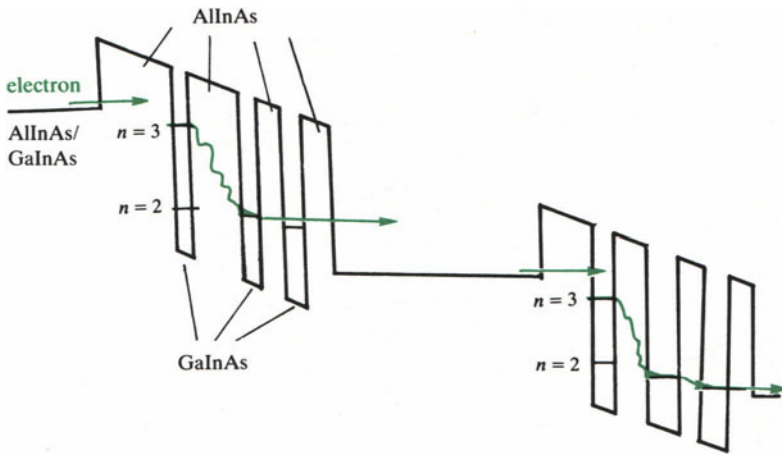


Figure 8.13 An energy level diagram for the conduction band of the region shown in Figure 8.12.

8.4 OPTICAL FIBRES

Optical fibres are used to transmit light in the way that metal wires are used to transmit electricity. For example, a telephone call can be sent along an optical fibre in the form of a series of light pulses from a laser. The intensity, time between pulses and length of pulse can be modified to convey the contents of the call in coded form. In order to transmit the information over useful distances (of the order of kilometres) the intensity of the light must be maintained so that there is still a detectable signal at the other end of the fibre. Thus much of the art of making commercial optical fibres lies in finding ways of reducing energy loss.

The first requirement is that the laser beam keeps within the fibre. Laser beams diverge less than conventional light beams so that using laser light is a help, but even so there is some tendency for the beam to stray outside the fibre. Therefore, fibres are usually constructed with a variable refractive index across the fibre. The beam is sent down a central core. The surrounding region has a lower refractive index than the core so that light deviating from a straight path is totally internally reflected and hence remains in the core (Figure 8.14).

In the simple case shown in Figure 8.14, the totally internally reflected rays travel a longer path than those that travel straight along the core. This will lead to a pulse being spread out in time. One way to keep the pulses together is to use very narrow cores so that essentially all the light travels the straight ray path. An alternative is the variable refractive index core. The refractive index is a measure of how fast light travels in a

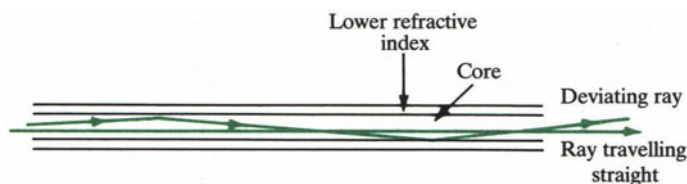


Figure 8.14 Rays of light travelling along an optical fibre.

medium; the lower the refractive index, the faster the speed of light. If the outer parts of the core, therefore, have a lower refractive index, the reflected light moves faster and this compensates for the longer pathlength.

There are bound to be some imperfections in the fibre and these are another source of energy loss. The imperfections cause scattering of the light of a type known as **Rayleigh scattering**. Rayleigh scattering does not cause any change in the wavelength of the light, only in its direction. The amount of scattering depends on $(1/\lambda^4)$, where λ is the wavelength, and so there is much less scattering for longer wavelengths. Even the reduction in going from blue to red light is significant and is responsible for the colour of the sky. To reduce Rayleigh scattering, the lasers employed for optical fibre systems usually emit infrared radiation.

A third source of energy loss is absorption of light by the fibre. In a fibre several kilometres long, a very small amount of impurity can give rise to substantial absorption. On looking at a sheet of window glass edge-on, instead of being clear, the glass appears green. This is due to absorption by Fe^{2+} ions in the glass. A window pane is only about 50 cm across, so in a fibre of a few kilometres in length there would be considerable loss due to such absorption. In a glass the spectrum of the impurity ions is similar to that in a crystal, but because the ions occupy several different types of site in a glass, the absorption bands are wider, each site giving rise to a band at a slightly different wavelength. In an optical fibre 3 km long operating at 1300 nm in the near infrared, the intensity of the Fe^{2+} absorption is still such that a concentration of 2 parts in 10^{10} would reduce the amount of radiation by one-half. Materials for optical fibres must therefore be very pure. One reason why silica has been widely used is because high purity silicon tetrachloride, developed for the semiconductor industry, is commercially available as a starting material.

Metal ions are not the only source of absorption, however. Using infrared radiation means there is likely to be loss due to absorption by molecular vibrations. In silica glass the structure may contain dangling SiO bonds which easily react with water to form OH bonds. The vibrational frequencies of OH bonds are high and close to the frequencies used for transmission. It is important, therefore, to exclude water when

manufacturing silica optical fibres. Even when water is excluded and there are no OH bonds, absorption by vibrational modes cannot be neglected. SiO bonds vibrate at lower frequencies than OH bonds, and so the maximum in the absorption does not interfere. However, the SiO absorption is very strong and the peak tails into the region of the transmission frequency. There has been some research into substances with lower vibrational frequencies than silica, particularly fluorides, but as yet such substances are not economically viable, being difficult to manufacture and more expensive than silica.

There are still losses in the fibres developed for commercial use; nonetheless these have been reduced to a point where transmission over several kilometres is possible. As well as transmission of information in telephone systems and similar applications, it has been suggested that optical devices may replace conventional electronics in more advanced applications such as computers. For such applications, optical switches, amplifiers and so on are needed. We conclude this chapter by looking at one such device.

8.4.1 Optical switches

The refractive index of a crystal is not always a fixed quantity, but can be made to vary. In some materials, an intense beam of light such as that produced by a laser can itself alter the refractive index. Another way to alter the value is to apply an electrical field, and this is the basis of a commercially available optical switch.

The lithium niobate switch consists of a crystal of lithium niobate (LiNbO_3) with two optical channels formed in it by diffusing in titanium (Figure 8.15). The titanium alters the refractive index and the radiation is contained within the channels in the same way as radiation is confined in optical fibres. That is, slightly deviating rays are totally internally reflected due to the different refractive index outside the channels. Applying an electric field alters the refractive index between the channels so that the radiation is no longer reflected and can switch from one channel to the other. To see why the refractive index is altered by composition and by applying an electric field, the atomic origin of the refractive index is considered briefly.

Electromagnetic radiation has associated with it an oscillating electric field. Even when the radiation is not absorbed, this field has an effect on the electrons in the solid. Think of an electrical field applied to an atom, and imagine the electrons pulled by the field so that the atom is no longer spherical. The applied field produces a separation of the centres of positive and negative charge, i.e. it induces an electric dipole moment. (A molecule in a solid may also have a permanent electric dipole moment

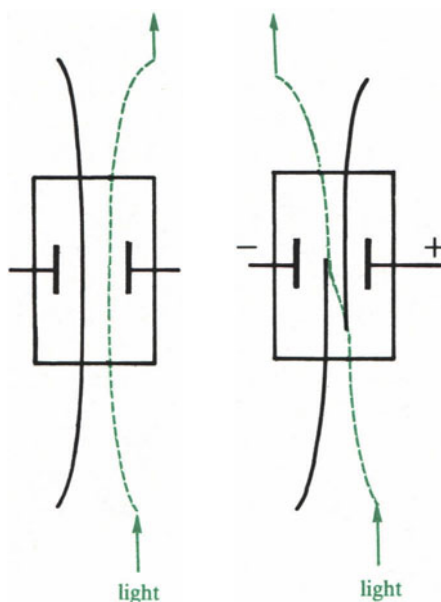


Figure 8.15 An electro-optical switch.

produced by an unequal distribution of bonding electrons between the nuclei but this is present in the absence of an applied field.)

The oscillating field of the radiation can be thought of as pulling the electrons alternately one way and then the other. The amount the electrons respond depends on how tightly bound the electrons are to the nucleus. This property is called the **polarizability** and is higher for large ions with low charge, e.g. Cs^+ , than for small, highly charged ions such as Al^{3+} . If there is a high concentration of polarizable ions in a solid, the radiation will be slowed down, i.e. its refractive index will increase. Lithium niobate contains Li^+ and (formally) ' Nb^{5+} ', which will have low polarizabilities; adding titanium (which formally goes into the solid as ' Ti^{4+} ') increases the refractive index because the titanium ions have a slightly higher polarizability. Applying an electric field across lithium niobate, which is ferroelectric (Chapter 9), moves the ion slightly and causes the refractive index to increase.

Adjusting the refractive index by adding carefully selected impurities is also useful in other applications. For example, controlling the refractive index of glass is very important when making lenses for telescopes, binoculars and cameras. Lead ions, Pb^{2+} , are highly polarizable and are used to produce glass of high refractive index, such as decorative crystal.

We have used the lithium niobate switch as an example of a currently available optical device for use in information storage and transmission.

Others are or will no doubt soon be available. Examples include CD ROMs, and an optical switch in which the intensity of the light itself is used to transfer radiation between paths. Many current devices, however, depend on electronic properties or on magnetic properties. Electronic properties were discussed in Chapter 4. Chapter 9 considers the nature and applications of magnetic properties. Closely related to the optical properties in this last section are dielectric properties which are also discussed in Chapter 9.

FURTHER READING

West, A.R. (1988) *Basic Solid State Chemistry*, Chapter 8, John Wiley, New York.

See comments following Chapter 4. The last part of chapter 8 deals with applications of luminescence and lasers.

Duffy, J.A. (1990) *Bonding, Energy Levels and Bands in Inorganic Solids*, Chapters 2, 3, 5 and 8, Longman, London.

See comments after Chapter 4. This book is of most use for optical properties, although much of it is written at a level more suitable for 3rd year undergraduates and postgraduates.

Moore, W.J. (1967) *Seven Solid States*, Chapter VI, W.A. Benjamin Inc.

See comments after Chapter 4. The description of the energy levels and the fundamental laser process are useful.

Nassau, K. (1983) *The Physics and Chemistry of Color*, Chapters 5, 8 and 14, New York.

See comments after Chapter 5.

The following three articles are very readable and at a suitable level.

Hill, C.G.A. (1983) Inorganic luminescent materials, *Chemistry in Britain*, September, 723.

Goodman, C.H.L. (1983) Optical fibres, *Chemistry in Britain*, September, 745.

Deluca, J.A. (1980) An introduction to luminescence in inorganic solids, *Journal of Chemical Education*, 57, 541.

QUESTIONS

1. In the oxide MnO , Mn^{2+} ions occupy octahedral holes in an oxide lattice. The degeneracy of the $3d$ levels of manganese are split into two, as for Ti^{3+} . The five d electrons of the Mn^{2+} ions occupy separate d orbitals and have parallel spins. Explain why the absorption lines due to transitions between the two $3d$ levels are very weak for Mn^{2+} .
2. Figure 8.16 shows the energy levels of Nd^{3+} in yttrium aluminium garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$) which are involved in the laser action of this crystal (known as the Nd YAG laser). Describe the processes that occur when the laser is working.

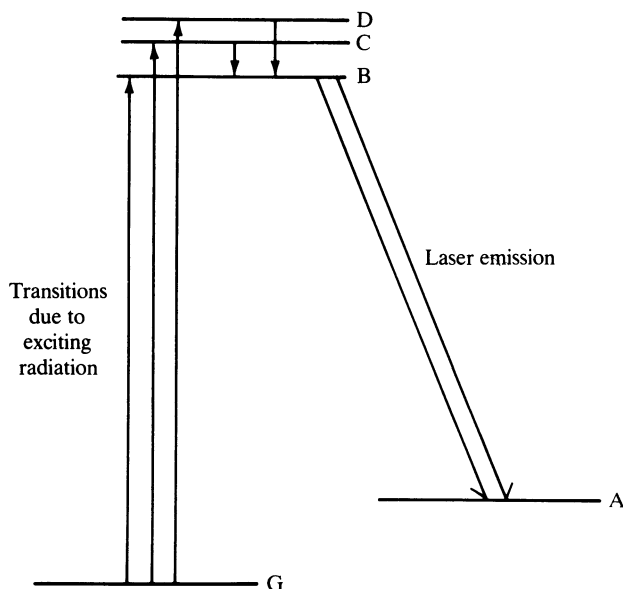


Figure 8.16 Energy levels of Nd^{3+} in yttrium aluminium garnet.

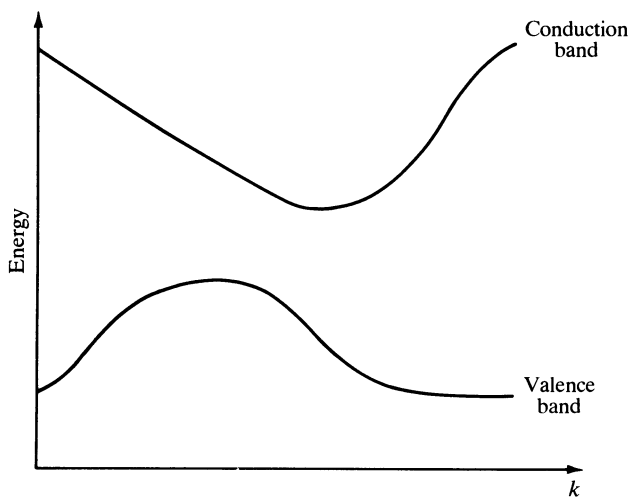


Figure 8.17 A plot of energy against k for two bands of a solid.

3. A phosphor commonly used on television screens is ZnS doped with Cu^+ . This is more efficient at transferring energy to the impurity sites for emission than are the phosphors based on phosphates as host. ZnS is a semiconductor. Suggest a reason for the efficiency of transfer in this solid.

4. In Chapter 5 the photographic process was described. Outline the processes leading to the formation of a silver atom when red light is absorbed by a grain of AgBr in an emulsion containing a sensitizer. AgBr has an indirect band gap. Explain why this is useful. Compare the processes you describe with those in phosphors.
5. Figure 8.17 shows two bands for a semiconductor. Is the band gap of this solid direct or indirect?
6. Explain why silicon is used for solar cells but not for LEDs.
7. The core of silica optical fibres contains some B_2O_3 , GeO_2 and P_2O_5 . How do these impurities increase the refractive index?

Magnetic and dielectric properties

9.1 INTRODUCTION

One consequence of the closeness of atoms in a solid is that properties of the individual atoms or molecules can interact cooperatively to produce effects not found in fluids. A well-known example of this is ferromagnetism. In a piece of iron used as a magnet, for example, the magnetism of the iron atoms aligns to produce a strong magnetic effect. Other cooperative magnetic effects lead to a cancelling (antiferromagnetism) or partial cancelling (ferrimagnetism) of the magnetism of different atoms. Ferro- and ferri- magnets have many commercial applications from compass needles and watch magnets to audio- and videotapes and computer memory devices.

Cooperative effects are not confined to magnetism; similar effects can occur for a crystal's response to mechanical stress and to electric fields. The electrical analogue of ferromagnetism is the ferroelectric effect, in which the material develops an overall electrical polarization, that is a separation of charge. Ferroelectric materials are important in the electronics industry as capacitors (for storing charge) and transducers (for converting, for example, ultrasound to electrical energy). Ferroelectric crystals are a sub-class of piezoelectric crystals and piezoelectric crystals have commercial uses of their own. For example, quartz watches use piezoelectric quartz crystals as oscillators.

We are going to look at the types of material that display cooperative magnetic and dielectric properties. To start with, though, we consider the weaker magnetic effects that can be found in all types of matter. Then we shall discuss the origin of the cooperative magnetic effects and their applications. Following magnetic effects, we look at dielectric effects, starting with the piezoelectric effect and its applications and then considering ferroelectric materials and in particular the oxide barium titanate, BaTiO_3 , which is widely used as a capacitor.

9.2 MAGNETIC SUSCEPTIBILITY

A magnetic field produces lines of force which penetrate the medium to which the field is applied. These lines of force show up, for example, when you scatter iron filings on a piece of paper covering a bar magnet. The density of these lines of force is known as the **magnetic flux density**, B . In a vacuum the magnetic field, H , and the magnetic flux density are related by the permeability of free space, μ_0 .

$$B = \mu_0 H. \quad (9.1)$$

If a magnetic material is placed in the field, however, it can increase or decrease the flux density. Diamagnetic materials reduce the density of the lines of force as shown in Figure 9.1. Paramagnetic materials increase the flux density.

The field of the sample in the applied field is known as its **magnetization** (M). The magnetic flux density is given by equation (9.2).

$$B = \mu_0(H + M). \quad (9.2)$$

The magnetization is usually discussed in terms of the **magnetic susceptibility**, χ , where $\chi = M/H$.

Diamagnetism is present in all substances but is very weak so that it is not normally observed if other effects are present. It is produced by circulation of electrons in an atom or molecule. Atoms or molecules with closed shells of electrons are diamagnetic. Unpaired electrons, however, give rise to paramagnetism. Simple paramagnetic behaviour is found for substances such as liquid oxygen or transition metal complexes in which

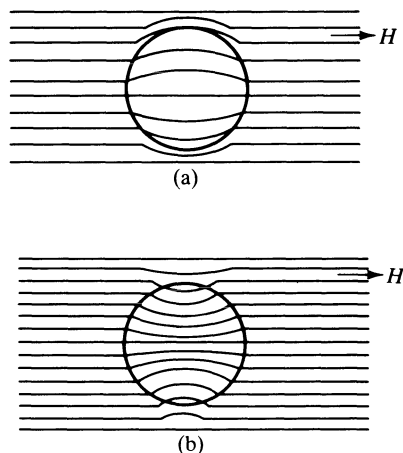


Figure 9.1 Flux density in (a) a diamagnetic and (b) a paramagnetic sample.

the unpaired electrons on different centres are isolated from each other. In a magnetic field the magnetic moments on different centres tend to align with the field and hence with each other, but this is opposed by the randomizing effect of thermal energy, and in the absence of a field the unpaired electrons on different centres are aligned randomly. The interplay of applied field and thermal randomization leads to the temperature dependence described by the **Curie law**:

$$\chi = C/T, \quad (9.3)$$

where χ is the magnetic susceptibility, C is a constant known as the Curie constant and T is the temperature in Kelvin.

Different temperature dependence is observed when there is cooperative behaviour. The changeover from independent to cooperative behaviour is associated with a characteristic temperature. For ferromagnetism the Curie law becomes

$$\chi = C/(T - T_C), \quad (9.4)$$

where T_C is the Curie temperature. For antiferromagnetism the temperature dependence is of the form

$$\chi = C/(T + T_N), \quad (9.5)$$

where T_N is the Néel temperature. These two behaviours are illustrated in Figure 9.2.

Ferrimagnetism has a more complicated form of temperature dependence with ions on different sites having different characteristic temperatures. The characteristics of the various types of magnetism that we shall be concerned with are given in Table 9.1.

9.3 PARAMAGNETISM IN METAL COMPLEXES

In solids containing metal complexes such that the unpaired electrons on the different metal atoms are effectively isolated, the susceptibility can be discussed in terms of magnetic moments. The isolated metal complex can be thought of as a small magnet. Each complex in a solid will produce its own magnetic field due to the unpaired electrons. If the solid consists of one type of complex, each complex produces the same magnitude magnetic field. However, thermal motion causes the orientation of these fields to be random. In the Curie law (9.3), the temperature dependence is the result of this thermal motion but the constant, C , gives us information on the value of the magnetic field, known as the **magnetic moment**, μ , of the complex. The magnetic moment, unlike the susceptibility, does not normally vary with temperature. The dimensionless quantity χ in equation (9.2) is the susceptibility per unit volume. To obtain the size of

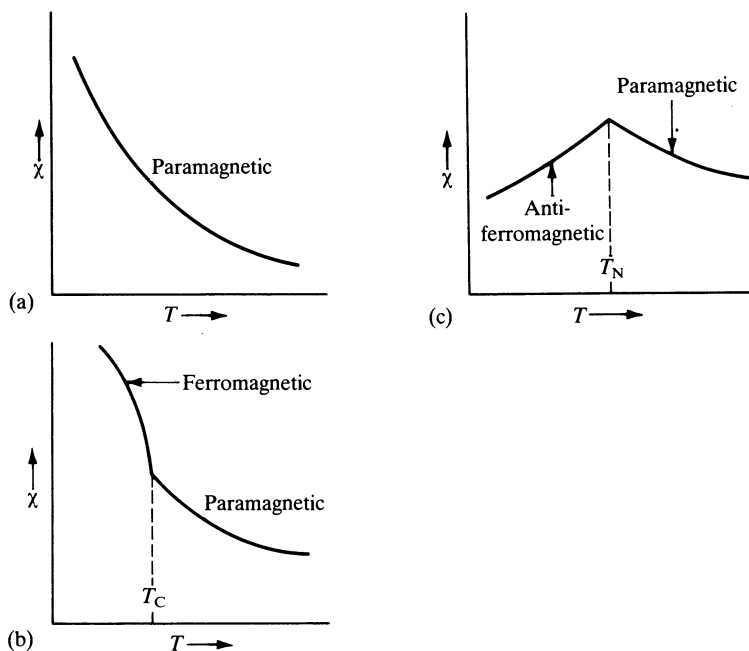


Figure 9.2 Variation of magnetic susceptibility with temperature for (a) a paramagnetic substance, (b) a ferromagnetic substance and (c) an antiferromagnetic substance.

the magnetic field due to an individual complex, χ is divided by the specific gravity to give the susceptibility per unit mass of the sample and then multiplied by the relative molecular mass to obtain the molar susceptibility, χ_m . Assuming that each complex has a fixed magnetic moment, μ , and that the orientation is randomized by thermal motion, it can be shown that χ_m is proportional to μ^2 as in equation (9.6).

$$\chi_m = \frac{N_A \mu_0}{3kT} \mu^2, \quad (9.6)$$

where N_A is Avogadro's number, k is Boltzmann's constant, μ_0 is the permeability of free space and T is the temperature in Kelvin. In SI units, χ_m is in $\text{m}^3 \text{mol}^{-1}$ and the magnetic moment in joules per tesla (J T^{-1}). It is usual to quote μ in Bohr magnetons (BM or μ_B) where one Bohr magneton has a value of $9.274 \times 10^{-24} \text{J T}^{-1}$.

The magnetic moment, μ , is a consequence of the angular momentum of the unpaired electrons. The electrons possess both spin and orbital angular momentum. For the first row transition elements the contribution from the orbital angular momentum is greatly reduced or 'quenched' as a consequence of the lifting of the fivefold degeneracy of the $3d$ orbitals. In

Table 9.1 Characteristics of the types of magnetism

Type	Sign of χ	Typical χ value (calculated using SI units)	Dependence of χ on H	Change of χ with increasing temperature	Origin
Diamagnetism	-	$-(1-600) \times 10^{-5}$	Independent	None	Electron charge Spin and orbital motion of electrons on individual atoms } Cooperative interaction between magnetic moments of individual atoms Spin and orbital motion of delocalized electrons
Paramagnetism	+	0-0.1	Independent	Decreases	
Ferromagnetism	+	$0.1-10^7$	Dependent	Decreases	
Antiferromagnetism	+	0-0.1	May be dependent	Increases	
Pauli paramagnetism	+	10^{-5}	Independent	None	

Table 9.2 Values of S and μ_s for unpaired $3d$ electrons

<i>No. of unpaired electrons</i>	<i>Spin quantum number (S)</i>	<i>Magnetic moment μ_s in Bohr magnetons</i>
1	$\frac{1}{2}$	1.73
2	1	2.83
3	$\frac{3}{2}$	3.87
4	2	4.90
5	$\frac{5}{2}$	5.92

complexes of these atoms the magnetic moment is often close to that predicted for spin angular momentum only:

$$\mu_s = g\sqrt{S(S+1)} \quad (9.7)$$

where g is a constant which for a free electron has the value 2.00023, and μ_s is in Bohr magnetons. The value of S depends on the number of unpaired electrons and Table 9.2 gives the values of S and μ_s for the possible numbers of unpaired $3d$ electrons. Contributions from orbital angular momentum cause deviations from these values.

