

Shin-ichi Uchida

High Temperature Superconductivity

The Road to Higher Critical Temperature



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Preface

At the time of writing this book, in the summer 2014, the highest superconducting transition temperature T_c remains 135 K which was recorded in 1993 for one of the copper oxide compounds. The “silence” period over 20 years is the longest since the recorded history of superconductivity started from 1911. The second longest silence was between 1973 and 1986, the period between the discovery of Nb_3Ge with $T_c=23$ K and the discovery of high- T_c superconductivity in copper oxides. During this period between 1973 and 1986, researchers of superconductivity were pessimistic for further rising T_c , and superconductivity at liquid nitrogen temperature was only a dream, as it was believed that superconductivity was a very low-temperature phenomenon. However, in the present silence period, researchers are no longer pessimistic, since they know that high- T_c superconductivity is real and that there is no reason that T_c does not increase beyond 135 K. So, it is a realistic challenge in material sciences to search for new superconducting materials with higher T_c and/or to enhance T_c of the known superconducting materials.

In contrast to the long silence in T_c , several material families have successively been found to show superconductivity at temperature higher than the old record 23 K such as MgB_2 and iron arsenides. Like copper oxides, most of them were not expected to be superconductors before their discovery. Notably, these superconductors are from completely different material families than copper oxides, encouraging researchers to search for new high- T_c superconductors in materials yet to be investigated.

To unravel the mechanism of high- T_c superconductivity in copper oxides remains a challenging problem of physics. Nevertheless, there has been well advanced understanding of their unusual physical properties, various ordering phenomena other than superconductivity, and