For complexes containing heavier metal ions, interaction of spin and orbital angular momenta is greater. For the lanthanides the magnetic moment depends on the total angular momentum of the electrons, $\mathbf{J}$, not just or mainly on the spin angular momentum. The total angular momentum, $\mathbf{J}$, is the vector sum of the orbital, $\mathbf{L}$, and spin, $\mathbf{S}$, angular momenta.

$$\mathbf{J} = \mathbf{L} + \mathbf{S}. \quad (9.8)$$

If $\mathbf{J}$ is the quantum number for the total electronic angular momentum, then the magnetic moment is given by

$$\mu = g\sqrt{J(J+1)} \quad (9.9)$$

where

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

This can give rise to large magnetic moments, especially for shells that are more than half full. For example, Tb^{3+} with an f^8 configuration has a magnetic moment from equation (9.9) of 9.72 Bohr magnetons.

9.4 FERROMAGNETIC METALS

When discussing the electrical conductivity of metals, we described them in terms of ionic cores and delocalized valence electrons. The core electrons contribute a diamagnetic term to the magnetic susceptibility, but the valence electrons can give rise to paramagnetism or one of the cooperative effects we have described.

In filling the conduction band, we have implicitly put electrons into energy levels with paired spins. Even in the ground state of simple molecules such as O_2 it can be more favourable to have electrons in different orbitals with parallel spins than in the same orbital with paired spins. This occurs when there are degenerate or nearly degenerate levels. In an energy band there are many degenerate levels and many levels very close in energy to the highest occupied level. It might well be favourable then to reduce electron repulsion by having electrons with parallel spin singly occupying levels near the Fermi level. To obtain a measurable effect the number of parallel spins would have to be comparable with the number of atoms; 10^3 unpaired spins would not be noticed in a sample of 10^{23} atoms. Unless the density of states is very high near the Fermi level, a large number of electrons would have to be promoted to high energy levels in the band in order to achieve a measurable number of unpaired spins. The resulting promotion energy would be too great to be compensated for by the loss in electron repulsion. In the wide bands of the simple metals the density of states is comparatively low so that, in the absence of a magnetic field, few electrons are promoted.

When a magnetic field is applied, the electrons will acquire an extra energy term due to interaction of their spins with the field. If the spin is parallel to the field, its magnetic energy is negative, i.e. the electrons are at lower energy than they were in the absence of a field. For an electron with spin antiparallel to the field, it is now worthwhile to go to a higher energy state and change spin so long as the promotion energy is not more than the gain in magnetic energy. This will produce a measurable imbalance of electron spins aligned with and against the field and hence the solid will exhibit paramagnetism. This type of paramagnetism is known as **Pauli paramagnetism** and is a very weak effect, giving a magnetic susceptibility much less than that due to isolated spins and comparable in magnitude to diamagnetism.

For a very few metals, however, the unpaired electrons in the conduction band can lead to ferromagnetism. In the whole of the periodic table, only iron, cobalt, nickel and a few of the lanthanides (Gd, Tb) possess this property. So, what is so special about these elements that confers this uniqueness on them? It is not their crystal structure; they each have different structures and the structures are similar to those of

other non-ferromagnetic metals. Iron, cobalt and nickel, however, do all have a nearly full, narrow $3d$ band.

The $3d$ orbitals are less diffuse than the $4s$ and $4p$, i.e. they are concentrated nearer the atomic nuclei. This leads to less overlap so that the $3d$ band is a lot narrower than the $4s/4p$ band. Furthermore, there are five $3d$ orbitals so that for a crystal of N atoms, $5N$ levels must be accommodated. With more electrons and a narrower band, the average density of states must be much higher than in ns/np bands. In particular the density of states near the Fermi level is high. In this case it is energetically favourable to have substantial numbers of unpaired electrons at the cost of populating higher energy levels. Thus these elements have large numbers of unpaired electrons, even in the absence of a magnetic field. For iron, for example, in a crystal of N atoms there are up to $2.2N$ unpaired electrons, all with their spins aligned parallel. Note the contrast with a paramagnetic solid containing transition metal complex ions where each ion may have as many as five unpaired electrons but in the absence of a magnetic field, electrons on different ions are aligned randomly.

Ferromagnetism thus arises from the alignment of electron spins throughout the solid, and this occurs for partially filled bands with a high density of states near the Fermi level. $4d$ and $5d$ orbitals are more diffuse than $3d$ and produce wider bands so that ferromagnetism is not observed in the second and third row transition elements. The $3d$ orbitals themselves become less diffuse across the transition series and lower in energy. In titanium the valence electrons are in the $4s/4p$ band with low density of states and, at the other end of the row in copper, the $3d$ band has dropped in energy so that the Fermi level is in the $4s/4p$ band. Thus it is only at the middle of the series that the Fermi level is in a region of high density of states. Schematic band diagrams for Ti, Ni and Cu are given in Figure 9.3. The occupied levels are indicated by shading.

The pure elements are not always suitable for applications requiring a metallic ferromagnet and many ferromagnetic alloys have been produced. Some of these contain one or more ferromagnetic elements and among these alloys of iron, cobalt and nickel with the lanthanides, e.g. SmCo_5 , $\text{Nd}_2\text{Fe}_{14}\text{B}$, have produced some of the most powerful permanent magnets known. In the lanthanide alloys, f electrons contribute to the magnetism. Potentially this could lead to a very high magnetization because there are seven f orbitals and so a maximum possible magnetization corresponding to seven electrons per atom. The theoretical maximum magnetization for the transition metals is five electrons per atom, as there are only five d orbitals. In practice this maximum is never reached. In the pure lanthanide metals the overlap of f orbitals is so small that they can be regarded as localized. In the ferromagnetic lanthanides the magnetism is produced by delocalized d electrons. The interaction between these d electrons and the localized f electrons causes alignment of the d and f electrons in order to

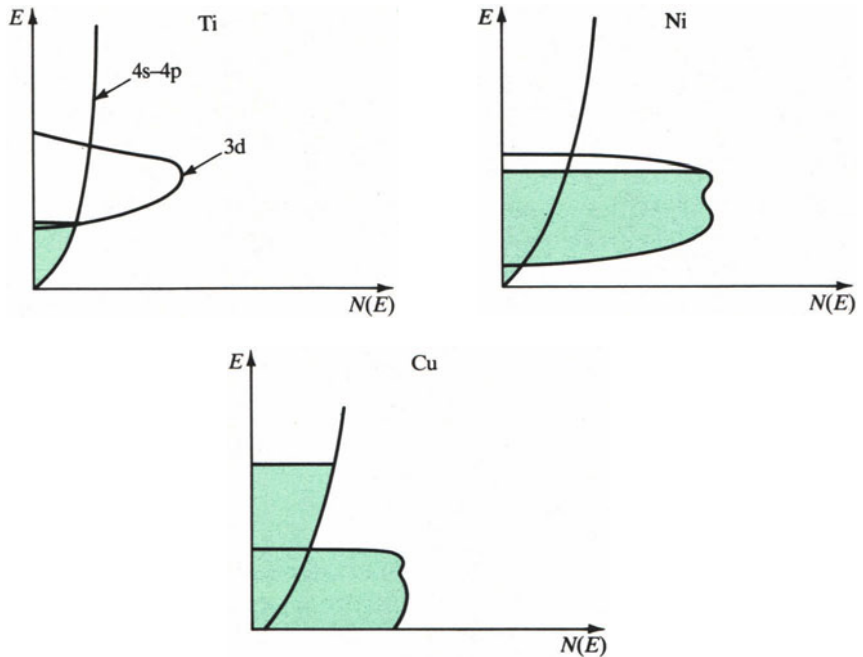


Figure 9.3 Schematic energy level diagrams for Ti, Ni and Cu. The shading represents occupied levels.

reduce electron repulsion. Thus f electrons on different atoms are aligned through the intermediary of the d electrons. In alloys the f electrons can align via the transition metal d electrons, and although not all the d and f electrons are aligned, it can be seen that high values of the magnetization could be achieved. It is not surprising, then, that it is these transition metal/lanthanide alloys that are the most powerful magnets. Other alloys can be made from non-magnetic elements such as manganese and in these the overlap of d orbitals is brought into the range necessary for ferromagnetism by altering the interatomic distance from that in the element.

The usefulness of a particular ferromagnetic substance depends on factors such as the size of the magnetization produced, how easily the solid can be magnetized and demagnetized and how readily it responds to an applied field. The number of unpaired electrons will determine the maximum field, but the other factors depend on the structure of the solid and the impurities it contains.

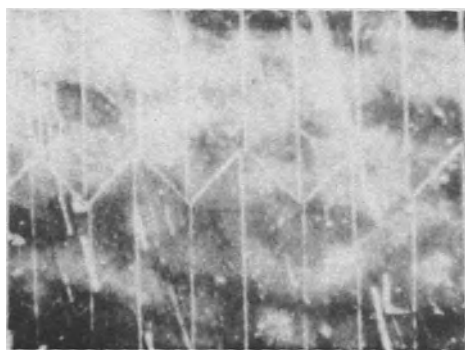
9.4.1 Ferromagnetic domains

A drawback to the explanation above may have occurred to you. If $2.2N$ electrons are all aligned in any sample of iron, why are not all pieces of

iron magnetic? The reason for this is that our picture only holds for small volumes of metal (about 10^{-14} m^3) within a crystal, called **domains**. Within each domain the spins are all aligned, but the different domains are aligned randomly with respect to each other. It is actually possible to see these domains through a microscope by spreading finely divided iron powder on the polished surface of a crystal (Figure 9.4). What then causes these domains to form?

The spins tend to align parallel because of short range **exchange interactions** stemming from electron–electron repulsion, but there is also a longer range **magnetic dipole interaction** tending to align the spins antiparallel. Consider building up a domain starting with just a few spins, initially the exchange interactions dominate and so the spins all lie parallel. As more spins are added, an individual spin will be subjected to a greater and greater magnetic dipole interaction. Eventually the magnetic dipole interaction overcomes the exchange interaction and the adjacent piece of crystal has the spins aligned antiparallel to the original domain. Thus within domains exchange forces keep the spins parallel, whereas the magnetic dipole interaction keeps the spins of different domains aligned in different directions.

When a magnetic field is applied to a ferromagnetic sample, the domains all tend to line up with the field. The alignment can be accomplished in two ways. Firstly a domain of correct alignment can grow at the expense of a neighbouring domain. Between the two domains is an area



(a)



(b)

Figure 9.4 (a) Domain patterns for a single crystal of iron containing 3.8% of silicon. The white lines show the boundaries between the domains. From R. Eisberg and R. Resnick (1985) *Quantum Physics of Atoms, Molecules, Solids, Nuclei and Particles*, © John Wiley (courtesy of H.J. Williams, Bell Telephone Laboratories). (b) Magnetic domain patterns on the surface of an individual crystal of iron. From W.J. Moore (1967) *Seven Solid States*, W.A. Benjamin Inc., © W.J. Moore.

of finite thickness known as the domain wall. Changeover from the alignment of one domain to that of the next is gradual within the wall. When the magnetic field is applied, the spins in the wall nearest the aligned domain alter their spins to line up with the bulk of the domain. This causes the next spins to alter their alignment. The net effect is to move the wall of the domain further out (Figure 9.5). This process is reversible; the spins return to their former state after the magnetic field is removed.

If impurities or defects are present it becomes harder for a domain to grow; there is an activation energy to aligning the spins through the defect and so a larger magnetic field is required. Once the domain has grown past the defect, however, it cannot shrink back once the magnetic field is removed because this will also need an energy input. In this case the solid retains magnetization. The amount retained depends on the number and type of defects. Thus steel (which is iron with a high impurity content) remains magnetic after the field is removed whereas soft iron (which is much purer) retains hardly any magnetization.

The second mechanism of alignment, which only occurs in strong magnetic fields, is that the interaction of the spins with the applied field becomes large enough to overcome the dipole interaction and entire

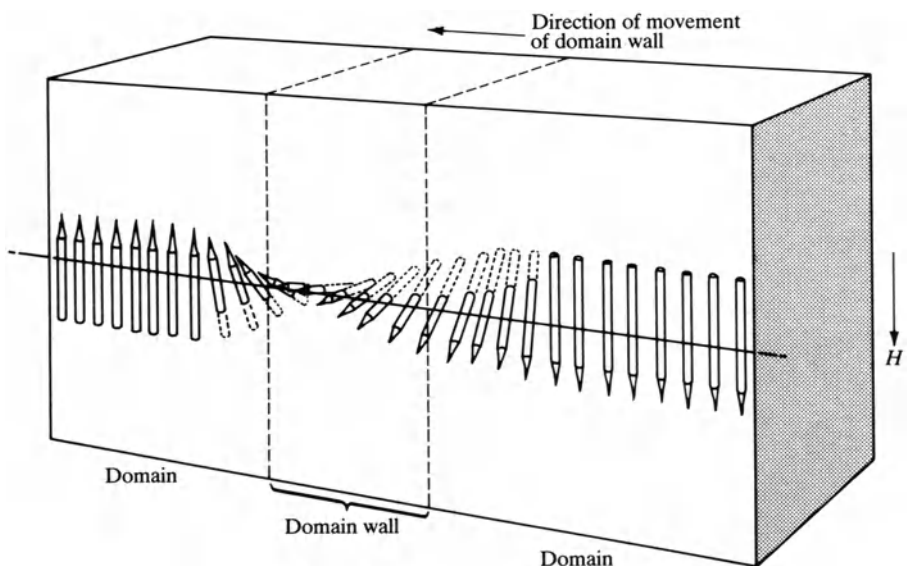


Figure 9.5 Movement of a domain wall. The broken lines show the domain wall, which separates two domains with magnetic moments lined up in opposite directions. The moments twist to align with the applied field, H , and the wall moves in the direction of the arrow.

domains of spins change their alignment simultaneously. The two mechanisms are compared in Figure 9.6.

The magnetic behaviour of different ferromagnetic substances is shown by their **hysteresis curves**. This is a plot of magnetic flux density, B , against applied magnetic field, H . If we start with a non-magnetic sample in which all the domains are randomly aligned, then in the absence of a magnetic field B and H are zero. As the field is increased, the flux density also increases. The plot of B against H is shown in Figure 9.7. Initially the curve is like 'oa', which is not simply a straight line because the magnetization is increasing with the field. At point 'a' the magnetization has reached its maximum value; all the spins in the sample are aligned. When the applied field is reduced the flux density does not follow the initial curve. This is due to the difficulty of reversing processes where domains have grown through crystal imperfections. A sufficiently large field in the reverse direction to provide the activation energy for realignment through the imperfection must be applied before the magnetization process can be reversed. At point 'b', therefore, where H is zero, B is not zero because there is still a contribution from the magnetization, M . The magnetization at this point is known as the **remanent magnetization**. The field that needs to be applied in the reverse direction to reduce the

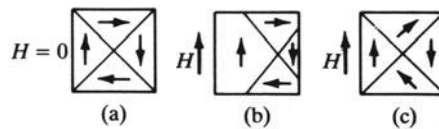


Figure 9.6 Magnetization processes according to the domain model: (a) unmagnetized; (b) magnetized by domain growth (boundary displacement); (c) magnetized by domain rotation (spin alignment).

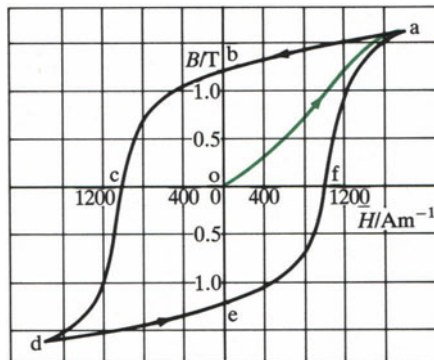


Figure 9.7 B - H curve for a typical hard steel.

magnetization to zero is the **coercive force** and is equal to the distance 'oc'.

9.4.2 Permanent magnets

Substances used as permanent magnets need a large coercive force, so that they are not easily demagnetized, and preferably should have a large remanent magnetization. These substances have fat hysteresis curves. They are often made from alloys of iron, cobalt or nickel which form with small crystals and include non-magnetic areas so that domain growth and shrinkage are difficult. Magnets for electronic watches, for example, are made from samarium/cobalt alloys. The best known of these alloys is SmCo_5 which has a coercive force of $6 \times 10^5 \text{ A m}^{-1}$ compared to 50 A m^{-1} for pure iron.

9.5 FERROMAGNETIC COMPOUNDS – CHROMIUM DIOXIDE

Chromium dioxide (CrO_2) crystallizes with a rutile structure and is ferromagnetic with a Curie temperature of 392 K. Like VO and TiO , CrO_2 has metal $3d$ orbitals which can overlap to form a band. In CrO_2 , however, this band is very narrow and so like iron, cobalt and nickel, CrO_2 displays ferromagnetism. The dioxides later in the row have localized $3d$ electrons (e.g. MnO_2) and are insulators or semiconductors. TiO_2 has no $3d$ electrons and is an insulator. VO_2 has a different structure at room temperature and is a semiconductor. It does, however, undergo a phase transition to a metal at 340 K, when it becomes Pauli paramagnetic. So CrO_2 occupies a unique position amongst the dioxides, similar to that of iron, cobalt and nickel amongst the first row transition metals, in which dioxides of elements to the left have wide bands of delocalized electrons and elements to the right have dioxides with localized $3d$ electrons. Because the metal atoms are further apart in the dioxides than in the elemental metals, the narrow bands that give rise to ferromagnetism occur earlier in the row than for the metallic elements.

9.5.1 Audiotapes

Commercial interest in CrO_2 lies in its use as a magnetic powder on audiotapes. Recording tape usually consists of a polyester tape impregnated with needle-like crystals of a magnetic material such as CrO_2 or $\gamma\text{-Fe}_2\text{O}_3$. The recording head has an iron core with a coil wrapped round it and a gap where the tape passes across it. Sound waves from the voice or music to be recorded hit a diaphragm in the microphone. The vibrations of the diaphragm cause a linked coil of wire to move in and out of a

magnetic field. This causes a fluctuating electric current in the coil; the current depends on the frequency of the motion of the coil and hence on the frequency of the sound waves. The varying current is passed to the coil on the recording head, producing a varying magnetic field in the (soft) iron core. This in turn magnetizes the particles on the tape and the strength and direction of this magnetization is a record of the original sound. To play the tape, the whole process is reversed.

Materials for recording tape therefore need to retain their magnetization so that the recording is not accidentally erased. Having needle-like crystals aligned with the recording field helps here, but the material should also have a high coercive force. Chromium dioxide fulfils these requirements and has a high magnetization giving a large range of response and thus a high quality of reproduction. It does have some drawbacks, however; it has a relatively low Curie temperature, so that recordings can be erased by heating, and it is toxic.

9.6 ANTIFERROMAGNETISM – TRANSITION METAL MONOXIDES

These oxides have been discussed in Chapter 4. They are all based on the sodium chloride structure but have varying electrical properties. In this section we shall see that their magnetic properties are equally varied. In TiO and VO the $3d$ orbitals are diffuse and form delocalized bands. These oxides are metallic conductors. The delocalized nature of the $3d$ electrons also determines the magnetic nature of these salts and, like the simple metals, they are Pauli paramagnetic. MnO, FeO, CoO and NiO have localized $3d$ electrons and are paramagnetic at high temperatures. On cooling, however, the oxides become antiferromagnetic. The Néel temperatures for this transition are 122, 198, 293 and 523 K, respectively.

In **antiferromagnetism** the spins on different nuclei interact cooperatively but in such a way as to cancel out the magnetic moments. Antiferromagnetic materials therefore show a drop in magnetic susceptibility at the onset of cooperative behaviour. The temperature which characterizes this process is known as the **Néel temperature** (Figure 9.2c).

The appearance of cooperative behaviour suggests that d electrons on different ions interact but the electronic properties are explained by assuming that the d electrons are localized. So how do we reconcile these two sets of properties?

The magnetic interaction in these compounds is thought to arise indirectly through the oxide ions; a mechanism known as **superexchange**. In a crystal of, say, NiO there is a linear Ni–O–Ni arrangement. The d_{z^2} orbital on the nickel can overlap with the $2p_z$ on oxygen, leading to partial covalency. The incipient NiO bond will have the d_{z^2} electron and a

$2p_z$ electron paired. The oxide ion has a closed shell and so there is another $2p_z$ electron which must have opposite spin. This electron forms a partial bond with the next nickel and so the d_{z^2} on this nickel pairs with the $2p$ electron of opposite spin. The net result is that adjacent nickel ions have opposed spins (Figure 9.8).

The alternating spin magnetic moments in antiferromagnets such as NiO can be observed experimentally using neutron diffraction. Because neutrons have a magnetic moment, a neutron beam used for diffraction responds not only to the nuclear positions but also to the magnetic moments of the atoms. X-rays, on the other hand, have no magnetic moment and respond to electron density and hence to atomic positions (see Chapter 2). The structure of NiO as found by X-ray diffraction is a simple NaCl structure. When the structure is determined by neutron diffraction, however, extra peaks appear which can be interpreted as giving a magnetic unit cell twice the size of the X-ray-determined unit cell. The positions of the nickel ions in this cell are shown in Figure 9.9.

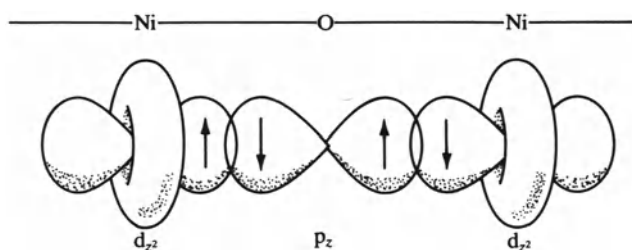


Figure 9.8 Overlap between Ni d_{z^2} orbitals and O p_z orbitals in NiO.

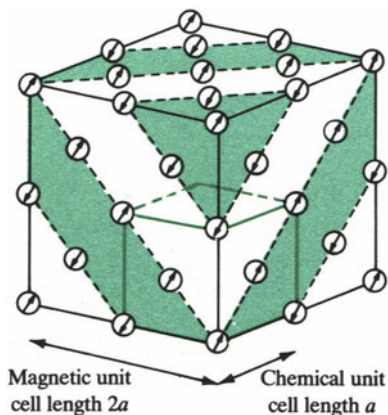


Figure 9.9 Magnetic unit cell of NiO, with the crystallographic or chemical unit cell indicated in colour.

The normal crystallographic unit cell is bounded by identical atoms. The magnetic unit cell is bounded by identical atoms with identical spin alignment. The shading indicates layers of nickel ions parallel to the body diagonal of the cube. The spins of all nickel ions in a given layer are aligned parallel but antiparallel to the next layer.

9.7 FERRIMAGNETISM – FERRITES

The name ferrite was originally given to a class of mixed oxides having an **inverse spinel structure** and the formula AFe_2O_4 , where A is a divalent metal ion. The term is sometimes extended to include other oxides, not necessarily containing iron, which have similar magnetic properties. In this section we shall concentrate on the original group.

The spinel structure is a common mixed oxide structure, typified by spinel itself, $MgAl_2O_4$, in which the oxide ions are in a face-centred cubic close-packed array. For an array of N oxide ions there are N octahedral holes (Al^{3+}) and the trivalent ions occupy half of the octahedral sites (Figure 9.10). In addition, there are $2N$ tetrahedral sites and the divalent ions (Mg^{2+}) occupy one-eighth of these. In the inverse spinel structure the oxide ions are also in a cubic close-packed arrangement, but the divalent metal ions occupy octahedral sites and the trivalent ions are equally divided amongst tetrahedral and octahedral sites.

Ions on octahedral sites interact directly with each other and their spins align parallel. The ions on octahedral sites also interact with those on tetrahedral sites but in this case they interact through the oxide ions and the spins align antiparallel as in NiO .

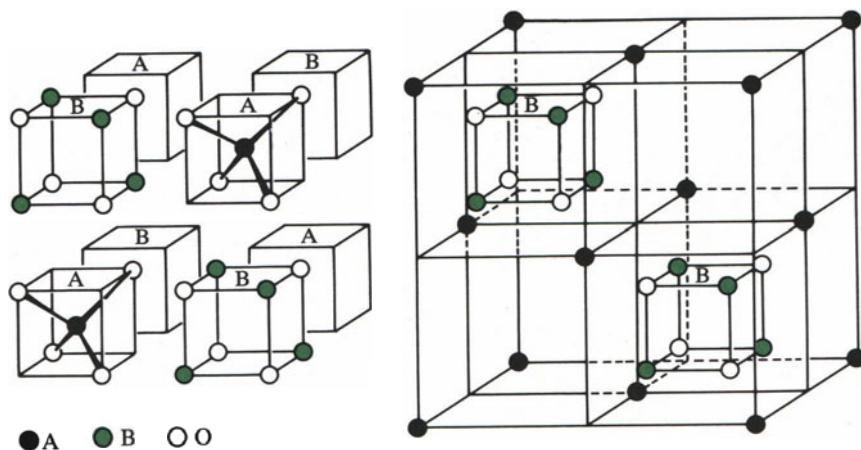


Figure 9.10 The spinel structure, AB_2O_4 .

In ferrites the Fe^{3+} ions on octahedral sites are aligned antiparallel to those on tetrahedral sites, so that there is no net magnetization from these ions. The divalent A ions, however, if they have unpaired electrons, tend to align their spins parallel with those of Fe^{3+} on adjacent octahedral sites, and hence with those of other A^{2+} ions. This produces a net ferromagnetic interaction for ferrites in which A^{2+} has unpaired electrons. The magnetic structure of a ferrimagnetic ferrite is shown in Figure 9.11.

In magnetite, Fe_3O_4 , the divalent ions are iron and the interaction between ions on adjacent octahedral sites is particularly strong. One way of looking at the electronic structure of this oxide is to consider it as an array of O^{2-} ions and Fe^{3+} ions with the electrons that would have made half the Fe ions divalent delocalized over all the ions on octahedral sites. Fe^{3+} ions have five 3d electrons, all with parallel spins. Since there can only be five 3d electrons of one spin on any atom, the delocalized spin must have the opposite spin. Being delocalized, it must also have the opposite spin to the 3d electrons on the next Fe ion. Hence the two ions must have their spins aligned, and these spins must be aligned with those of all other Fe ions on octahedral sites. Delocalization will be less for other ferrites.

Magnetite is the ancient lodestone used as an early compass. More recently ferrites have found use as memory devices in computers, as magnetic particles on recording tapes and as transformer cores. A simple sketch of the main parts of a transformer is shown in Figure 9.12. The importance of ferrites in transformer cores stems from their combination of low electrical conductivity, low coercive force and high magnetization.

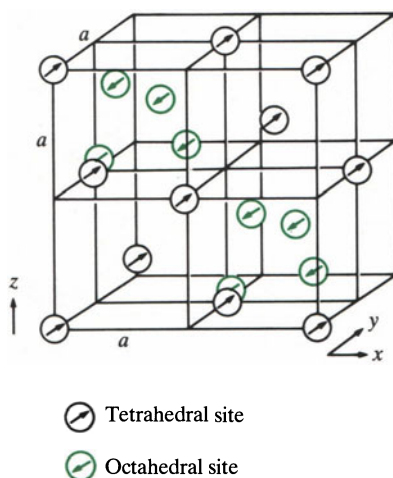


Figure 9.11 Magnetic structure of ferrimagnetic inverse spinel.

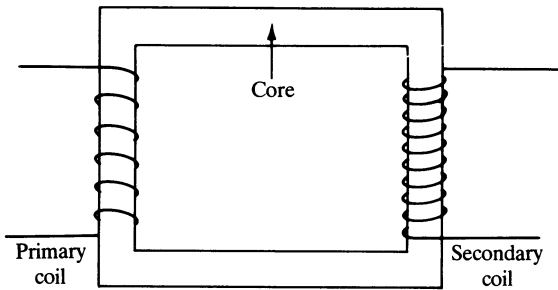


Figure 9.12 Sketch of the basic parts of a transformer.

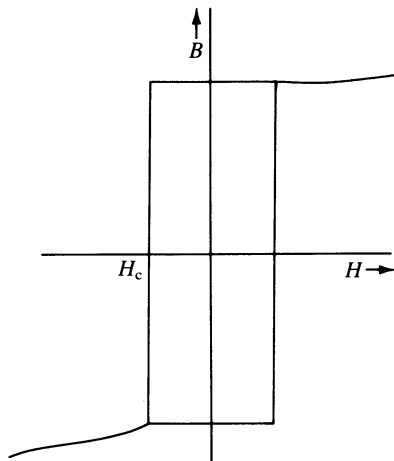


Figure 9.13 Idealized hysteresis curve of ferrite used for information storage.

The low electrical conductivity, which is further reduced by laminating the core, reduces energy losses due to eddy currents. The high maximum magnetization ensures that the cores are not easily saturated and the low coercive force provides good linkage between the primary and secondary circuits.

9.7.1 Computer memory devices

In early computers ferrites were employed as memory devices. For this purpose they needed to switch cleanly between two different states which are read as 0 and 1 and to stay in one state until switched to the other. An almost square hysteresis curve (Figure 9.13) possessed by some ferrites, fulfils these requirements.

More recently, magnetic bubble devices have been used. These consist of very thin films of magnetic material which are manufactured to be magnetically anisotropic, i.e. their magnetization is not the same in different directions. In the absence of an applied field, magnetic domains magnetized up and down with respect to an axis at right-angles to the film are formed (Figure 9.14). When a magnetic field in, say, the down direction is applied, the up domains will shrink and the down domains grow. As the applied field is increased the up domains shrink further until they are only a few micrometres in diameter and become cylindrical.

These cylindrical domains are known as **magnetic bubbles** because their behaviour is described by equations similar to those used to describe soap bubbles. The films used are only thick enough to contain one bubble at any point. The bubbles move through the film towards regions of lower applied field and this effect is used to transmit information. A magnetic bubble is read as 1 and the absence of one as 0, giving a binary code as in other similar devices. Magnetic bubble devices can carry more information per unit area than older devices, but are being challenged by the optical

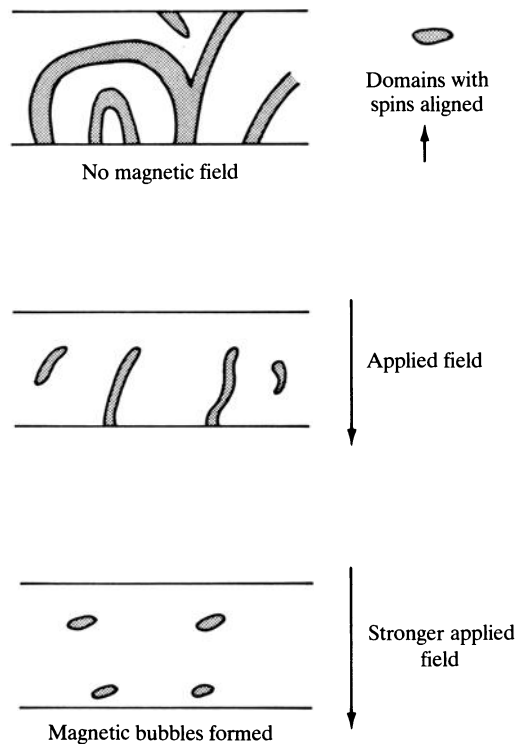


Figure 9.14 Domains in thin films giving rise to magnetic bubbles.

storage devices as described in Chapter 8. The materials usually used are based on the garnet structure, a complex oxide structure with iron ions in octahedral and tetrahedral sites and lanthanide ions in (eight-coordinate) dodecahedral sites. Such an eight-coordinate site can be thought of as a distorted cube (Figure 9.15). The iron ions on the two types of site have their spins aligned antiparallel, and the lanthanide ions are aligned parallel to the iron ions on octahedral sites (Figure 9.16).

The anisotropy of the magnetism and the size of the bubbles is controlled by careful substitution of different ions, for example a garnet of composition $\text{Sm}_{0.4}\text{Y}_{2.6}\text{Ga}_{1.2}\text{Fe}_{3.8}\text{O}_{12}$ was used to develop $8\mu\text{m}$ diameter bubble devices.

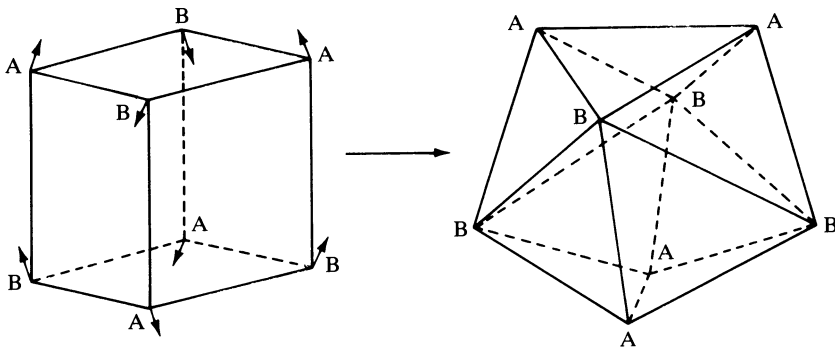


Figure 9.15 An eight-coordinate dodecahedral site.

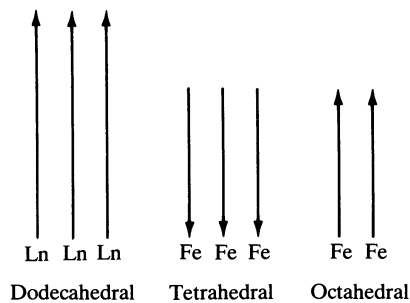


Figure 9.16 Alignment of spins in lanthanide iron garnet.

9.8 ELECTRICAL POLARIZATION

Although solids consist of charged particles (nuclei and electrons) a solid has no overall charge. For most solids there is also no net separation of

positive and negative charges; that is there is no net dipole moment. Even if a solid is composed of molecules with permanent dipole moments, for example ice, the molecules are generally arranged in such a way that the unit cell of the crystal has no net dipole moment and so the solid has none. If such a solid is placed in an electric field then a field is induced in the solid which opposes the applied field. This field arises from two sources: a distortion of the electron cloud of the atoms or molecules and slight movements of the atoms themselves. The average dipole moment per unit volume induced in the solid is the electrical polarization, P , and is proportional to the field, E :

$$P = \epsilon_0 \chi_e E, \quad (9.10)$$

where ϵ_0 is the permittivity of free space ($= 8.85 \times 10^{-12} \text{ F m}^{-1}$) and χ_e is the (dimensionless) dielectric susceptibility. For most solids the electric susceptibility lies between 0 and 10. The susceptibility is often determined experimentally by determining the capacitance of an electric circuit with and without the solid present. The ratio of these two capacitances is the relative permittivity or dielectric constant of the solid, ϵ_r :

$$C/C_0 = \epsilon_r, \quad (9.11)$$

where C is the capacitance in farads in the presence of the solid and C_0 is that in the absence of the solid. The dielectric constant, ϵ_r , is related to the susceptibility by

$$\epsilon_r = 1 + \chi_e. \quad (9.12)$$

If the experiment is performed using a high frequency alternating electric field, the atoms cannot follow the changes in the field and only the effect due to electron displacement is measured. Electromagnetic radiation in the visible and ultraviolet regions provides such a field and the refractive index of a material is a measure of the electron contribution to the dielectric constant. Substances with high dielectric constants also tend to have high refractive indices, so that you will find that similar types of material will be considered in the following sections as were discussed at the end of Chapter 8 in connection with optical devices.

Although most solids do not have a dipole moment in the absence of an electric field, the classes of solids that do are commercially important and so form the subject matter of the rest of this chapter.

9.9 PIEZOELECTRIC CRYSTALS – α -QUARTZ

A piezoelectric crystal is one that develops an electrical voltage when subject to mechanical stress for example if pressure is applied to it, and conversely develops strain when an electric field is applied across it. Application of an electric field causes a slight movement of atoms in the

crystal so that a dipole moment develops in the crystal. In order for it to be piezoelectric, a crystal must be made up from units that are non-centrosymmetric, that is they do not possess a centre of symmetry. Of the 32 crystal classes (Chapter 1), 11 possess a centre of symmetry and one other cannot be piezoelectric because of other symmetry elements it possesses.

α -Quartz is based on SiO_4 tetrahedra. Tetrahedra do not have centres of symmetry and in α -quartz the tetrahedra are distorted so that each unit has a net dipole moment. However these tetrahedra are arranged in such a way (Figure 9.17) that normally the crystal does not have an overall polarization. External stress changes the Si—O—Si bond angles between tetrahedra so that the dipole moments no longer cancel and the crystal has a net electrical polarization. The effect in α -quartz is small; the output electrical energy is only 0.01 of the input strain energy whereas for Rochelle salt (another commercially used piezoelectric crystal) the ratio of output to input energy is 0.81. α -Quartz however is useful in applications where an oscillator of stable frequency is needed, such as in quartz watches. An electric field causes distortion of quartz and if an alternating electric field is applied the crystal vibrates. When the frequency of the electric field matches a natural vibration frequency of the crystal then

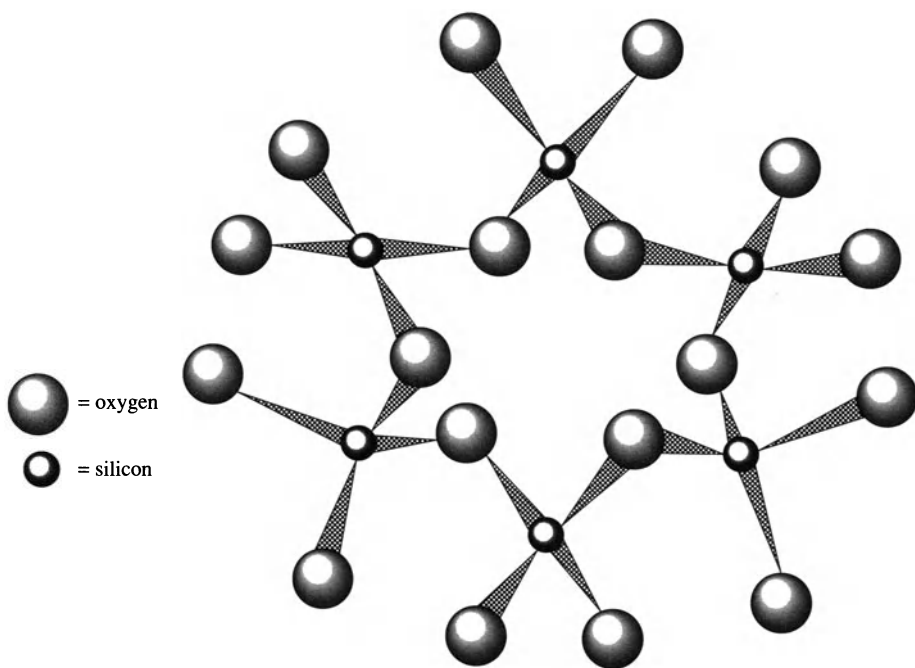


Figure 9.17 Structure of α -quartz.

resonance occurs and a steady oscillation is set up with the vibrating crystal feeding energy back to the electrical circuit. The importance of α -quartz in devices such as watches is due to the fact that, for some crystallographic cuts, a natural frequency of the crystal is independent of temperature and so the crystal will oscillate at the same frequency, and the watch will keep time, however hot or cold the day is.

For other applications, such as ultrasonic imaging, it is more important that the conversion of mechanical to electrical energy is high.

Some piezoelectric crystals are electrically polarized in the absence of mechanical stress; one example is gem-quality tourmaline crystals. Normally this effect is unnoticed because the crystal does not act as the source of an electric field. Although there should be a surface charge, this is rapidly neutralized by charged particles from the environment and from the crystal itself. However, the polarization decreases with temperature and this can be used to reveal the polar nature of the crystal. If tourmaline is heated its polarization decreases and it loses some of its surface charges. On rapid cooling it has a net polarization and will attract small electrically charged particles such as ash. Such crystals are known as pyroelectric, of which ferroelectric crystals are a special sub-class.

9.10 THE FERROELECTRIC EFFECT

Ferroelectric crystals possess domains of different orientation of electrical polarization that can be reorientated and brought into alignment by an electric field. Among the most numerous ferroelectrics are the perovskites (Chapter 1), of which a classic example is barium titanate, BaTiO_3 . This substance has a very large dielectric constant (about 1000) and is widely used in capacitors. Above 393 K BaTiO_3 has a cubic structure as in Figure 1.35, with Ba^{2+} ions in the centre, Ti^{4+} ions at the cube corners and an octahedron of O^{2-} ions around each titanium ion. The Ti^{4+} ion is small (75 pm radius) and there is room for it to move inside the O_6 cage. At 393 K the structure changes to a tetragonal one in which the Ti atom moves off-centre along a Ti—O bond. At 278 K a further change occurs in which the Ti moves off-centre along a diagonal between two TiO bonds and at 183 K a rhombohedral phase is formed in which there is distortion along a cube diagonal. The three distortions are shown in Figure 9.18. This figure magnifies the effect: the Ti atom is moved about 15 pm off-centre. In these three phases the TiO_6 octahedra have a net dipole moment. To illustrate how ferroelectricity arises we use the tetragonal structure as an example. If all the Ti atoms were slightly off-centre in the same direction, then the crystal would have a net polarization. Like ferromagnetics, however, ferroelectrics have domains within which there is a net polarization but different domains have their polarization in

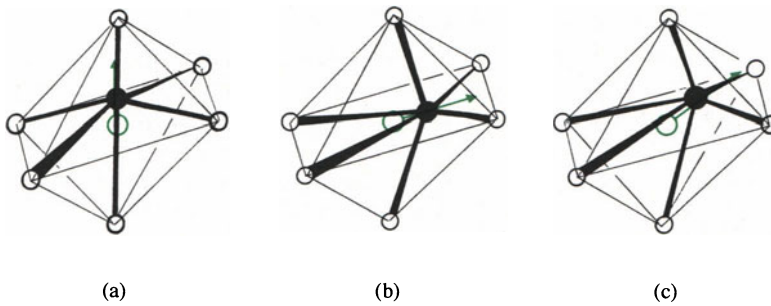


Figure 9.18 Distortions of TiO_6 octahedra in (a) the tetragonal structure, (b) the orthorhombic and (c) the rhombohedral structures of barium titanate.

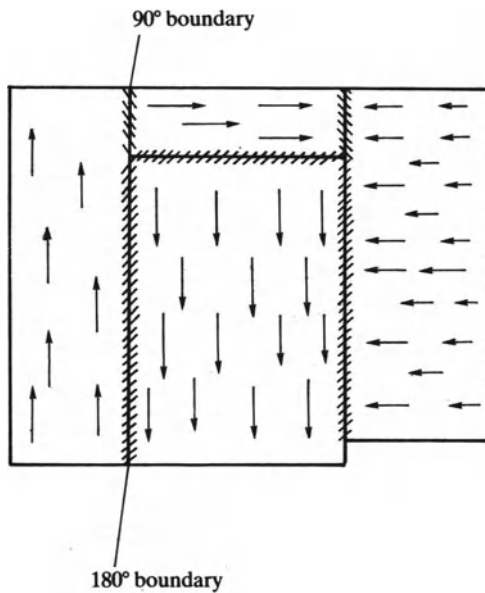


Figure 9.19 Sketch of domains in barium titanate showing 90° and 180° boundaries.

different directions, thus giving a net zero polarization. In the tetragonal phase of BaTiO_3 the Ti atom can be off-centre in six directions along any one of the Ti—O bonds. Neighbouring domains, as a result, have polarizations that are either at 90° or at 180° to each other, e.g. Figure 9.19.

A domain can be of the order 10^{-5} m, or even more. Several methods can be used to obtain pictures of the domains. Figure 9.20 is a photograph taken of a thin slice of barium titanate under a polarizing microscope in which different domains can clearly be seen. Note the sharpness of the domain boundaries.

When an external electric field is applied, domains aligned favourably grow at the expense of others. As with ferromagnetics, the response to the field exhibits hysteresis; the polarization grows until the whole crystal has its dipoles aligned, this polarization remains while the field is reduced to zero and only declines as a field of opposite polarity is applied. Figure 9.21 shows a hysteresis curve for barium titanate.

The electric susceptibility and dielectric constant of ferroelectric substances obey a Curie law dependence on temperature (equation 9.13):

$$\epsilon_r = \epsilon_\infty + C/(T - T_C), \quad (9.13)$$

where ϵ_∞ is the permittivity at optical frequencies and T_C is the Curie temperature. The origin of the Curie temperature in barium titanate is quite easy to see as the Curie temperature is the temperature, 393 K, at which barium titanate undergoes a phase transition to a cubic structure. Above the Curie temperature the structure has a centre of symmetry and no net dipole moment. The dielectric constant is still high because the

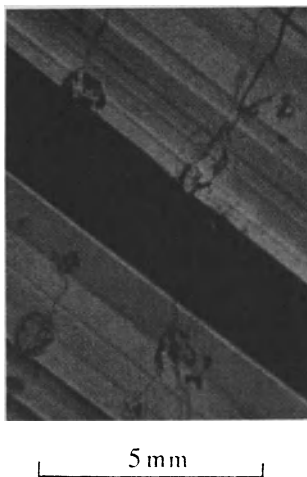


Figure 9.20 A photograph of a thin slice of barium titanate taken under the polarizing microscope, showing domains of different polarization. (From A. Guinier and R. Jullien (1989) *The Solid State from Superconductors to Super-alloys*, Oxford University Press/International Union of Crystallography, Oxford, Figure 2.9, p. 67. Reproduced by permission of Oxford University Press.)

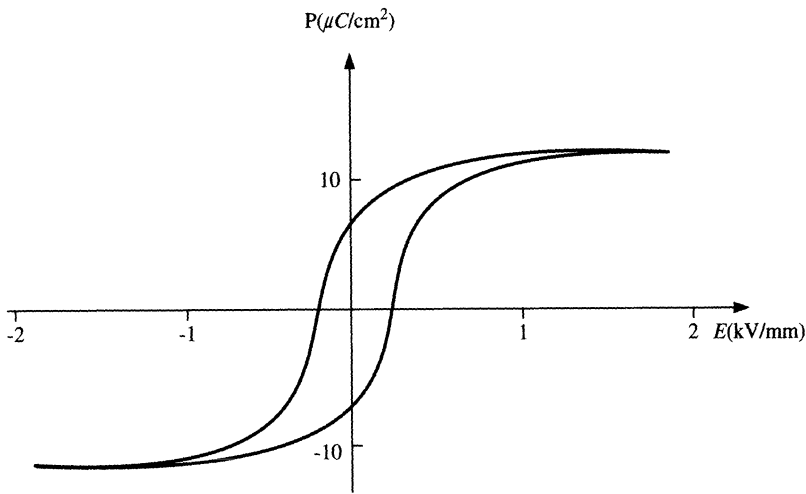


Figure 9.21 A plot of polarization versus applied electrical field for barium titanate of grain size 2×10^{-5} – 1×10^{-4} m.

atoms can be moved off-centre by an applied electric field, but the polarization is lost as soon as the field is removed.

9.10.1 Multilayer ceramic capacitors

Capacitors are used to store charge. An electric field is applied to induce charge in the capacitor. The capacitor then remains charged until a current is required. To be useful in modern electronic circuits, for computers, space shuttles, TV sets and many other applications, a capacitor must be small. In order to retain a high capacitance, i.e. to store a large amount of electrical energy whilst remaining small, a material needs a high permittivity. Hence barium titanate with its very high permittivity has proved invaluable for this purpose. Pure barium titanate has a high permittivity (about 7000) close to the Curie temperature, but this rapidly drops with temperature to the room temperature value of 1000–2000. Whilst this is still high, for electronic circuits it would be useful to retain the higher value so that the size of the capacitor could be reduced. For some applications it is also necessary for the permittivity to be constant with temperature over a range of 180 K from 218 K to 398 K. Barium titanate with some of the titanium substituted by zirconium or tin has a Curie temperature nearer room temperature and a flatter permittivity versus temperature curve. Further improvements can be made by partially substituting the barium ions. Materials made in this way consist of several phases mixed together, each with a different Curie temperature, and it is this that gives rise to the flatter permittivity versus temperature curve.

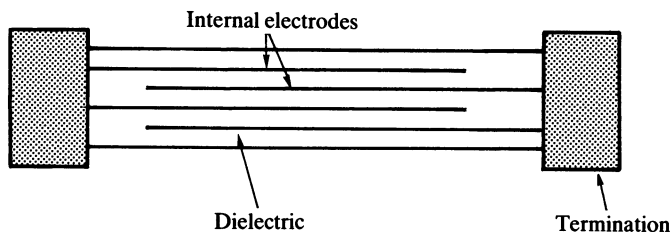


Figure 9.22 A section through a multilayer capacitor.

For example, a sample made by sintering 95% BaTiO_3 and 5% CaZrO_3 together at 1720 K in the presence of 0.6% niobium had a permittivity of 3000 over the range 223–403 K. The phases produced had the general formula $\text{Ba}_{1-x}\text{Ca}_x\text{Ti}_{1-y}\text{Zr}_y\text{O}_3$ and structures close to that of tetragonal BaTiO_3 . The role of the niobium seems to be to prevent the attainment of the thermodynamically stable phase. Another factor that affects the dielectric properties of barium titanate is the grain size. On the surface of the tetragonal crystals the structure is cubic, so that for small particles with a large surface to volume ratio there is a high proportion of cubic material. This leads to a higher room temperature permittivity but a smaller Curie temperature permittivity. For very small particles there is no ferroelectric effect. It is therefore important to produce grains of a suitable size to give the properties needed. In Chapter 3 we discussed preparative methods for barium titanate which give more suitable grain sizes than ceramic methods. To manufacture multilayer capacitors, barium titanate of suitable grain size and appropriately doped is interleaved with conducting plates (Figure 9.22). This enables one device to be used in place of several single disc capacitors in parallel.

Barium titanate is one example of a ferroelectric material. Other oxides with the perovskite structure are also ferroelectric, for example lead titanate and lithium niobate. These, like barium titanate, have small ions in O_6 cages which are easily displaced. Other ferroelectric solids include hydrogen-bonded solids, such as KH_2PO_4 and Rochelle salt ($\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$), and salts with anions which possess dipole moments, such as NaNO_2 . In the final chapter we look at the exciting field of superconductors, including high-temperature superconductors, many of which have structures related to the perovskite structure.

FURTHER READING

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See comments after Chapter 4. Concentrates on paramagnetism in metal complexes but also covers magnetic ordering.

Rao, C.N.R. and Gopalakrishnan, J. (1986) *New Directions in Solid State Chemistry*, Chapter 6, Cambridge University Press, Cambridge.

An interesting, though rather higher level, description of the interplay of structure and properties and their effect on applications.

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A readable article explaining how these devices work. This issue of Chemistry in Britain contains several articles relevant to solid state chemistry.

Guinier, A. and Jullien, R. (1989) *The Solid State from Superconductors to Superalloys*, Chapters 2 and 3, Oxford University Press/International Union of Crystallography, Oxford.

This translation of a French text book is very clearly written and at about the same level as the present volume.

Cheetham, A.K. and Day, P. (1992) *Solid State Chemistry Compounds*, Chapter 8, Oxford University Press, Oxford.

Written by experts in the field, this is a useful introduction to the field of ferroics, including ferromagnetics and ferroelectrics.

Newnham, R.E., Trolier-McKinstry, S. and Giniewicz, J.R. (1993) Piezoelectric, pyroelectric and ferroic crystals, *Journal of Materials Education*, **15**, 189–223.

A clear and readable article written for materials scientists, covering ferromagnetism and ferroelectricity as well as the piezoelectric effect.

QUESTIONS

1. Although manganese is not ferromagnetic, certain alloys such as Cu_2MnAl are ferromagnetic. The Mn–Mn distance in these alloys is greater than in manganese metal. What effect would this have on the $3d$ band of manganese? Why would this cause the alloy to be ferromagnetic?
2. The compound EuO has the NaCl structure and is paramagnetic above 70 K but magnetically ordered below it. Its neutron diffraction patterns at high and low temperatures are identical. What is the nature of the magnetic ordering?
3. ZnFe_2O_4 has the inverse spinel structure at low temperatures. What type of magnetism would you expect it to exhibit?

4. In transition metal pyrite disulphides, MS_2 , the M^{2+} ions occupy octahedral sites. If a d band is formed it will split into two as in the monoxides. Consider the information on some sulphides given below and decide whether the $3d$ electrons are localized or delocalized, which band the electrons are in if delocalized, and, in the case of semiconductors, between which two bands the band gap of interest lies.

MnS_2 antiferromagnetic ($T_N = 78\text{ K}$), insulator: above T_N
paramagnetism fits five unpaired electrons per manganese.

FeS_2 diamagnetic, semiconductor.

CoS_2 ferromagnetic ($T_C = 115\text{ K}$), metal.

5. In hydrogen-bonded ferroelectrics, the Curie temperature and permittivity alter when deuterium is substituted for hydrogen. What does this suggest about the origin of the ferroelectric transition in these compounds?

10.1 INTRODUCTION

In the late 1980s the amount of research effort in the field of superconductors increased dramatically due to the discovery of so-called 'high-temperature' superconductors by Bednorz and Muller in 1986. Their findings were thought to be so important that it was only a year later that they were awarded the Nobel Prize for Physics by the Royal Swedish Academy of Sciences.

Superconductors have two unique properties that could be very important for technology if methods can be found for exploiting them. First, they have zero electrical resistance and so carry current with no energy loss: this could revolutionize the national grid for instance, and is already exploited in the windings of superconducting magnets as used in NMR experiments. Second, they expel all magnetic flux from their interior and so are forced out of a magnetic field. The superconductors can float or 'levitate' above a magnetic field: the Japanese have an experimental frictionless train that floats above magnetic rails and has achieved speeds of over 500 km h^{-1} (300 mph). However, until 1986 the highest temperature a superconductor operated at was 23 K, and so they all had to be cooled by liquid helium (boiling temperature $\sim 4 \text{ K}$). This, of course, made any use of superconductors extremely expensive.

For many years workers have sought to find a superconductor that will operate at the very least at liquid nitrogen temperatures (above 77 K) so that the less expensive liquid nitrogen can be used instead of liquid helium as coolant. It is hoped that eventually a room-temperature superconductor will be found. The discoveries of 1986 and the years since then have achieved the aim of an operating temperature at liquid nitrogen temperatures. No one has yet reported a room-temperature superconductor.

10.2 THE DISCOVERY OF SUPERCONDUCTORS

In 1908 Kamerlingh Onnes succeeded in liquefying helium, and this paved the way for many new experiments to be performed on the behaviour of materials at low temperatures. For a long time, it had been known from conductivity experiments that the electrical resistance of a metal decreased with temperature. In 1911 Onnes was measuring the variation of the electrical resistance of mercury with temperature when he was amazed to find that at 4.2 K the resistance suddenly dropped to zero. He called this effect **superconductivity** and the temperature at which it occurs is known as the **(superconducting) critical temperature**, T_c . This effect is illustrated for tin in Figure 10.1. One effect of the zero resistance is that there is no power loss in an electrical circuit made from a superconductor. Once an electrical current is established, it shows no discernible decay for as long as experimenters have been able to watch – a maximum of $2\frac{1}{2}$ years so far!

For more than 20 years little progress was made in the understanding of superconductors and only more substances exhibiting the effect were found. More than 20 metallic elements can be made superconducting under suitable conditions (Figure 10.2), as can thousands of alloys. It was not until 1933 that a new effect was observed by Meissner.

10.3 THE MAGNETIC PROPERTIES OF SUPERCONDUCTORS

Meissner and Ochsenfeld found that when a superconducting material is cooled below its critical temperature, T_c , it expels all magnetic flux from within its interior (Figure 10.3a); the magnetic flux, B , is thus zero

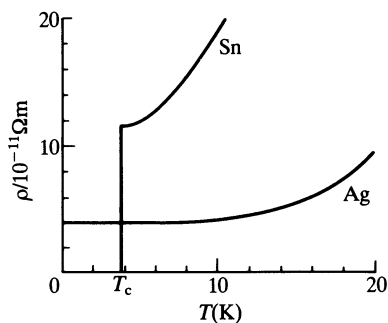


Figure 10.1 A plot of resistivity, ρ , versus temperature, T , showing the drop to zero at the critical temperature, T_c , for a superconductor, and the finite resistivity of a normal metal at absolute zero.

H																	He				
Li	Be															B	C	N	O	F	Ne
Na	Mg															Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
Fr	Ra																				

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ac	Th	Pa	U	Np	Pu								



Al Superconducting



B Non-metallic elements



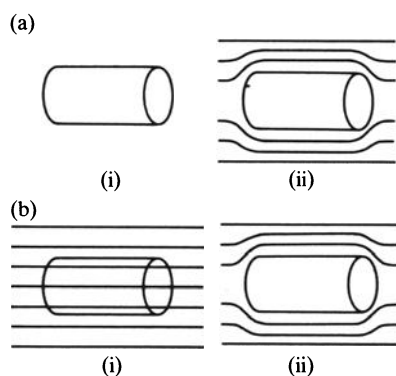
Si Superconducting under high pressure or in thin films



Fe Elements with magnetic order



Li Metallic but not yet found to be superconducting

Figure 10.2 The superconducting elements.**Figure 10.3** (a) (i) Superconductor with no magnetic field. When a field is applied in (ii) the magnetic flux is excluded. (b) (i) Superconducting substance above the critical temperature, T_c , in a magnetic field. When the temperature drops below the critical temperature (ii), the magnetic flux is expelled from the interior. Both are called Meissner effects.

inside a superconductor. Since $B = \mu_0 H(1 + \chi)$, when $B = 0$, χ must equal -1 , i.e. superconductors are perfect diamagnets. If a magnetic field is applied to a superconductor, the magnetic flux is excluded (Figure 10.3b) and the superconductor repels a magnet. This is shown in Figure 10.4, where a magnet is seen floating in mid-air above a superconductor.

It is also found that T_c changes in the presence of a magnetic field. A typical plot of T_c against increasing magnetic field is shown in Figure 10.5;

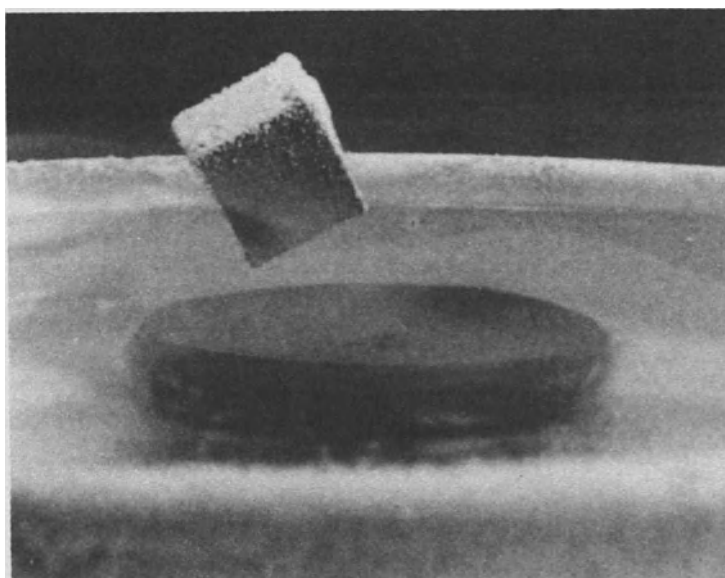


Figure 10.4 A permanent magnet floating over a superconducting surface.

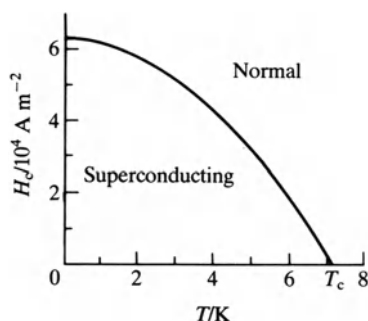


Figure 10.5 The variation with temperature of the critical field strength, H_c , for lead. Note that H_c is zero when the temperature, T , equals the critical temperature, T_c .

as the applied field increases, the critical temperature drops. It follows that a superconducting material can be made non-superconducting by the application of a large enough magnetic field. The minimum value of the field strength required to bring about this change is called the **critical field strength**, H_c ; its value depending on the material in question and on the temperature.

Similarly, if the current in the superconductor exceeds a **critical current**, the superconductivity is destroyed. This is known as the **Silsbee effect**. The size of the critical current is dependent on the nature and geometry of the particular sample.

10.4 THE THEORY OF SUPERCONDUCTIVITY

The theory of superconductivity is extremely complex, lying firmly in the realm of theoretical physics. This section attempts to give a qualitative picture of the ideas involved and also to give some familiarity with the terminology.

Physicists worked for many years to find a theory that explained superconductivity. To begin with, it looked as though the lattice played no part in the superconducting mechanism as X-ray studies showed that there was no change in either the symmetry or the spacing of the lattice when superconductivity occurred. However, in 1950 an **isotope effect** was first observed: for a particular metal the critical temperature was found to depend on the isotopic mass, M , such that

$$T_c \propto \frac{1}{\sqrt{M}} \quad (10.1)$$

The frequency, ν , of vibration of a diatomic molecule is known to be given by

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (10.2)$$

where μ is the reduced mass of the molecule, and k is the force constant of the bond. We can see that a vibration also changes frequency on isotopic substitution such that the frequency, ν , is proportional to $1/\sqrt{\text{mass}}$. This suggested to physicists that superconductivity was in some way related to the vibrational modes of the lattice and not just to the conduction electrons. The vibrational modes of a lattice are quantized, as are the modes of an isolated molecule, the quanta of the lattice vibrations being called **phonons**.

Frohlich suggested that there could be a strong phonon–electron interaction in a superconductor that leads to an attractive force between two

electrons that is strong enough to overcome the Coulomb repulsion between them. Very simply, the mechanism works like this: as a conduction electron passes through the lattice, it can disturb some of the positively charged ions from their equilibrium positions, pushing them together and giving a region of increased positive charge density. As these oscillate back and forth a second electron passing this moving region of increased positive charge density is attracted to it. The net effect is that the two electrons have interacted with one another, using the lattice vibration as an intermediary. Furthermore, the interaction between the electrons is attractive because each of the two separate steps involved an attractive Coulomb interaction.

It is the scattering of conduction electrons by the lattice vibrations, phonons, that produces electrical resistance at room temperature. (At low temperatures it is predominantly the scattering by lattice defects that gives electrical resistance.) Contrary to what we might have expected intuitively, a superconductor will have high resistance at room temperature, because it has strong electron–phonon interactions. Indeed, the best room-temperature electronic conductors, silver and copper, do not superconduct at all! Superconductors do not have low electrical resistance above the superconducting T_c .

In 1957 Bardeen, Cooper and Schrieffer published their theory of superconductivity, known as the **BCS theory**. It predicts that under certain conditions the attraction between two conduction electrons due to a succession of phonon interactions can slightly exceed the repulsion that they exert directly on one another due to the Coulomb interaction of their like charges. The two electrons are thus weakly bound together, forming a so-called **Cooper pair**. It is these Cooper pairs that are responsible for superconductivity.

BCS theory shows that there are several conditions that have to be met for a sufficient number of Cooper pairs to be formed and superconductivity to be achieved. It is beyond the scope of this book to go into this in any depth. Suffice it to say that the electron–phonon interaction must be strong and that low temperature favours pair formation, hence high-temperature superconductors are not predicted by BCS theory.

Cooper pairs are weakly bound, with typical separations of 10^6 pm for the two electrons. They are also constantly breaking up and reforming (usually with other partners). There is thus enormous overlap between different pairs and the pairing is a complicated dynamic process. The ground state of a superconductor therefore is a ‘collective’ state, describing the ordered motion of large numbers of Cooper pairs. When an external electrical field is applied, the Cooper pairs move through the lattice under its influence. However, they do so in such a way that the ordering of the pairs is maintained. The motion of each pair is locked to the motion of all

the others, and none of them can be individually scattered by the lattice. Because the pairs cannot be scattered by the lattice the resistance is zero and the system is a superconductor.

10.5 JOSEPHSON EFFECTS

In 1962 Josephson predicted that if two superconducting metals were placed next to each other, separated only by a thin insulating layer (such as their surface oxide coating), then a current would flow in the absence of any applied voltage. This effect is indeed observed because if the barrier is not too thick then electron pairs can cross the junction from one superconductor to the other without dissociating. This is known as the **d.c. Josephson effect**. He further predicted that the application of a small d.c. electric potential to such a junction would produce a small alternating current, the **a.c. Josephson effect**. These two properties are of great interest to the electronics and computing industries, where they can be exploited for fast-switching purposes.

10.6 THE SEARCH FOR A HIGH-TEMPERATURE SUPERCONDUCTOR

By 1973 the highest temperature found for the onset of superconductivity was 23.3 K. This was for a compound of niobium and germanium, Nb_3Ge , and here it stayed until 1986 when Georg Bednorz and Alex Müller reported their findings. Their Nobel Prize citation states 'Last year, 1986, Bednorz and Müller reported finding superconductivity in an oxide material at a temperature 12°C higher than previously known.' The compound that prompted their initial paper has been shown to be $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, where $x = 0.2$, with a structure based on that of K_2NiF_4 , a perovskite-related layer compound: they observed the onset of superconductivity at 35 K. (We will look at the detailed structure in the next section.) The insight that they brought to this field was to move away from the investigation of metals and their alloys and to study systematically the solid state physics and chemistry of metallic oxides.

The idea was soon born that it might be possible to raise the temperature even further by substitution with different metals. Using this technique, it was Chu's group at Houston, Texas, that finally broke through the liquid nitrogen temperature barrier with the superconductor that is now known as '1-2-3'. This superconductor replaces lanthanum with yttrium and has the formula $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. The onset of superconductivity for 1-2-3 occurs at 93 K.

10.7 THE CRYSTAL STRUCTURES OF HIGH-TEMPERATURE SUPERCONDUCTORS

The perovskite structure is named after the mineral CaTiO_3 (section 1.5.3). Many oxides of general formula ABO_3 , for example LiNbO_3 (Chapter 8) and BaTiO_3 (Chapter 9), adopt this structure (also fluorides, ABF_3 , and sulphides, ABS_3). The so-called perovskite A-type unit cell (with the A-type atom in the centre of the cell) is shown in Figure 10.6. The central A atom (Ca) is coordinated by eight titaniums at the corners of the cube and by 12 oxygens at the midpoints of the edges. The perovskite structure can be equally well represented by moving the origin of the unit cell to the body centre. This has the effect of putting Ca (A) atoms at each corner, Ti (B) atoms at the body centre and an O atom in the centre of each face (Figure 10.7).

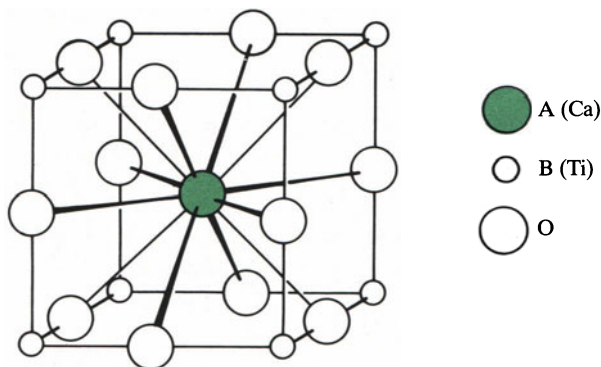


Figure 10.6 The A-type unit cell of the perovskite structure for compounds ABO_3 , such as CaTiO_3 .

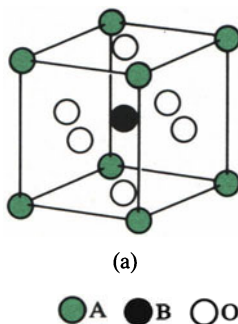


Figure 10.7 B-type cell for the ABO_3 perovskite structure.

The K_2NiF_4 structure is adopted by the Bednorz/Müller superconductor $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$. Its unit cell, and its relationship to the perovskite structure is illustrated in Figure 10.8. The structure has a body-centred tetragonal cell. We can get more insight into the structure by dividing it up into three sections along its c direction (Figure 10.8a). The central section is a B-type perovskite unit cell, and this is sandwiched by two A-type cells that have their bottom and top layers, respectively, missing (they are shown by dotted atomic positions). The lanthanum and barium atoms are similar in size and they are randomly distributed amongst the K (A) atom positions in the structure. Cu takes the Ni (B) positions. Notice that the A-type atoms (K or La/Ba) are surrounded by only nine oxygens in this structure whereas A was coordinated by 12 equidistant oxygens in the basic perovskite structure.

For the sake of simplicity each section of the unit cell has been shown as a cube. In practice the central section is slightly elongated in the c direction and the Cu atoms are coordinated by an elongated octahedron of six Os (and by eight La/Bas at the corners). This elongation is a Jahn–Teller effect and is the reason that Bednorz and Müller chose to investigate these copper oxides for superconductivity. The copper atoms and the four closest oxygen atoms lie in the ab planes forming networks of copper and oxygen atoms separated by planes of other atoms. It is this planar arrangement of copper and oxygen atoms that confers the superconducting properties on the crystal.

The parent compound, La_2CuO_4 (without any barium in the lattice), has no superconductivity. This is because the parent compound is antiferromagnetic. This crystal contains Cu^{2+} ions and the unpaired electrons on the copper ions align antiparallel throughout the structure. The presence of this interaction locks the electrons to the lattice, stopping both conductivity and superconductivity very effectively. When some barium (Ba^{2+}) is introduced into the lattice replacing lanthanum (La^{3+}) obviously some charge compensation has to be made in order to preserve electrical neutrality. For every Ba^{2+} present one Cu^{II} must be oxidized to Cu^{III} , or one O^{2-} to O^- , and this breaks up the alignment of the unpaired spins. When the average oxidation state of the copper atoms reaches a critical value of ~ 2.2 the antiferromagnetism disappears and superconductivity appears. (Substitution with strontium or calcium also produces superconductivity.) It has been observed that if pressure is applied to the compound, such that the Cu–O distance decreases, then T_c increases. There is also a general correlation of higher T_c with higher Cu(III) content: a Cu(III)–O bond is shorter than a Cu(II)–O bond because the electron is removed from an antibonding e_g orbital. These two observations are not necessarily related because the high-pressure studies show an increase of T_c with decrease in Cu–O distance, without any change in the Cu(III) content of the compound.

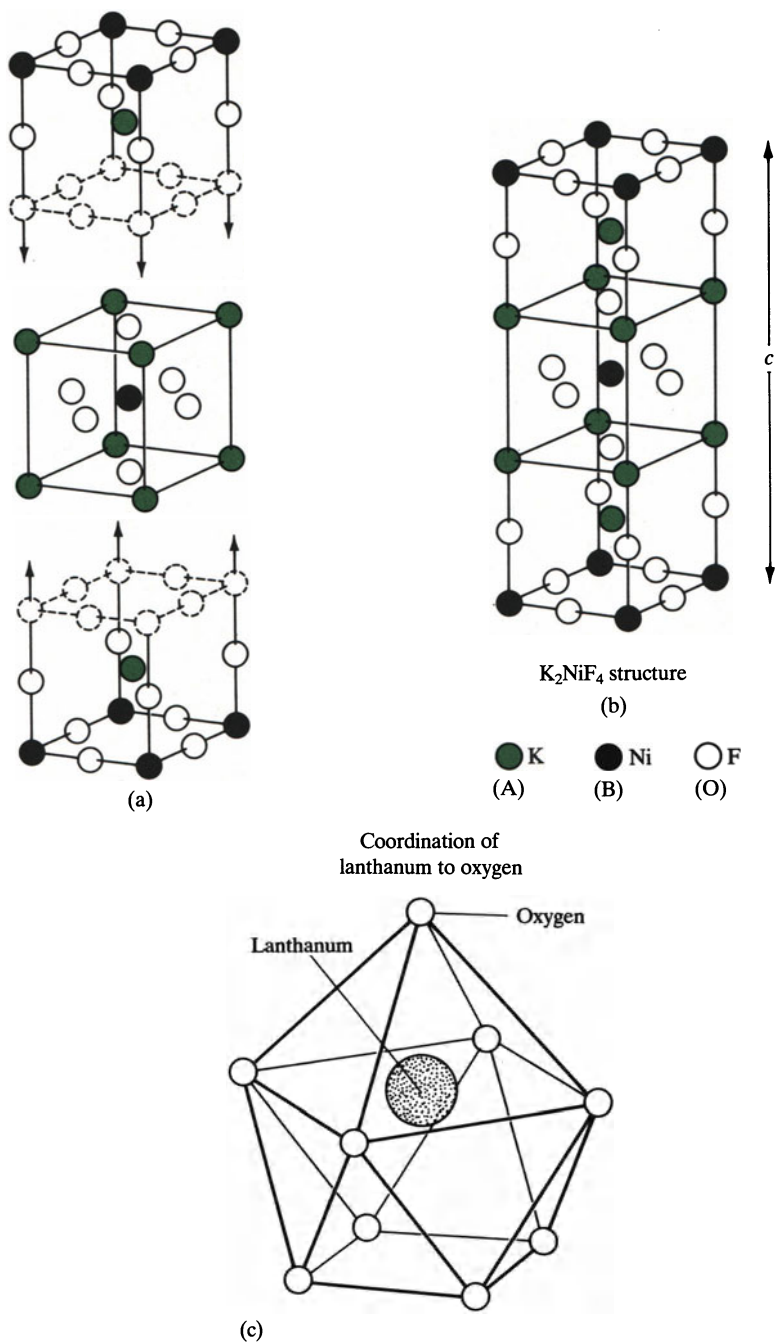


Figure 10.8 (a) and (b) show the K_2NiF_4 structure derived from perovskite-type (ABO_3) unit cells, as adopted by $La_{2-x}Ba_xCuO_4$. (c) The ninefold coordination of lanthanum by oxygen in this structure.

The crystal structure of the 1-2-3 superconductor, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, is shown in Figure 10.9. Figure 10.9a shows only the positions of the metal atoms: note the strong similarity between this and the structure of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$. If, as before, we discuss it in terms of the perovskite structure ABO_3 , where $\text{B} = \text{Cu}$, the central section is now an A-type perovskite unit cell and above and below it are also A-type perovskite unit cells with their bottom and top layers missing. This gives copper

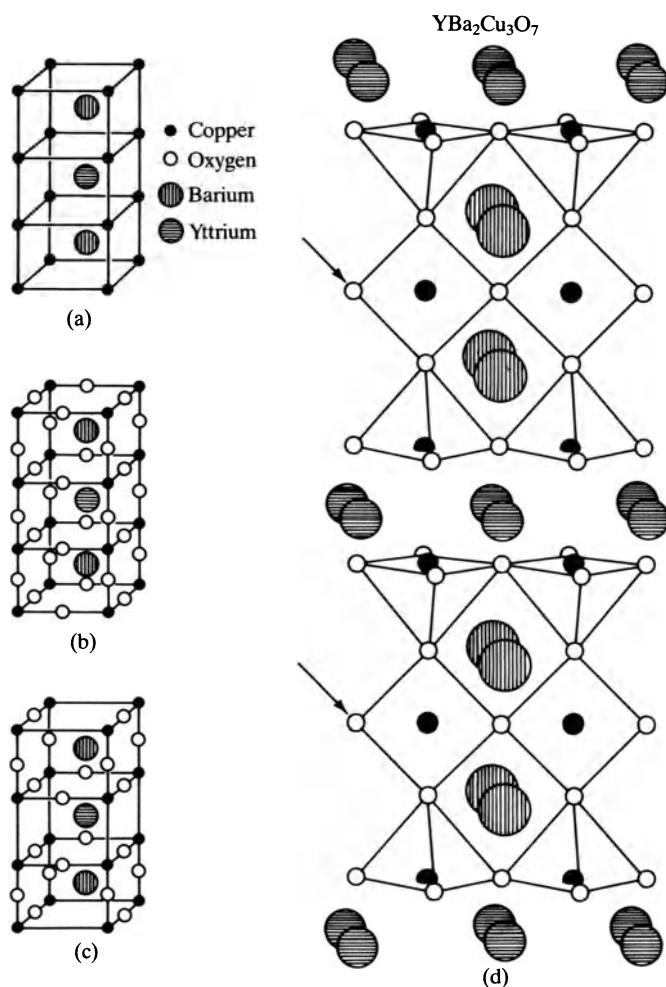


Figure 10.9 The structure of 1-2-3; (a) the metal positions; (b) an idealized unit cell of the hypothetical $\text{YBa}_2\text{Cu}_3\text{O}_9$, based on three perovskite A-type unit cells; (c) idealized structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$; (d) the structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$, showing copper-oxygen planes formed by the bases of the pyramids, with the copper-oxygen diamonds in between.

atoms at the unit cell corners and on the unit cell edges at fractional coordinates $\frac{1}{3}$ and $\frac{2}{3}$. The atom at the body centre of the cell (i.e. in the centre of the middle section) is now **yttrium**. The atoms in the centres of the top and bottom cubes are **barium**.

If, in this structure, all three sections were based exactly on perovskite unit cells, we would expect to find the oxygen atoms in the middle of each cube edge (Figure 10.9b). This would give an overall formula of $\text{YBa}_2\text{Cu}_3\text{O}_9$. This formula is improbable because it gives an average oxidation state for the three copper atoms of $\frac{11}{3}$, implying that the unit cell contains both Cu(III) and Cu(IV), which is unlikely as Cu(IV) complexes are extremely rare. The unit cell in fact contains only approximately seven oxygen atoms ($\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$). When $x = 0$, the oxygen atoms on the vertical edges of the central cube are not there and there are also two missing from both the top and bottom faces (Figure 10.9c). A unit cell containing seven oxygen atoms has an average copper oxidation state of 2.33 indicating the presence of Cu(II) and Cu(III) in the unit cell (but no longer Cu(IV)).

In the 1-2-3 structure (when $x = 0$) the yttrium atom is coordinated by eight oxygens and the barium atoms by 10 oxygens. The oxygen vacancies in the 1-2-3 superconductor create sheets and chains of linked copper and oxygen atoms running through the structure (this is shown slightly idealized in the diagrams as, in practice, the copper atoms lie slightly out of the plane of the oxygens); the copper is in fourfold square-planar or fivefold square-pyramidal coordination (Figure 10.9d). The superconductivity is found in directions parallel to the copper planes which are created by the bases of the Cu–O pyramids and which are separated by layers of yttrium atoms. These Cu–O nets seem to be a common feature of all the new high-temperature superconductors. If this superconductor is made more deficient in oxygen, at $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ ($x = 0.5$) the superconducting T_c drops to 60 K and at $\text{YBa}_2\text{Cu}_3\text{O}_6$ the superconductivity disappears. The oxygen is not lost at random but goes from specific sites, gradually changing the square-planar coordination of the copper along the c direction into the twofold linear coordination characteristic of Cu^+ . The sites from which the oxygen atoms are lost are indicated by arrows in Figure 10.9d. The arrangement of the copper and oxygen atoms in the base of the pyramids is not affected. However, when the formula is $\text{YBa}_2\text{Cu}_3\text{O}_6$ all the square planar units along c have become chains containing Cu^+ and the pyramid bases contain only Cu^{2+} ; the unpaired spins of the Cu^{2+} are aligned antiparallel and the compound is antiferromagnetic. It is not until the oxygen content is increased to $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ that the antiferromagnetic properties are destroyed and the compound becomes a superconductor.

In both of the superconductors discussed here the average oxidation state of the copper is greater than two and positive holes are formed in the CuO_2 sheets. The charge is carried by the positive holes and as a

consequence these materials are known as ***p*-type superconductors**. Until 1988 all the high-temperature superconductors that had been found were *p*-type and it was assumed by many that this would be a feature of high-temperature superconductors. However, some ***n*-type superconductors** have now also been discovered, where the charge carriers are electrons. The first to be found was based on the compound Nd_2CuO_4 with small amounts of the three-valent neodymium substituted by four-valent cerium, $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$, where $x \sim 0.17$ (samarium, europium or praseodymium can also be substituted for the neodymium). Other similar compounds have since been found, based on this structure where the three-valent lanthanide is substituted by, for example, four-valent thorium in $\text{Nd}_{2-x}\text{Th}_x\text{CuO}_{4-y}$. The superconductivity occurs at $T_c \leq 25\text{ K}$ for these compounds.

At the time of writing (1995) the superconductor with the highest known critical temperature is formed from mercury, barium, calcium, copper and oxygen. Again the characteristic Cu–O planes are present, interspersed by ones containing mercury and oxygen. The T_c reported is 135 K, rising to 164 K under pressure. This compound, $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$, has a structure similar to that of other copper–oxide superconductors. There are layers of copper–oxygen pyramids as in Figure 10.9d, with the barium ions in similar positions to those in this diagram. However, between the two layers forming the pyramid bases are a layer of calcium ions, a layer of copper ions and then another layer of calcium ions. The planes beyond the apices of the pyramids and the barium ions are occupied by mercury and oxygen atoms (Figure 10.10).

Most high-temperature superconductors, like the ones described above, are layered oxygen-deficient perovskites containing CuO_2 sheets (the pyramids in Figure 10.9). The parent compounds, for example $\text{La}_2\text{Cu}_2\text{O}_4$, are antiferromagnetic with electrons on the copper ions interacting via a superexchange mechanism (see Chapter 9) through the oxygen. When these are doped to give *n*- or *p*-type superconductors, it is believed that this destroys the superexchange interaction. The copper–oxygen sheets become superconducting and the insulating layers separating them act as reservoirs of charge. Although it is believed that electron pairs are responsible for the superconduction as in conventional superconductors, there is as yet no agreement on the mechanism by which the pairs interact. Phonon coupling would not give superconduction above about 40 K.

Whatever the mechanism, however, it must also accommodate the few high-temperature superconductors that are not copper oxide-based, such as $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ ($T_c = 36\text{ K}$). Another exciting group of such compounds are based on buckminsterfullerene (Chapter 1). The highest temperature recorded for these alkali metal fullerenes of general formula A_3C_{60} is $\text{Rb}_2\text{CsC}_{60}$ with $T_c = 35\text{ K}$. These are unusual in being carbon-based and may herald an era of organic superconductors.

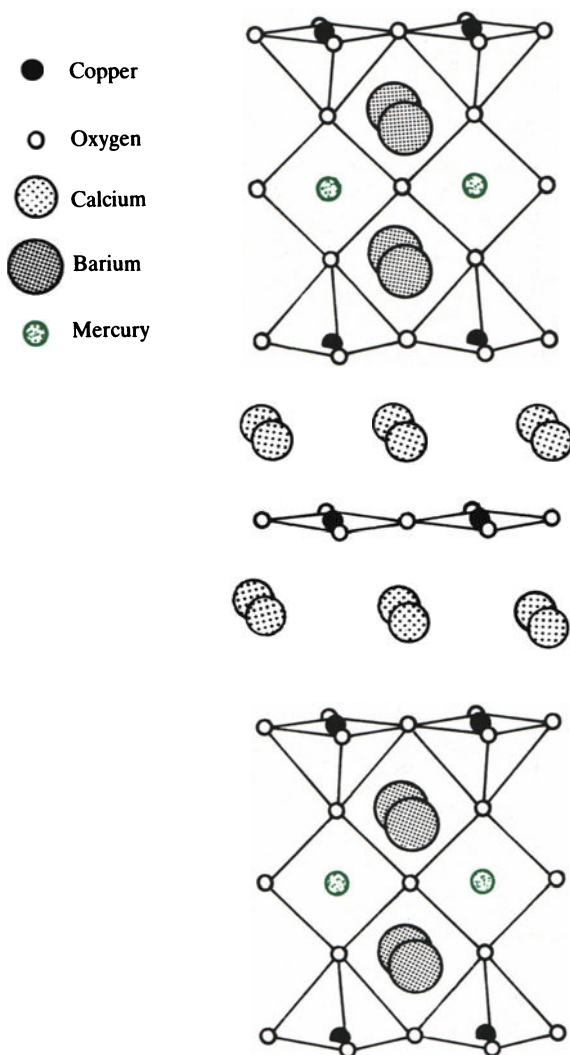


Figure 10.10 A simplified structure of the high-temperature superconductor $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$.

10.8 APPLICATIONS OF HIGH-TEMPERATURE SUPERCONDUCTORS

In order to be useful in many of the possible applications of superconductors, the new high-temperature superconductors have to meet some fairly stringent criteria: they have to be able to carry currents of more

than 10^9 A m^{-2} ($100\,000 \text{ A cm}^{-2}$); withstand strong magnetic fields (up to 5 T); and be physically strong enough to be used in motors and generators. Some of the criteria for these different uses are summarized in Figure 10.11. For some of the uses, bulk samples will not be useful and the material will need to be available in the form of wire, tape or thin film. Added to this, the benefits of using the new materials (better performance or cheaper running costs, for instance) have to outweigh any extra capital costs that may be needed to change to the new technology.

Making useful products in the form of wire or tape has proved to be difficult. They are made from a powdered mixture of superconductor and polymer which is formed into the appropriate shape, sintered and then annealed; unfortunately the product tends to be brittle. Another problem is that the 1-2-3 superconductor tends to lose oxygen, and therefore its superconductivity at the same time; other ceramics may not have this same problem. It has proved possible to make thin films that can carry large currents – of the order of 10^6 A cm^{-2} (10^{10} A m^{-2}) – and these have found uses.

The uses of superconductors are based around four main properties: the Meissner effect, the lack of electrical resistance, the ability to create

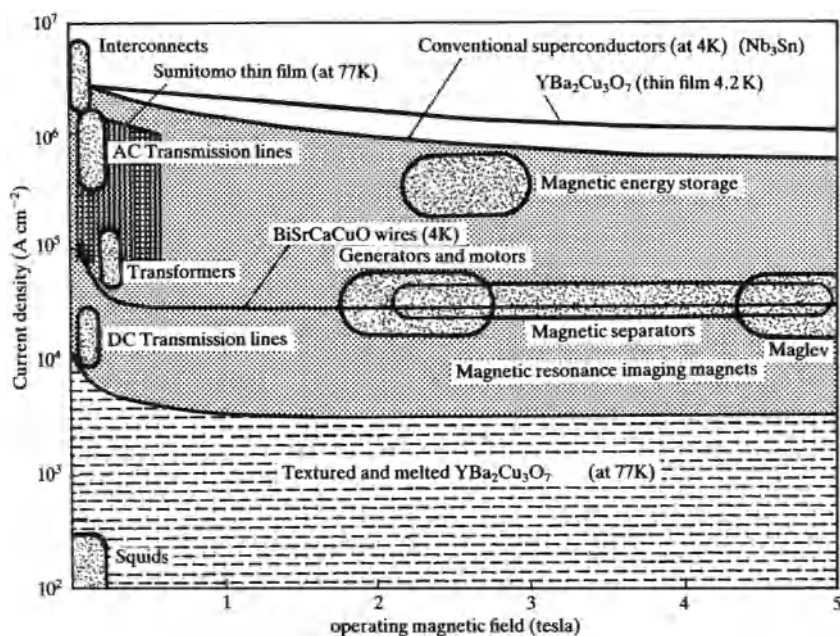


Figure 10.11 The graph shows the necessary performance of superconductors for various devices, based on present designs.

superconducting magnets and the Josephson effect. We will look at each area in turn.

The property of superconductors that has received most publicity is the Meissner effect, the ability to expel magnetic flux from the interior and so float or levitate above a magnet. The Japanese have been developing a magnetically levitating train, the so-called '**maglev**', using low-temperature superconducting magnets. Use of the new high-temperature superconductors instead should reduce the refrigeration costs of the project. Unfortunately refrigeration is only a very small percentage of both the capital and running costs and so will probably not make the difference as to whether this becomes a viable mode of transport or not. The hope is to produce a train that can travel at several hundreds of kilometres per hour and so compete with flying over short and medium length journeys.

Conventional electromagnets (made by passing an electric current through insulated copper wire wound around an iron core) can produce fields of about 2 T. Low-temperature superconducting magnets are manufactured from both NbTi and Nb₃Sn wires, which can carry much higher currents than copper wire ($\sim 400\,000\text{ A cm}^{-2}$) and so eliminate the need for the amplifying iron core. Such superconducting magnets are both lighter and more powerful ($\sim 10\text{ T}$) than their conventional counterparts, consume very little power, and produce little heat, but they have to be cooled to 4 K to become superconducting. If the windings could be replaced by high-temperature superconductors the liquid helium coolant (priced in £ per litre) could be replaced by liquid nitrogen (priced in pence per litre), thus dramatically reducing the running costs. It might also be possible to produce even larger value magnetic fields than currently achieved.

Low-temperature superconducting magnets are currently employed for several important uses. Strong magnets are used to remove impurities from food and raw materials; for instance, the magnetic impurities in china clay discolour the manufactured product if not removed. The latest NMR spectrometers employ superconducting magnets to provide large magnetic fields, so improving sensitivity. They are an important tool in fundamental scientific research, and are increasingly being used in body scanners for NMR imaging used in medical diagnosis.

Electrical generators produce power by spinning a magnet inside a coil; an electrical current is produced in the coil. It is thought that the use of a superconducting magnet would make the process more efficient, and the electricity a little cheaper. As with many of the other possible uses for the high-temperature superconductors, the percentage savings would be quite small, perhaps 1%, and whether this will ever offset the immense capital investment required is not clear.

Although superconductors carry direct current (d.c.) with no loss of power and without generating heat, there is a small loss of power when

they carry alternating current (a.c.), due to the production of radio waves. This absence of electrical resistance could be extremely useful in the distribution of electricity throughout the country, as the copper and aluminium wires now used lose 5–8% of the power due to the resistance of these elements. The superconducting wire (once it could be manufactured) is unlikely to be strong enough to be suspended from pylons; this means that all the cables, together with the cooling system, would have to be at ground level or buried underground – an expensive capital outlay! On the other hand, the environmental pressure groups would be greatly in favour of this, both for aesthetic and for safety reasons.

A supermagnetic energy storage unit (SMES) has been designed that could store a massive amount of direct current with no energy loss. The design currently uses NbTi alloy and a liquid helium cooling system. It would be used to store electricity generated at times of low demand, at night or in the summer for instance. A liquid nitrogen cooling system would be cheaper to build and to run.

Josephson junctions have been of great interest to the electronics industry because they can be used for switching voltages very quickly. As they do so they consume very little power and thus do not heat up. This means that they can be packed very close together without the need for elaborate cooling, giving the potential of making smaller and faster computers. IBM expended much time and research on building a Josephson computer based on these junctions. Sadly, the project was eventually abandoned because they found the memory cells unreliable. Japanese workers are still continuing the research, but in the meantime semiconductor technology reigns supreme.

Josephson junctions are used in superconducting quantum interference devices (SQUIDS). These consist of a loop of superconductive wire with either one built-in Josephson junction (RF SQUID) or two (DC SQUID). The device is extremely sensitive to changes in magnetic field, and can measure voltages as small as 10^{-18} V, currents of 10^{-18} A and magnetic fields of 10^{-14} T. SQUIDS are being used in medical research to detect small changes in magnetic field in the brain. Geologists are able to employ SQUIDS in prospecting for minerals and oil where deposits can cause small local changes in the earth's magnetic field; they also use the device for research into plate tectonics, collecting magnetic data on rocks of different ages. Physicists use SQUIDS for research into fundamental particles, and it is thought that there may be military applications in detecting the change in the earth's magnetic field caused by submarines. Clearly SQUIDS with their remarkable sensitivity have a myriad of potential uses. SQUIDS are one of the few high-temperature superconductor devices commercially available. The most common material used is $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. These liquid nitrogen-cooled SQUIDS do not achieve such high resolution as those using liquid helium, but can be used where liquid

helium is unobtainable or too expensive. For example, geophysical measurements in the field would generally be impractical with liquid helium devices since liquid helium is only available in major built-up areas and needs replenishing every few days due to evaporation.

Work still continues, however, and other commercial applications may emerge soon.

FURTHER READING

*This field has moved very rapidly in recent years and this chapter may well date quite rapidly. To keep up with current developments, the reader is referred to journals such as **Angewandte Chemie**, **New Scientist**, **Science** and **Scientific American**.*

Vanderah, T. (ed.) *Chemistry of Superconductor Materials: Preparation, Chemistry, Characterization and Theory*, Noyes Publications, 1992.

Ellis, A.B. (1987) Superconductors: better levitation through chemistry, *Journal of Chemical Education*, **64**, 836–41.

Cava, R.J. (1990) Superconductors beyond 1-2-3, *Scientific American*, August, 24–31.

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Khurana, A. (1989) Electron superconductors challenge theories, start a new race, *Physics Today*, April, 17–9.

*The September 1994 issue of **Chemistry in Britain** is devoted to superconductors and is a good presentation of the current state of research in this field.*

QUESTIONS

1. A party of late-night revellers, returning home, decide to take a short cut across a field. Unfortunately, the night is dark and moonless and the field is known to contain deep potholes. Someone has the bright idea that if everyone links arms and advances together across the field, then if one of the company does encounter a pothole she will be lifted clear by dint of collective support! Taking this story as an analogy (not a perfect one of course) with BCS theory, try to identify as many components as possible with corresponding components of BCS theory.

2. Draw a packing diagram (section 1.5.8) of the perovskite A-type cell ($\text{CaTiO}_3/\text{ABO}_3$), determine the number of ABO_3 formula units, and describe the coordination geometry around each type of atom. Repeat this procedure for the perovskite B-type unit cell.
3. The unit cell of the K_2NiF_4 crystal structure is shown in Figure 10.8. Draw packing diagrams for layers at fractional coordinates $\frac{1}{6}$ and $\frac{1}{3}$ in c .

Answers

ANSWERS TO CHAPTER 1

1. There are $2n$ tetrahedral holes and n octahedral holes; the same is true for an *hcp* array.
2. Twelve. Again, this is the same for a *hcp* array.
3. The coordination number of each atom is six.
4. (a) NF_3 . Figure 1.62a shows the threefold (C_3) axis and three planes of symmetry.
(b) SF_4 . Figure 1.62b shows the twofold (C_2) axis and two planes of symmetry.
(c) ClF_3 . Figure 1.62c shows the twofold (C_2) axis and two planes of symmetry.
5. No. Tetrahedral molecules do not have a centre of inversion. If you draw a line from any F atom and extend it through the C atom and for the same distance the other side, you do not meet with another F atom. A twofold (C_2) axis of symmetry is coincident with the $\bar{4}$ (S_4).
6. P: the corner of each unit cell is shared with eight other unit cells. The unit cell has eight corners and, therefore, contains one molecule.
I: the body-centred cell has ($8 \times \frac{1}{8}$) molecules at the corners, and one molecule in the centre which is not shared, making two molecules in all.
A: the A-centred cell has only two faces centred, contributing ($2 \times \frac{1}{2}$) molecules, and ($8 \times \frac{1}{8}$) at the corners, making a total of two molecules.
F: each face is shared by two unit cells, therefore the face-centred cell has ($6 \times \frac{1}{2}$) molecules on the faces and ($8 \times \frac{1}{8}$) at the corners, making a total of four molecules.
7. There are four. Unit cell (2) contains two lattice points; (3a) and (3b) each contain three lattice points; (4) contains four lattice points.

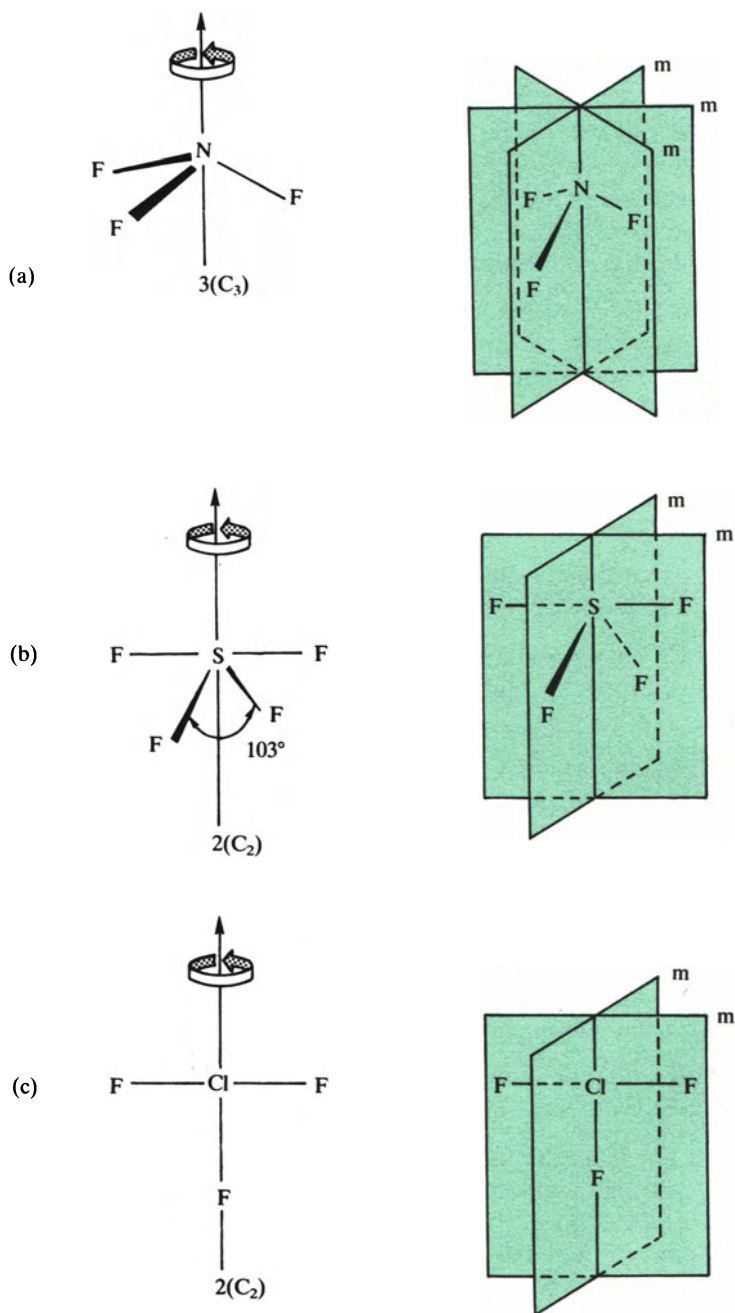
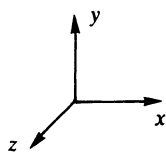


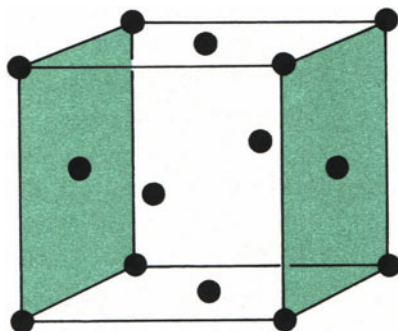
Figure 1.62 Threefold (C_3) axis in NF_3 . (b) Three planes of symmetry in NF_3 . (c) Twofold (C_2) axis in SF_4 . (d) Two planes of symmetry in SF_4 . (e) Twofold (C_2) axis in ClF_3 . (f) Two planes of symmetry in ClF_3 .

8. The indices are B – $1\bar{1}$; C – 01 ; D – 21 ; E – $2\bar{1}$. (By choosing a different line, you may have come up with the answers: $\bar{1}1$, $0\bar{1}$, $2\bar{1}$ and $\bar{2}1$. These are equally valid answers.)
9. Figure 1.26b shows the 200 planes: the planes are parallel to y and z and divide a into two.
Figure 1.26c shows the $11\bar{1}$ planes: they leave, a , b and c undivided.
Figure 1.26d shows the 110 planes: the planes are parallel to z and leave both a and b undivided.
10. Figure 1.63 shows the three planes: (a) 100 (b) 110 (c) 111 . The area of the 100 plane shown is a^2 and contains $(1 + 4 \times \frac{1}{4}) = 2$ atoms. The 110 plane contributes an area $a^2\sqrt{2}$ and contains $(2 \times \frac{1}{2} + 4 \times \frac{1}{4}) = 2$ atoms. The 111 plane contributes an area of $a^2(\sqrt{3}/2)$ and contains $(3 \times \frac{1}{2} + 3 \times \frac{1}{6}) = 2$ atoms.
The relative densities per unit area for these three planes are thus
$$100:110:111 = 2 : 1.414 : 2.31.$$

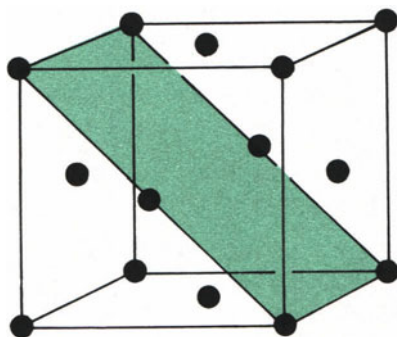
Notice that the 111 planes are the close-packed layers of the structure and so have the densest packing of atoms, as we would expect.
11. Both Cs^+ and Cl^- have a coordination number of eight, as each ion is surrounded by eight equivalent oppositely charged ions at the corners of the cube.
12. CsCl has a primitive lattice. If you find this answer difficult to understand and think that CsCl is body-centred, look back to the definition of a lattice on p. 14. This structure would be body-centred only if the ion in the centre of the cell were the same as the ions at the corners.
There is one formula unit of CsCl in the unit cell. This is made up from one Cl^- in the centre of the cell, plus eight Cs^+ ions at the corners which all contribute one-eighth of a Cs^+ ion to the cell, as they are shared by eight adjacent unit cells.
13. The coordination number is six for both Na^+ and Cl^- ions; each ion is octahedrally coordinated by the other.
14. There are four Na^+ ions: eight at cube corners shared with eight unit cells, and six at cube faces each shared with two unit cells, making a total of $(8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) = 4$. There are four Cl^- ions: 12 at midpoints of cube edges shared with four unit cells, one unshared at the body-centre position, making a total of $(12 \times \frac{1}{4}) + 1 = 4$. Thus, there are four formula units of NaCl in the cell.
15. The Ni atoms are octahedrally coordinated by six As atoms. The As atoms sit in the centre of a trigonal prism of six Ni atoms. The coordination number of both As and Ni is six.



(a)



(b)



(c)

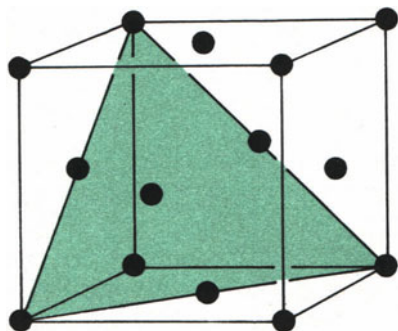


Figure 1.63 The diagrams show different planes in the face-centred unit cell of the *ccp* structure: (a) *100*, (b) *110*, (c) *111*.

16. The coordination number is four in each case. Each Zn atom is surrounded tetrahedrally by four S atoms and vice versa. This is also true for the wurtzite structure.
17. (a) The unit cell projection for CsCl is shown in Figure 1.64a. (b) The unit cell projection for NaCl is shown in Figure 1.64b. This is a view looking down c on the unit cell, showing ions at level 0.5 in c in black and at levels 0 and 1 in c in colour. (c) The unit cell projection for ZnS (zinc blende) is shown in Figure 1.64c.
18. Four. If the sulphur atoms in Figure 1.38 are black circles, there are $(6 \times \frac{1}{2}) = 3$ at the centres of the faces and $(8 \times \frac{1}{8}) = 1$ at the corners. These four are matched by the four zincs entirely enclosed in the cell.
19. (a) Figure 1.65a shows the hexagonal unit cell for *hcp*. (b) Figure 1.65b shows a possible unit cell for *ccp*, which has threefold symmetry. A more usual unit cell for this structure is a cubic one which is more difficult to visualize because the close-packed planes lie parallel to a body diagonal of the cell (see Figure 1.31).
20. Assuming that anion–anion contact occurs as in Figure 1.48b, the iodide ion radius is $300/\sqrt{2}$ or 212 pm.
21. From the internuclear distance in NaI, $r(\text{Na}^+) = (323 - 212) \text{ pm} = 111 \text{ pm}$. Then from the internuclear distance in NaF, $r(\text{F}^-) = (231 - 111) \text{ pm} = 120 \text{ pm}$. The same procedure for RbI and RbF gives $r(\text{Rb}^+) = 154 \text{ pm}$ and $r(\text{F}^-) = 128 \text{ pm}$.
22. The *100* and *111* planes are the same as the planes for the cubic close-packed structure in Question 10, Figure 1.63. The only plane that has changed is the *110* (Figure 1.66) which now has two additional atoms. Thus the relative densities per unit area become

$$100:110:111 = 2 : 2.83 : 2.31.$$

(Note that the structure is no longer truly close-packed, i.e. the carbon atoms are not touching, because the *110* planes are now more densely packed than the *111*. Remember that the radius of a tetrahedral hole is only $0.225r$, and the carbon atoms here all have the same radius, so although we can think in terms of the carbon atoms occupying tetrahedral holes in a close-packed structure, they are actually too big to do so, and so this description is only useful in terms of the relative geometry, in the same way as we discussed for the fluorite structure.)

23. $L_0(\text{CaCl}_2(\text{s})) = -2255.8 \text{ kJ mol}^{-1}$. From equation (1.21) we can write

$$\begin{aligned} \Delta H_f^\circ(\text{CaCl}_2(\text{s})) &= \Delta H_{\text{atm}}^\circ(\text{Ca}(\text{s})) + I_1(\text{Ca}) + I_2(\text{Ca}) \\ &\quad + D(\text{Cl}-\text{Cl}) - 2E(\text{Cl}) + L_0(\text{CaCl}_2(\text{s})). \end{aligned}$$

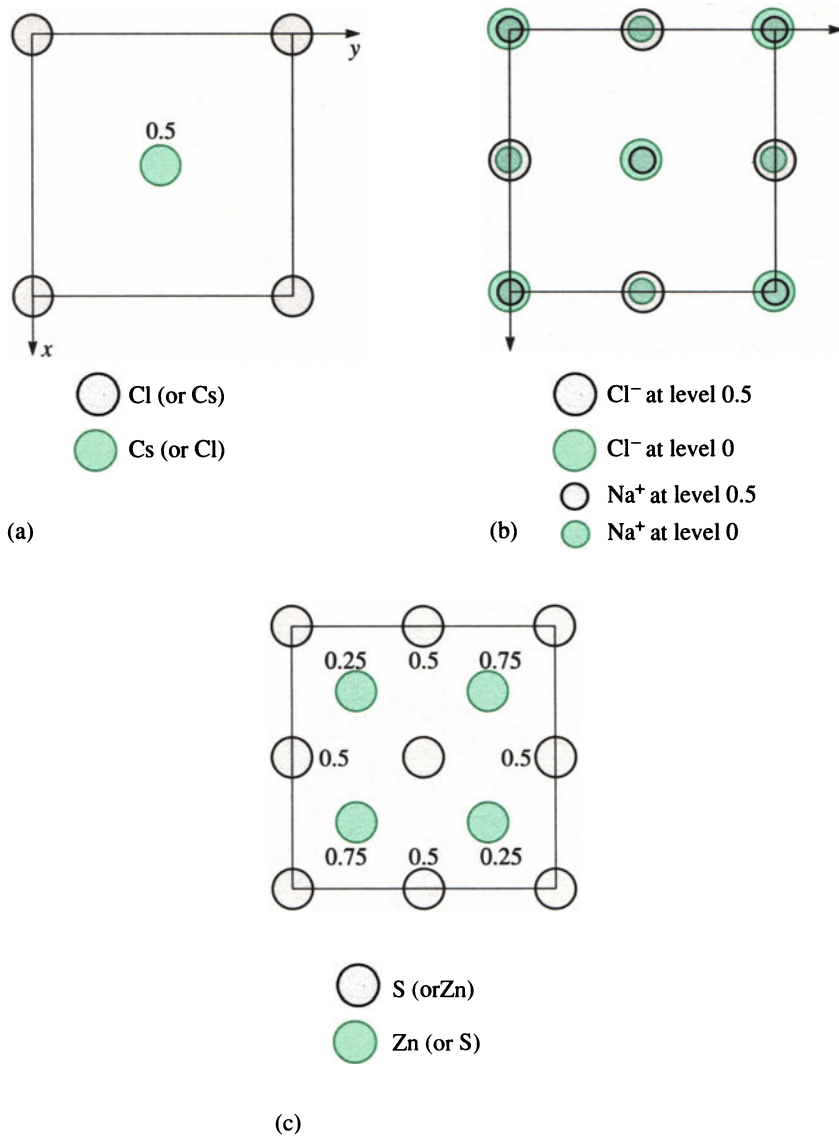


Figure 1.64 (a) Plan of the CsCl structure. (b) Plan of the NaCl structure. (c) Plan of the zinc blende, ZnS, structure.

Rearranging and inserting the values from Table 1.16 gives the answer. The lattice energy for CaCl_2 has a large negative value. Note how dominant in the cycle is the second ionization energy of calcium.

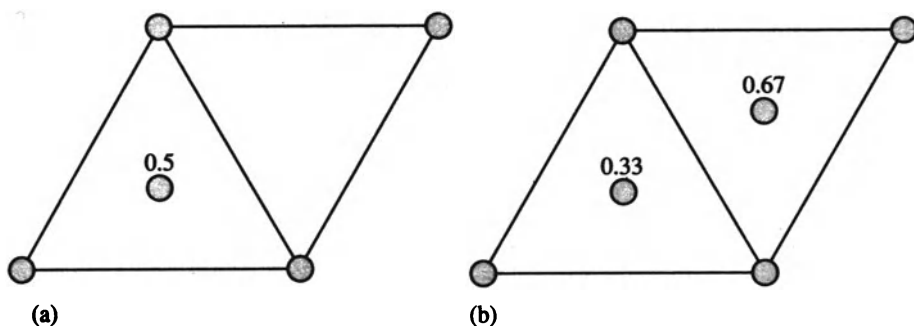


Figure 1.65 (a) Hexagonal close-packing. (b) Cubic close-packing.

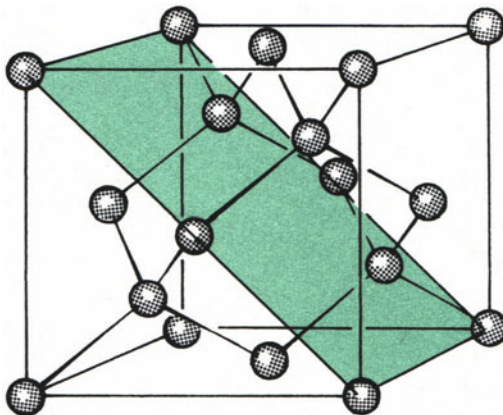
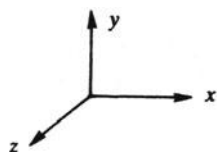


Figure 1.66 The 110 plane of the diamond structure.

24. The Madelung constant, $A = -3.99$. There are seven ions in the structure in Figure 1.61: six cations and one anion. First calculate the contribution to the potential energy of interactions of the six cations with the central anion. Each cation is distance r_0 from the central ion.

$$E_1 = -\frac{6e^2}{4\pi\epsilon_0 r_0}.$$

Each cation also interacts with a diametrically opposite cation (distance $2r_0$). There are three such interactions, so

$$E_2 = +\frac{3e^2}{4\pi\epsilon_0 2r_0}.$$

Finally, E_3 is calculated from interactions between adjacent cations (distance $\sqrt{2}r_0$), of which there are 12:

$$E_3 = +\frac{12e^2}{4\pi\epsilon_0 \sqrt{2}r_0}$$

$$\begin{aligned} E &= E_1 + E_2 + E_3 \\ &= -\frac{e^2}{4\pi\epsilon_0 r_0} \left(6 - \frac{3}{2} - \frac{12}{\sqrt{2}} \right) \\ &= -\frac{Ae^2}{4\pi\epsilon_0 r_0} \end{aligned}$$

so

$$A = 6 - \frac{3}{2} - \frac{12}{\sqrt{2}}$$

$$A = -3.99.$$

25. The appropriate Born–Haber cycle is shown in Figure 1.56 and leads to the relationship in equation (1.2):

$$\begin{aligned} \Delta H_f^\circ(\text{MCl(s)}) &= \Delta H_{\text{atm}}^\circ(\text{M(s)}) + I_1(\text{M}) + \frac{1}{2}D(\text{Cl–Cl}) \\ &\quad - E(\text{Cl}) + L_0(\text{MCl(s)}). \end{aligned}$$

Using the data in Table 1.17 we have

$$\begin{aligned} L_0 &= (-436.7 - 89.1 - 418 - 122 + 349) \text{ kJ mol}^{-1} \\ &= -717 \text{ kJ mol}^{-1}. \end{aligned}$$

From equation (1.17):

$$L_0 = -\frac{1.214 \times 10^5 v Z_+ Z_-}{r_+ + r_-} \left(1 - \frac{34.5}{r_+ + r_-} \right),$$

for KCl, $Z_+ = 1$, $Z_- = 1$, $r_{\text{K}^+} = 152 \text{ pm}$, $r_{\text{Cl}^-} = 167 \text{ pm}$, $v = 2$, giving $L_0 = -679 \text{ kJ mol}^{-1}$. There is a discrepancy of 38 kJ mol^{-1} between the calculated value and the thermodynamic value.

26. An appropriate cycle is shown in Figure 1.67. Note that sulphur is a solid in its standard state, not a gas. We wish to calculate $[E(\text{S}) + E(\text{S}^-)]$, which we can do if $L_0(\text{FeS(s)})$ can be calculated. Values of all the other terms in the cycle are known. The lattice energy relationship of equation (1.17) will be needed:

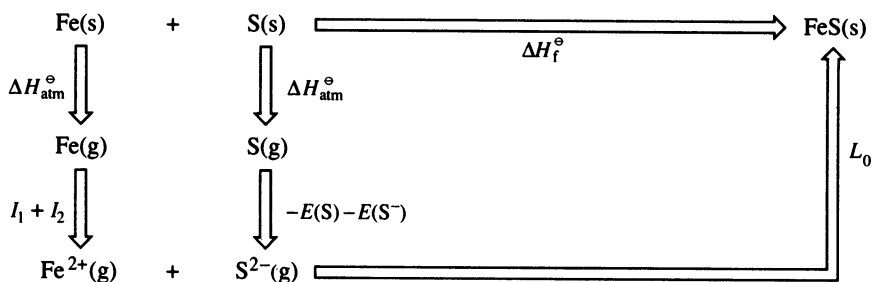


Figure 1.67 Born-Haber cycle for the calculation of the electron affinity of sulphur.

$$L_0 = -\frac{1.214 \times 10^5 v Z_+ Z_-}{r_+ + r_-} \left(1 - \frac{34.5}{r_+ + r_-} \right)$$

Substituting $v = 2$, $Z_+ = 2$, $Z_- = 2$, $r_+ = 92$, $r_- = 170$, gives $L_0 = -3219 \text{ kJ mol}^{-1}$. From the cycle in Figure 1.67

$$\begin{aligned} E(S) + E(S^-) &= -\Delta H_f^\ominus(\text{FeS(s)}) + \Delta H_{\text{atm}}^\ominus(\text{Fe(s)}) \\ &\quad + (I_1 + I_2) + \Delta H_{\text{atm}}^\ominus(\text{S(s)}) \\ &\quad + L_0(\text{FeS(s)}) \\ &= (100.0 + 416.3 + 761 + 1561 + 278.8 \\ &\quad - 3219) \\ &= -101.9 \text{ kJ mol}^{-1} \end{aligned}$$

$$E(S) = 200, \text{ so } E(S^-) = -101.9 - 200 = -301.9 \text{ kJ mol}^{-1}.$$

The value of the electron affinity is the heat given out on the addition of an electron, so this implies that the enthalpy change for the addition of an electron to the $\text{S}^-(\text{g})$ anion is endothermic:

$$\text{S}^-(\text{g}) + \text{e}^-(\text{g}) = \text{S}^{2-}(\text{g}); \quad \Delta H_m^\ominus = 301.9 \text{ kJ mol}^{-1}.$$

Not surprisingly it appears to be energetically unfavourable to add an electron to a negatively charged ion.

27. An appropriate cycle is shown in Figure 1.68. We wish to calculate $[E(\text{O}) + E(\text{O}^-)]$, which we can do if $L_0(\text{MgO(s)})$ can be calculated. Values of all the other terms in the cycle are known. The lattice energy relationship of equation (1.17) will be needed:

$$L_0 = -\frac{1.214 \times 10^5 v Z_+ Z_-}{r_+ + r_-} \left(1 - \frac{34.5}{r_+ + r_-} \right)$$

Substituting $v = 2$, $Z_+ = 2$, $Z_- = 2$, $r_+ = 86$, $r_- = 126$, gives $L_0 = -3836 \text{ kJ mol}^{-1}$. From the cycle in Figure 1.68

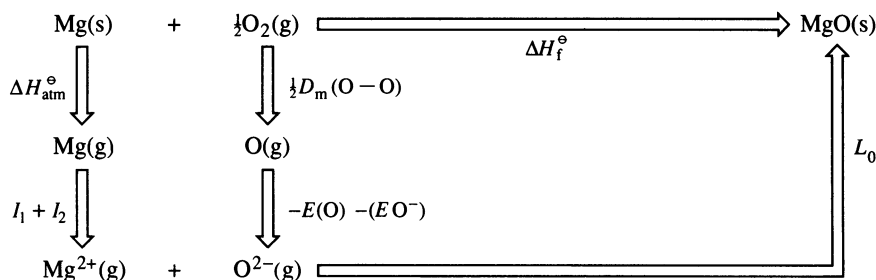


Figure 1.68 Born-Haber cycle for magnesium oxide.

$$\begin{aligned}
 E(\text{O}) + E(\text{O}^-) &= -\Delta H_f^\ominus(\text{MgO(s)}) + \Delta H_{\text{atm}}^\ominus(\text{Mg(s)}) \\
 &\quad + (I_1 + I_2) + \frac{1}{2}D_m(\text{O}-\text{O}) \\
 &\quad + L_0(\text{MgO(s)}) \\
 &= (601.7 + 147.7 + 736 + 1452 + 249 \\
 &\quad - 3836) \\
 &= -649.6 \text{ kJ mol}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 E(\text{O}) &= 141, \text{ so } E(\text{O}^-) = -649.6 - 141 \\
 &= -790.6 \text{ kJ mol}^{-1}.
 \end{aligned}$$

This implies that the enthalpy change for the addition of an electron to the $\text{O}^-\text{(g)}$ anion is also endothermic:

$$\text{O}^-\text{(g)} + \text{e}^-\text{(g)} = \text{O}^{2-}\text{(g)}; \quad \Delta H_m^\ominus = 790.6 \text{ kJ mol}^{-1}.$$

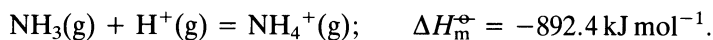
28. First we use equation (1.17) to calculate a value for the lattice energy:

$$L_0 = -\frac{1.214 \times 10^5 v Z_+ Z_-}{r_+ + r_-} \left(1 - \frac{34.5}{r_+ + r_-} \right)$$

For NH_4Cl , $v = 2$, $Z_+ = 1$, $Z_- = 1$, $r_+ = 151 \text{ pm}$, $r_- = 167 \text{ pm}$, giving $L_0 = -681 \text{ kJ mol}^{-1}$. From Figure 1.58:

$$\begin{aligned}
 P(\text{NH}_3\text{(g)}) &= -\Delta H_f^\ominus(\text{NH}_4\text{Cl(s)}) + \Delta H_f^\ominus(\text{NH}_3\text{(g)}) \\
 &\quad + \frac{1}{2}D_m(\text{H}-\text{H}) + I(\text{H}) + \frac{1}{2}D_m(\text{Cl}-\text{Cl}) - E(\text{Cl}) \\
 &\quad + L_0(\text{NH}_4\text{Cl(s)}) \\
 &= (314.4 - 46.0 + 218 + 1314 + 122 - 349 \\
 &\quad - 681) \text{ kJ mol}^{-1} \\
 &= 892.4 \text{ kJ mol}^{-1}.
 \end{aligned}$$

The addition of a proton to the ammonia molecule is an exothermic process



(The experimentally determined value is $871 \pm 15 \text{ kJ mol}^{-1}$, quite good agreement!)

29. The Born–Haber cycle for a chloride, MCl, is given in Figure 1.56 and leads to equation (1.2):

$$\Delta H_{\text{f}}^{\ominus}(\text{MCl}(\text{s})) = \Delta H_{\text{atm}}^{\ominus}(\text{M}(\text{s})) + I_1(\text{M}) + \frac{1}{2}D(\text{Cl}-\text{Cl}) - E(\text{Cl}) + L_0(\text{MCl}(\text{s}))$$

giving a value for the lattice energy of NaCl of $L_0 = -786 \text{ kJ mol}^{-1}$. Assuming that this is also the value of L_0 for MgCl and AlCl, we can calculate that

$$\Delta H_{\text{f}}^{\ominus}(\text{MgCl}(\text{s})) = -129 \text{ kJ mol}^{-1}$$

and

$$\Delta H_{\text{f}}^{\ominus}(\text{AlCl}(\text{s})) = -110 \text{ kJ mol}^{-1}.$$

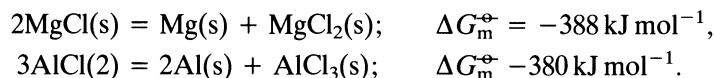
$\Delta S_{\text{f}}^{\ominus}(\text{NaCl}(\text{s})) = -90.6 \text{ J K}^{-1} \text{ mol}^{-1}$, and using this value for MgCl and AlCl gives

$$\Delta G_{\text{f}}^{\ominus}(\text{MgCl}(\text{s})) = -102 \text{ kJ mol}^{-1}$$

and

$$\Delta G_{\text{f}}^{\ominus}(\text{AlCl}(\text{s})) = -83 \text{ kJ mol}^{-1}.$$

This may seem a surprising result as it tells us that both MgCl(s) and AlCl(s) are stable with respect to decomposition into their elements under standard conditions and yet we know that they do not exist! The answer is that there is in each case another thermodynamically favourable decomposition route, a **disproportionation**, that can take place:



ANSWERS TO CHAPTER 2

1. The spacings for these planes are $d_{100} = a$, $d_{110} = a/\sqrt{2}$ and $d_{111} = a/\sqrt{3}$, and so their reflections occur in the order *100*, *110* and *111*.
2. Since the separation of planes decreases as $h^2 + k^2 + l^2$ increases, it follows that the value of $\sin\theta$ increases as $h^2 + k^2 + l^2$ increases. The $h^2 + k^2 + l^2$ values are therefore: for *220*, 8; for *300*, 9 and for *211*, 6. The sequence of reflections is *211*, *220*, *300*.

3. If the *100* and *110* reflections are absent then the crystal is likely to be face-centred cubic.
4. In this case the common factor of the first two lines is 0.05. Dividing all the $\sin^2\theta$ values by .05 gives the series 3, 4, 8, 11, 12, 16, 19 . . . , which is characteristic of face-centring.

The common factor 0.05 is equal to $\frac{\lambda^2}{4a^2}$, and so

$$a^2 = \frac{\lambda^2}{4 \times 0.05} = \frac{154.2^2}{0.2}$$

$$a = 345 \text{ pm}$$

5. The $\sin^2\theta$ values do not have the ratio 1:2:3:4:5:6:8 . . . , or 1:2:3:4:5:6:7:8 . . . so the cell is not primitive or body-centred. If it is face-centred then the common factor A will be $0.0746 - 0.0560 = 0.0186$. Dividing the $\sin^2\theta$ values by the common factor gives the $h^2 + k^2 + l^2$ values and these are listed in Table 2.6, rounded to the nearest integer. *h k l* only takes values where *h k l* are either all even or all odd, so the data fits a face-centred cubic structure.

Table 2.6 Powder diffraction data for NaCl

θ_{hkl}	$\sin^2\theta$	$h^2 + k^2 + l^2$	<i>hkl</i>
13°41'	0.0560	3	111
15°51'	0.0746	4	200
22°44'	0.1492	8	220
26°56'	0.2052	11	311
28°14'	0.2239	12	222
33°7'	0.2984	16	400
36°32'	0.3544	19	331
37°39'	0.3731	20	420
42°0'	0.4477	24	422
45°13'	0.5036	27	511, 333
50°36'	0.5972	32	440
53°54'	0.6529	35	531
55°2'	0.6715	36	600, 442
59°45'	0.7462	40	620

6. The mean value of the common factor, A, is 0.01875 and this is equal to $\lambda^2/4a^2$. This gives

$$a^2 = \frac{154.2^2}{4 \times 0.01875}$$

$$a = 563.1 \text{ pm}$$

7. If the mass of the unit cell contents is M and the unit cell volume is V then the density, ρ , is given by

$$\rho = \frac{M}{V} = 2.17 \times 10^3 \text{ kg m}^{-3}$$

but

$$V = (563.1 \times 10^{-12})^3 \text{ m}^3.$$

The mass of one mole of NaCl = $(22.99 + 35.45) \times 10^{-3}$ kg, dividing by the Avogadro constant we get that the mass of one formula unit of

$$\text{NaCl} = \frac{(22.99 + 35.45) \times 10^{-3}}{6.022 \times 10^{23}} \text{ kg}, \text{ and if there are } Z \text{ formula}$$

units in one unit cell, then the mass of the unit cell contents is

$$M = \frac{Z(22.99 + 35.45) \times 10^{-3}}{6.022 \times 10^{23}} \text{ kg}$$

so

$$\rho = 2.17 \times 10^3 = \frac{Z(22.99 + 35.45) \times 10^{-3}}{6.022 \times 10^{23} \times (563.1 \times 10^{-12})^3}$$

and rearranging gives

$$Z = \frac{2.17 \times 10^3 \times 6.022 \times 10^{23} \times (563.1 \times 10^{-12})^3}{(22.99 + 35.45) \times 10^{-3}}$$

$$Z = 3.99, \text{ or } Z = 4 \text{ (rounding to the nearest whole number).}$$

8. $\theta = 19.1^\circ$
 $\sin \theta = 0.327$

From the Bragg equation

$$\lambda = 2d_{III} \sin \theta_{III}$$

so

$$d_{III} = \frac{\lambda}{2 \sin \theta_{III}} = \frac{154.2}{0.654} = 235.8 \text{ pm}$$

The d spacing between the III planes is $\frac{a}{\sqrt{3}}$

so

$$a = (\sqrt{3} \times 235.8) \text{ pm}$$

$$= 408.4 \text{ pm}$$

$$\text{Density } \rho = \frac{M}{V}$$

$$V = (408.4 \times 10^{-12})^3 \text{ m}^3$$

$$M = \frac{Z \times 107.9 \times 10^{-3}}{N_A}, \text{ where } Z = 4, \text{ the number of atoms of}$$

silver in the unit cell, and N_A is the Avogadro constant.

$$\begin{aligned} \text{So } N_A &= \frac{4 \times 107.9 \times 10^{-3}}{10.5 \times 10^3 \times (408.4 \times 10^{-12})^3} \\ &= 6.03 \times 10^{23} \text{ mol}^{-1} \end{aligned}$$

$$9. \quad \rho = \frac{M}{V}$$

$$3.35 \times 10^3 = \frac{Z(40.08 + 15.99) \times 10^{-3}}{6.022 \times 10^{23}} \div (481 \times 10^{-12})^3$$

$$Z = \frac{3.35 \times 10^3 \times (481 \times 10^{-12})^3}{9.311 \times 10^{-26}}$$

$$Z = 4$$

$$10. \quad \rho = \frac{M}{V}$$

$$\begin{aligned} 8.5 \times 10^3 &= \frac{Z(232.04 + 2(78.96)) \times 10^{-3}}{6.022 \times 10^{23}} \\ &\div (442.0 \times 761.0 \times 906.4 \times (10^{-12})^3) \end{aligned}$$

$$Z = \frac{8.5 \times 10^3 \times 3.049 \times 10^{-28}}{6.476 \times 10^{-25}}$$

$$Z = \frac{2.591 \times 10^{-24}}{6.476 \times 10^{-25}}$$

$$Z = 4$$

11. From equation (2.7) we know that $\sin^2\theta_{hkl} = \lambda^2/4a^2(h^2 + k^2 + l^2)$. A cubic close-packed structure has a face-centred unit cell. The first two reflections observed will therefore be the *111* and the *200*, with $h^2 + k^2 + l^2$ values of 3 and 4 respectively. Thus $\sin^2\theta_{111} = 3\lambda^2/4a^2$ and $\sin^2\theta_{200} = 4\lambda^2/4a^2$, and $\lambda^2/4a^2 = \sin^2\theta_{200} - \sin^2\theta_{111} = 0.181 - 0.136 = 0.045$

$$a = 363.5 \text{ pm}$$

In a close-packed structure where the atoms are considered to be in contact, the radius of an atom, r , is $\frac{1}{4}$ of the length of the body-diagonal.

$$r = \frac{1}{4}\sqrt{3}a$$

$$r = \left(\frac{1}{4} \times 1.732 \times 363.5\right) \text{ pm}$$

$$r = 157.4 \text{ pm}$$

12. The scattering power is determined by the number of electrons possessed by each atom, i.e. the atomic number. In increasing order this is: H, O, F, Na, Cl, Co, Cd, Pt, Tl.
13. If the coordinates of the two Pt atoms are given by Pt₁ at x, y, z and Pt₂ at $-x, -y, -z$, then the coordinates of the vector will be $2x, 2y, 2z$. Dividing by 2 gives values of $x = 0.26, y = 0.02$ and $z = 0.24$. The coordinates of the two Pt atoms are therefore:
- Pt₁ 0.26, 0.02, 0.24
 Pt₂ -0.26, -0.02, -0.24 (this can also be expressed as 0.74, 0.98, 0.76).
14. Figure 2.19 shows a diagram of the six vectors between the four atoms in the unit cell. Notice that the vector between Pt₁ and Pt₂ has the same length and direction as the vector between Pt'₁ and Pt'₂, and similarly the vectors between Pt₁ and Pt'₂ and between Pt₂ and Pt'₁ are the same. Thus we expect that the two *smaller* peaks in the Patterson map will belong to the vectors between Pt₁ and Pt'₁ ($2x_1, 2y_1, 2z_1$) and Pt₂ and Pt'₂ ($2x_2, 2y_2, 2z_2$) respectively. Thus we can calculate a position of 0.40, 0.38, 0.22 for Pt₁ and 0.12, 0.25, 0.29 for Pt₂. These two positions double check with the vector $u, v, w = (x_1 - x_2, y_1 - y_2, z_1 - z_2) = (0.40 - 0.12, 0.38 - 0.25, 0.22 - 0.29) = 0.28, 0.13, -0.07$ and with the vector $u, v, w = (-x_1 - x_2, -y_1 - y_2, -z_1 - z_2) = (0.60 - 0.12, 0.62 - 0.25, 0.78 - 0.29) = 0.48, 0.37, 0.49$.

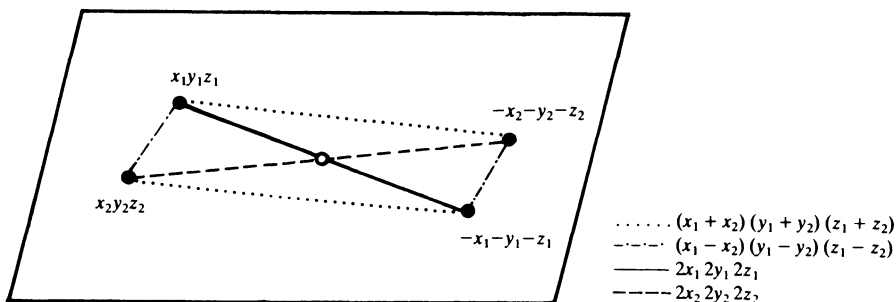


Figure 2.19 Projection of a triclinic unit cell that contains two pairs of platinum atoms, Pt₁ and Pt'₁, and Pt₂ and Pt'₂, respectively, where each pair is related by a centre of symmetry. The six vectors connecting each pair of atoms are indicated.

ANSWERS TO CHAPTER 3

1. This compound could be made from the elements in the correct stoichiometric proportions. The reactants would have to be very well mixed and the reaction vessel would have to be closed to prevent loss of the volatile sulphur (see SmS preparation).
2. Of the methods described in the chapter the following are suitable: a) sol-gel because the gel can be sliced thinly; CVD methods; b) hydrothermal synthesis, vapour phase and molecular beam epitaxy; c) vapour phase and molecular beam epitaxy; d) sol-gel precursor method.
3. Advantages – more homogeneous product with a smaller range of grain sizes; thin layers can be formed for microcapacitors.
Disadvantages – the process is more complex and would be expensive to set up on an industrial scale.
4. The compound given could be used as a precursor as it has a ratio of Cu:Cr of 1:2. Heating would pyrolyse the ammonia and ammonium, which would be driven off as nitrogen oxides and water.
The product would be more homogeneous than a ceramic product because the components are mixed at a molecular level. The temperature needed to pyrolyse the ammonia and ammonium is less than that required to enable the solid state reaction to proceed at a reasonable rate.
The precursor compound contains ammonia of solvation and was probably therefore precipitated from liquid ammonia.
5. β -TeI is metastable and contains Te in an unusual oxidation state. A method that employs temperatures of this order and can produce compounds in unusual oxidation states is hydrothermal synthesis.
6. Alumina is insoluble in water even under hydrothermal conditions but needs to be dissolved for the synthesis. However alumina is amphoteric and will dissolve in alkali. OH^- ions from the alkali coordinate to the aluminium, forming aluminate ions $\text{Al}(\text{OH})_4^-$ which are soluble.
7. At least one component of the reaction mixture must absorb microwave radiation strongly. Splitting the mixed oxides up into their component oxides which would be used as starting materials, we get $\text{CaO} + \text{TiO}_2$, $\text{BaO} + \text{PbO}_2$, $\text{ZnO} + \text{Fe}_2\text{O}_3$, $\text{ZrO}_2 + \text{CaO}$, $\text{K}_2\text{O} + \text{V}_2\text{O}_5$. PbO_2 , ZnO , V_2O_5 absorb microwaves strongly and so BaPbO_3 , ZnFe_2O_4 , $\text{Zr}_{1-x}\text{Ca}_x\text{O}_{2-x}$ and KVO_3 are good candidates.
8. Since the reaction is exothermic it is driven to the left by raising the temperature. Thus the crystals grow at the hotter end of the tube.

9. Niobium is in a high oxidation state in lithium niobate; the addition of oxygen to the carrier would prevent any tendency for decomposition to a lower oxidation state plus oxygen. The hydrogen in the preparation of mercury telluride would act to reduce the tellurium (in HgTe it is an oxidation state of -2) and form hydrocarbons with the ethyl radicals.

ANSWERS TO CHAPTER 4

1. For the Fermi level in sodium $E = 4.5 \times 10^{-19} \text{ J}$ (2.8 eV) and the mass of an electron is $9.11 \times 10^{-31} \text{ kg}$, this gives

$$\begin{aligned} 4.5 \times 10^{-19} &= \frac{1}{2} \times 9.11 \times 10^{-31} \times v^2 \\ v &= (2 \times 4.5 \times 10^{-19} / 9.11 \times 10^{-31})^{1/2} \\ &= 9.9 \times 10^5 \text{ ms}^{-1}. \end{aligned}$$

2. 10^{-12} m^3 of metal contains $970 \times 10^{-12} \text{ kg}$ of sodium, but one atom of sodium weighs $23/6.022 \times 10^{23} \text{ g} = 23 \times 10^{-3}/6.022 \times 10^{23} \text{ kg}$. So there are

$$\begin{aligned} &970 \times 10^{-12} \times 6.022 \times 10^{23} / 23 \times 10^{-3} \text{ atoms of sodium} \\ &= 2.5 \times 10^{16} \text{ atoms.} \end{aligned}$$

3. (a) $N = \frac{10^{-12} \times (2 \times 9.11 \times 10^{-31} \times 2.8 \times 1.602 \times 10^{-19})^{3/2}}{3 \times \pi^2 \times (1.055 \times 10^{-34})^3}$
 $= 2.125 \times 10^{16}.$

(b) $2.125 \times 10^{22}.$

(c) $0.2.$

Each level can take two electrons and a crystal of N atoms of sodium has N electrons to fill the band. As one can see, the agreement between the number of filled levels predicted by this very simple theory and the number needed to accommodate the available electrons is very good. Note also that this question illustrates how the energy level spacing increases as the electrons are confined to a smaller and smaller volume.

4. The band gap lies in the energy range for visible photons and so photons of visible light can promote electrons from the valence band to the conduction band. Electrons in both bands can then conduct electricity.
5. Si, Ge.

6. (a) *n*-type, (b) neither, (c) *p*-type, (d) *p*-type.
7. Carborundum, like silicon and germanium, has $4N$ valence electrons for a crystal of N atoms. The tetrahedral diamond structure will be favoured because all $4N$ electrons will then be in bonding orbitals and the energy is lower than in the higher coordination structure.

ANSWERS TO CHAPTER 5

1. $n_s \approx N \exp^{-\Delta H_s/2RT}$, where $\Delta H_s = 200 \text{ kJ mol}^{-1}$ and $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.

Table 5.9 Schottky defect concentration in MX compound at various temperatures

Temperature ($^{\circ}\text{C}$)	Temperature (K)	n_s/N	$n_s/(\text{mol}^{-1})$
27	300	3.87×10^{-18}	2.33×10^6
227	500	3.57×10^{-11}	2.15×10^{13}
427	700	3.45×10^{-8}	2.08×10^{16}
627	900	1.57×10^{-6}	9.45×10^{17}

2. Rearrange equation (5.4) and take logs:

$$\frac{n_s}{N} \approx \exp^{-\Delta H_s/2RT}$$

$$\ln \frac{n_s}{N} = -\frac{\Delta H_s}{2RT}$$

or

$$\log \frac{n_s}{N} = -\frac{\Delta H_s}{2.303 \times 2RT}$$

A plot of $\log n_s/N$ against $1/T$ gives a straight line plot passing through the origin. The slope of this graph, $-(\Delta H_s)/(2.303 \times 2R)$, gives a value of $183.4 \text{ kJ mol}^{-1}$ for ΔH_s . Dividing by Avogadro's number, 6.022×10^{23} , gives the enthalpy of formation of one Schottky defect, $3.045 \times 10^{-19} \text{ J}$.

3. Increasing the impurity levels does not affect the intrinsic (left-hand side) of the graph. It does, however, increase the value of σ (and thus of $\ln \sigma$) in the extrinsic region. As the activation energy, E_a , for cation movement stays the same, the slope of the graph is unchanged (Figure 5.38). The purer the crystal, the lower the transition temperature at which thermally generated defects take over.

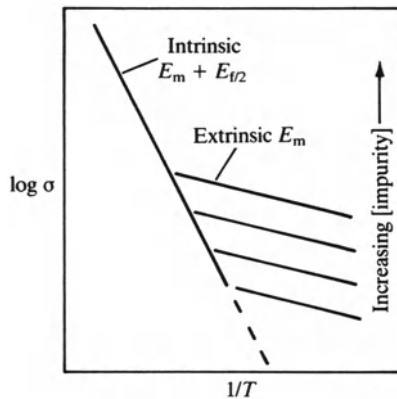


Figure 5.38 Schematic ionic conductivity of doped NaCl crystals. Parallel lines in the extrinsic region correspond to different dopant concentrations. (After West, A.R. (1984) *Solid State Chemistry and its Applications*, Wiley, 1984.)

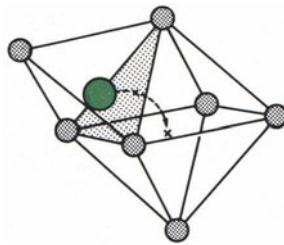


Figure 5.39 Path taken by an anion moving from tetrahedral coordination into an octahedral hole.

4. (a) Almost none. (b) Conductivity increases as two Na^+ ions are replaced by each Mg^{2+} ion, thus creating a vacancy each time. (c) Almost none. (d) Two Cl^- ions are replaced by each O^{2-} ion, creating anion vacancies; this will result in a small increase in conductivity because, although the major charge carrier is Na^+ , some current can be carried by the chloride ions.
5. The oxide has more highly charged ions (M^{4+} and O^{2-}) than a fluoride. This means that the coulombic interactions will be stronger and thus the energy of defect formation will be higher (see Table 5.1), so reducing the defect concentration at a given temperature.
6. The path is shown in Figure 5.39. The anion jumps from the tetrahedral site, through a trigonal position on the common triangular face and into the octahedral site at the body centre.

7. The anion at the body centre of the unit cell in Figure 5.3c is surrounded by six anions at distance $a/2$ and by four cations at a distance of $0.43a$. The interstitial site at the body centre of the unit cell in Figure 5.3a is surrounded by eight anions at a distance of $0.43a$ and by six cations at a distance of $a/2$.

For the normal anion site:

$r = 0.43 \times 537 \times 10^{-12} \text{ m}$ and $Z = +2$, for interaction with four cations. $r = 0.5 \times 537 \times 10^{-12} \text{ m}$ and $Z = -1$, for interaction with the six anions.

$$\begin{aligned} E &= -\left(\frac{2.31 \times 10^{-28} \text{ J m}}{537 \times 10^{-12} \text{ m}}\right)\left(\frac{4 \times 2}{0.43} + \frac{6 \times (-1)}{0.5}\right) \\ &= -(4.302 \times 10^{-19} \text{ J})(6.605) \\ &= -2.84 \times 10^{-18} \text{ J.} \end{aligned}$$

For the interstitial site

$$\begin{aligned} E &= -(4.302 \times 10^{-19} \text{ J})\left(\frac{8 \times (-1)}{0.43} + \frac{6 \times 2}{0.5}\right) \\ &= -(4.302 \times 10^{-19} \text{ J})(5.395) \\ &= -2.32 \times 10^{-18} \text{ J.} \end{aligned}$$

The energy of defect formation is the difference in energy between the two sites and so is given by

$$(-2.32 \times 10^{-18} \text{ J}) - (-2.84 \times 10^{-18} \text{ J}) = 5.2 \times 10^{-19} \text{ J.}$$

The experimental value for fluorite is given in Table 5.1 as $4.49 \times 10^{-19} \text{ J}$. This calculation gives a very good level of agreement considering that we have ignored all the more distant interactions, internuclear repulsion, lattice vibrations and lattice relaxation!

8. Both structures contain Ag^+ ions in tetrahedral sites, but in $\gamma\text{-AgI}$ half of the tetrahedral holes are occupied, so there is only one vacant equivalent site per Ag^+ ion, whereas in $\alpha\text{-AgI}$ there are five. Both structures contain vacant octahedral and trigonal sites. In $\gamma\text{-AgI}$ the octahedral holes lie at the body centre and at the midpoint of each edge. The trigonal sites lie on the triangular faces of the octahedra, where adjacent octahedra and tetrahedra join (Figure 5.40). Both structures have the same monovalent ions and a polarizable anion.

The jump from one tetrahedral site to another in $\gamma\text{-AgI}$ could take either of the routes sketched out in Figure 5.40, which first pass through a trigonal face and then through an octahedral hole. Alternatively (not shown) if the ion passed through only the top half of the octahedron it would be five-coordinate before passing through

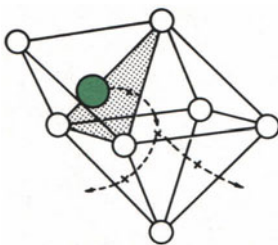


Figure 5.40

another three-coordinate face. All these routes would be of higher energy than the pathways we looked at for α -AgI.

9. I^- , S^{2-} , Se^{2-} and Te^{2-} are all polarizable anions.
10. In undoped β -alumina the excess Na^+ ions are balanced by additional oxygens in the conduction plane. Beyond a certain point, it seems likely that these will begin to block the motion of the Na^+ ions, as observed. By contrast, doping with Mg^{2+} suggests an alternative charge compensation mechanism: simple substitution for Al^{3+} ions in the spinel-like blocks allows extra Na^+ ions into the conduction planes without the need for oxygen interstitials. This is what happens in practice.
11. Unit cell volume is $(428.2 \text{ pm})^3 = 7.8513 \times 10^{-29} \text{ m}^3$. Mass of contents for iron vacancies:

$$[(4 \times 55.86 \times 0.910) + (4 \times 16.00)] / (N_A \times 10^3) \text{ kg giving a density of } 5.6534 \times 10^{-3} \text{ kg m}^{-3}.$$

Mass of contents for oxygen interstitial:

$$[(4 \times 55.85) + (4 \times 16.00 \times 1/0.910)] / (N_A \times 10^3) \text{ kg giving a density of } 6.2126 \times 10^{-3} \text{ kg m}^{-3}.$$

Comparing these theoretical values with the experimental value, we again see that the evidence supports an iron vacancy model.

12. From Table 5.6 we see that as the Fe:O ratio decreases the unit cell volume also decreases; this is the trend we would expect to see as more vacancies are introduced. If the interstitial model were correct, as the Fe:O ratio decreases, the number of interstitial oxygens rises and we would expect to see a slight increase in lattice parameter.
13. A crystal containing F-centres contains anion vacancies. We would expect, therefore, that the density would be lower than that of the colourless crystal.

14. (a) The central section has two Fe^{3+} ions in tetrahedral sites and seven vacancies, so it is known as a 7:2 cluster. (b) There are 32 oxide anions. There are seven octahedral vacancies and two $\text{Fe}_{\text{tet}}^{3+}$ interstitial ions, so there will be a total of 27 Fe cations. (There are two Fe^{3+} ions and six Fe_{oct} ions enclosed within the cluster. The outer layer will be the same as the Koch–Cohen cluster with $(8 \times \frac{1}{8}) = 1 \text{ Fe}_{\text{oct}}$ at the corners; $(12 \times \frac{1}{4}) = 3 \text{ Fe}_{\text{oct}}$ at the midpoints of the edges; and $(30 \times \frac{1}{2}) = 15 \text{ Fe}_{\text{oct}}$ on the faces; this makes 27 Fe ions in total.) The formula would be $\text{Fe}_{27}\text{O}_{32}$. (c) The 32 oxide ions provide 64 negative charges to be balanced. The two tetrahedral Fe^{3+} ions reduce this to 58 to be balanced by the ions in octahedral positions. Setting up simultaneous equations, we know that if x is the number of Fe^{2+} ions and y the number of Fe^{3+} , then

$$x + y = 25$$

and adding up the charges we get

$$2x + 3y = 58.$$

Solving gives $x = 17$ and $y = 8$.

15. **Titanium vacancies:** there are eight at the corners $(8 \times \frac{1}{8}) = 1$, and $(2 \times \frac{1}{2}) = 1$ on cell faces. **Titanium ions:** cell edges, $(4 \times \frac{1}{4}) = 1$. Cell faces, $(8 \times \frac{1}{2}) = 4$ on the top and bottom. There are five ions contained within the cell boundary, making 10 in total. The titanium stoichiometry of the unit cell is obviously representative of the whole structure: of the 12 sites, 10 are occupied and two are vacant. This is also true for oxygen. **Oxygen vacancies:** cell faces, $(4 \times \frac{1}{2}) = 2$. **Oxide ions:** cell faces, $(8 \times \frac{1}{2}) = 4$. Cell edges, $(8 \times \frac{1}{4}) = 2$. There are four ions contained within the cell boundary, making 10 in all.
16. Taking the titanium positions first: there are vacancies at all eight corners $(8 \times \frac{1}{8}) = 1$ and one vacancy in the centre of the cell, making two vacancies in all. There are no Ti^{2+} on cell edges. There are Ti^{2+} on only two of the faces, the top and bottom, which have four each, contributing $(2 \times 4 \times \frac{1}{2}) = 4$. There are four Ti^{2+} enclosed within the cell. Four edges have O^{2-} ions giving $(4 \times 1 \times \frac{1}{4}) = 1$; only the top and bottom faces have O^{2-} ions, and these have five each contributing $(2 \times 5 \times \frac{1}{2}) = 5$; there are four O^{2-} ions enclosed within the cell, making 10 in all. The overall content of this unit cell is thus Ti_8O_{10} , which corresponds to $\text{TiO}_{1.25}$.
17. The structure has Ti vacancies, every fifth Ti is missing. For every absent Ti^{2+} ion there must be two Ti^{3+} present or one Ti^{4+} .
18. The effects of sharing are shown in Figure 5.41.

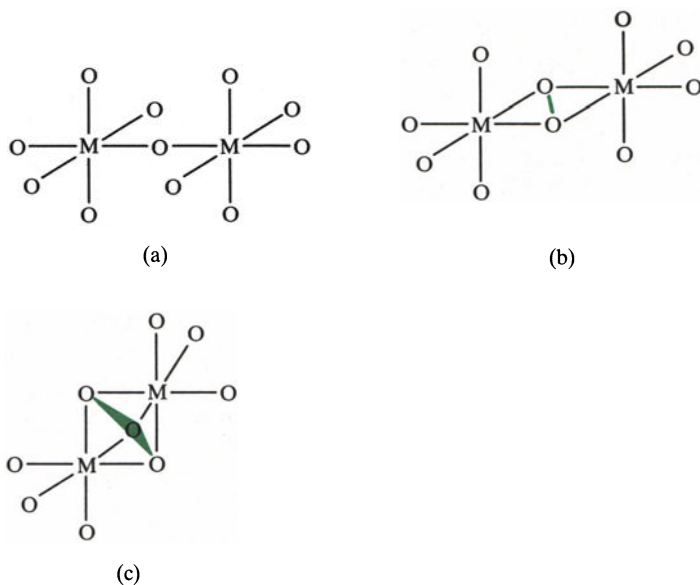


Figure 5.41 (a) Sharing a corner M_2O_{11} . (b) Sharing an edge M_2O_{10} . (c) Sharing a face M_2O_9 .

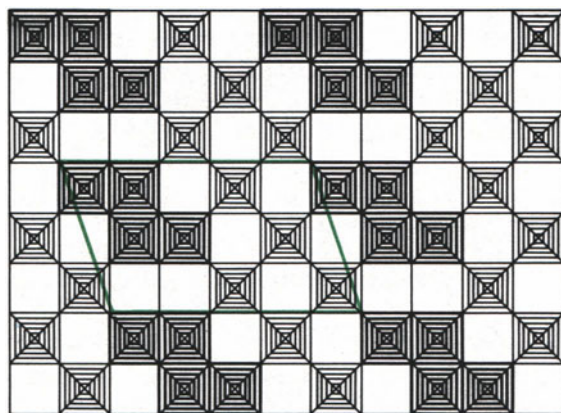
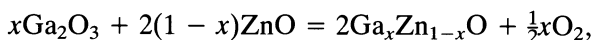


Figure 5.42 The structure of W_8O_{23} with the projection of a unit cell marked in colour.

19. Figure 5.42 shows the shear structure with a unit cell added. Within the boundary there is one group of four edge-sharing octahedra and four $[WO_6]$ octahedra. The formula is thus $W_4O_{11} + 4WO_3 = W_8O_{23}$.

20. Non-stoichiometric ZnO is an n -type semiconductor. Gallium ions entering the structure of ZnO have a charge of +3. If the Ga^{3+} substitutes for Zn^{2+} and the crystal maintains its stoichiometry, oxygen will be lost during the reaction. The electrons made available from the oxide ions becoming oxygen molecules will remain in the structure to effect the necessary charge compensation, thus enhancing the n -type semiconduction. An equation for the reaction is



where for simplicity we have used 1:1 ZnO.

ANSWERS TO CHAPTER 6

1. Polyphenylenevinylene has a π system delocalized over the benzene ring. It is likely that this is also delocalized over the conjugated double bond and hence to the benzene ring of the next unit. Thus, like polyacetylene, this polymer will have a delocalized π system, but it will include the π ring orbitals.
2. (a) Rb would lose an electron to the polyacetylene, forming Rb^+ , and give n -type polymer with a partially full conduction band. (b) H_2SO_4 would act as an electron acceptor and give p -type polyacetylene.
3.
$$8(\text{CH})_n + 9\delta n\text{HClO}_4 = 8[(\text{CH})^{\delta+}(\text{ClO}_4)^{\delta-}]_n + \delta n\text{HCl} + 4\delta n\text{H}_2\text{O}. \quad (6.7)$$
4. The potassium ions have oxidation state +1, the cyanide ions will contribute -1 and the bromine ions -1 also. Since the net oxidation state is 0, that of platinum is $-2 + 4 + 0.3 = 2.3$. Note that oxidation state is a formal concept and that the above result does not imply that there is a charge of 2.3 on each platinum.
5. If there were no interaction between the chains, $(\text{SN})_x$ would be a one-dimensional conductor and it would be expected at low-temperatures to obey Peierls' theorem. This would result in an insulating or semiconducting solid. The observation of low-temperature conductivity suggests that Peierls' theorem is not obeyed and one ready explanation of this is that the chains interact so that the solid no longer behaves like a one-dimensional system.
6. The alternating bond length suggests a partial localization of the d electrons. In polyacetylene, such bond alternation is the means by which a band gap is opened up and the same is probably true here. Thus, instead of the partly full band expected if the oxide were to adopt the TiO_2 structure, the d band splits so that there is a full band and an empty band.

7. Fluorine tends to attract electrons to itself and so TCNQF₄ is likely to be a stronger electron acceptor than TCNQ. The conducting properties of solids like TTF–TCNQ arise from partial transfer of electrons from one type of molecule to the other. TCNQF₄ is a sufficiently good acceptor to enable transfer of one electron per unit, thus completely filling the conduction band in one stack and completely emptying it in the other stack. So HMTTF–TCNQF₄ has no partially full bands and hence is not a metallic conductor.

ANSWERS TO CHAPTER 7

1. The peaks in the spectrum maximize at approximately –88, –93, –99 and –105 ppm. If you mark these values on the chart in Figure 7.13, then you will see that the best correspondence is to the four linkages: Si(OAl)₃(OSi), Si(OAl)₂(OSi)₂, Si(OAl)(OSi)₃ and Si(OSi)₄.
2. There is only one peak in the new spectrum at approximately –108 ppm. Reference to the chart in Figure 7.13 suggests that this is due to a Si(OSi)₄ environment. Clearly the treatment with SiCl₄ has removed all the tetrahedral Al from the framework. The intensity measurements on this peak indicate a Si/Al ratio of 55.
3. The starting sample (a) clearly shows the presence of tetrahedral Al in the framework (peak at 61 ppm). After treatment with SiCl₄ (b) the amount of Al in the framework has been reduced considerably but there is a very strong peak due to [AlCl₄][–] (at 100 ppm) and also a peak due to octahedral aluminium at 0 ppm. The first washings (c) remove Na⁺[AlCl₄][–] from the sample and repeated washing (d) also removes some of the octahedrally coordinated Al.
4. The chart in Figure 7.13 shows that the most likely Si environment for zeolite-A is Si(OAl)₃(OSi). However, we know that the Si/Al ratio is 1, so this coordination is not possible without systematically breaking Loewenstein's rule. It was spectroscopic work on this structure (and on zeolite ZK-4) that eventually confirmed the Si(OAl)₄ structure of zeolite-A with strict alternation of Si and Al and led to the extended ranges shown in the chart.
5. This system demonstrates reactant-selective catalysis. The branched hydrocarbons are too bulky to pass through the pore-openings in the catalyst.
6. We see here product-selective catalysis in operation: both reactant molecules are small enough to diffuse into the pores and be hydrogenated, but the slightly larger propane molecule cannot leave.

7. Zeolite-A (Ca) shows reactant selectivity. The straight-chain *n*-hexane can pass through the windows and undergo reaction but the branched-chain 3-methylpentane is excluded. The selective cracking of straight-chain hydrocarbons in the presence of branched chains is an important industrial process known as **selectoforming**, which improves the octane number of the fuel.
8. There are two possible reasons for the increased percentage of *para*-xylene. First, the increased crystal size increases the distance travelled by the diffusing molecules along the channels, giving more time for isomerization to the *para*-form. Second, the shape-selective reactions take place in the internal pores of the zeolites, rather than on the surface. Larger crystals have a higher ratio of internal to external sites, and so we would expect selectivity to improve.
9. As the Si/Al ratio increases, the —OH stretching frequency falls. This indicates a decrease in the covalent bond strength making ionization of H^+ easier, i.e. an increase in acid strength.

ANSWERS TO CHAPTER 8

1. In Mn^{2+} an electron can only go from one $3d$ level to another if it changes its spin. Transitions in which an electron changes its spin are forbidden and so give rise to weak spectral lines.
2. Radiation from a lamp excites electrons from the ground state, G, to states B, C and D. Electrons in states C and D undergo non-radiative transitions to state B. Radiative transitions from B to lower states are forbidden and so a large population of electrons in state B builds up. Eventually a photon is emitted and an electron goes to state A. This photon induces further emission from B to A, eventually producing a beam of laser light. Transitions from B to both A and G must be forbidden for a large population to build up in B, but the transition $B \rightarrow A$ must be less forbidden than the transition $B \rightarrow G$ as it is $B \rightarrow A$ that gives rise to laser action, and hence must be the more likely to occur.
3. ZnS is a semiconductor with a full valence band and empty conduction band. When the phosphor is illuminated, electrons are promoted to the conduction band. Since the orbitals in this band are delocalized, the energy can easily be transferred to other parts of the crystal, in particular to the dopant atoms.
4. The sensitizer acts like an impurity. It absorbs the radiation and goes to an excited state. The excited electron undergoes a radiationless

transition to a level in the conduction band of AgBr. Since it is now in a delocalized level, the electron can travel through the crystal until it combines with an interstitial Ag^+ ion to form a silver atom. The indirect band gap helps by reducing the probability of the electron in the conduction band dropping into a vacancy in the valence band. The process is similar to that of phosphors. However, with phosphors it is the light emitted by the impurity that is important whereas for photography it is the light absorbed by the sensitizer that matters.

5. The solid has an indirect band gap because the lowest energy inter-band transition (that is from the highest energy level in the valence band to the lowest energy level in the conduction band) does not correspond to $\Delta\mathbf{k} = 0$ and is therefore forbidden.
6. Silicon is an indirect band gap solid with an available non-radiative pathway from the conduction band to the valence band. In photovoltaic cells electrons are promoted from the valence band to the conduction band and are then used to do electrical work. The promoted electrons do not return directly to the valence band either by emitting energy or by a non-radiative pathway. In LEDs it is the return of the electrons to the valence band by emitting light that is important. This return has low probability because of the indirect band gap and the electrons use the non-radiative pathway instead. Promotion to the conduction band in the solar cell will also be of low probability but there is no competing non-radiative route.
7. These oxides (at least formally) contain small highly charged ions. These have low polarizability and hence impart high refractive indices.

ANSWERS TO CHAPTER 9

1. Because the manganese atoms are further apart, the overlap of the $3d$ orbitals will be less. The $3d$ band will therefore be narrower than in manganese metal. With a narrower band there is a larger inter-electronic repulsion and a state with a number of unpaired spins comparable to the number of atoms becomes favourable. The alloy is thus ferromagnetic.
2. The magnetically ordered unit cell is identical to the high-temperature (paramagnetic) unit cell, so that all the layers of europium ions must be aligned with their spins parallel, giving a ferromagnetic compound.
3. The Zn^{2+} and half the Fe^{3+} ions are on octahedral sites with spins aligned, and the remaining Fe^{3+} ions are on tetrahedral sites aligned antiparallel. The net moment of the Fe^{3+} ions is zero. As all the

electron spins are paired in Zn^{2+} ions, there is no overall magnetic moment and the compound is antiferromagnetic.

4. In MnS_2 the $3d$ electrons are localized on the evidence given. Above the Néel temperature, the solid is an insulator with a paramagnetic susceptibility corresponding to five unpaired electrons per Mn and this could be explained on the basis of filled bands below the $3d$ level and localized $3d$ electrons. Below the Néel temperature, the localized electrons on different Mn ions interact to cancel out magnetic moments, possibly through a superexchange mechanism involving the disulphide ions.

The properties of FeS_2 suggest that all spins are paired, either in a band or localized on the iron ions. There are six $3d$ electrons per Fe ion and this is just enough to fill the lower t_{2g} band. The semiconducting properties suggest that there is an empty band not much higher in energy. This is probably the e_g band.

In CoS_2 there are enough electrons to partly occupy the e_g band and thus this compound is metallic. The band is narrow and so gives rise to ferromagnetism.

5. The effect of deuterium substitution suggests that the hydrogen atoms are displaced when the ferroelectric phase is formed.

ANSWERS TO CHAPTER 10

- In the analogy, each person represents a Cooper pair and the linking of arms denotes the overlap between the pairs, giving an ordered system. Because of the ordered collective motion, scattering from defects – tripping over potholes – cannot take place! The analogy breaks down in that it allows for overlap only between adjacent pairs rather than over large numbers; also, the loss of superconductivity leads to the scattering of individual electrons, not of individual Cooper pairs.
- The packing diagram for the A-type unit cell is shown in Figure 10.12. The contents of the unit cell are as follows: 12 O atoms midway on cell edges, each shared by four unit cells; one Ca atom at the body centre, eight Ti atoms at the cube corners, each shared by eight unit cells: $[(12 \times \frac{1}{4})\text{O} + 1\text{Ca} + (8 \times \frac{1}{8})\text{Ti}] = 3\text{O} + 1\text{Ca} + 1\text{Ti} = 1$ formula unit. The Ca in the centre is surrounded by 12 O atoms, and eight Ti atoms at the corners of a cube. A Ti atom is surrounded octahedrally by six O atoms, and by eight Ca atoms at the corners of a cube. An O atom is linearly coordinated by two Ti atoms and by four Ca atoms in a square-planar configuration.

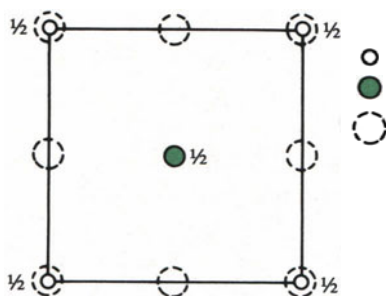


Figure 10.12 Packing diagram for a unit cell of perovskite, $\text{ABO}_3/\text{CaTiO}_3$.

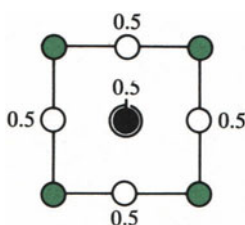


Figure 10.13 Packing diagram for a perovskite B-type cell.

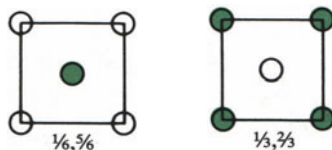


Figure 10.14 Layer sequences for K_2NiF_4 .

The packing diagram for the B-type cell is shown in Figure 10.13. This has the Ti/B atom at the centre of the cell and the Ca/A atoms at the corners, each shared by eight other unit cells; there are six face-centred oxygen atoms, each shared by two unit cells. Counting up as before gives $[(8 \times \frac{1}{8})\text{Ca} + 1\text{Ti} + (6 \times \frac{1}{2})\text{O}] = 1\text{Ca} + 1\text{Ti} + 3\text{O} = 1$ formula unit. The coordination geometry of course remains identical; we have only moved the origin of the unit cell.

3. The packing diagrams for the layers at $\frac{1}{6}$ and $\frac{1}{3}$ (and $\frac{5}{6}$ and $\frac{2}{3}$) in c are shown in Figure 10.14.

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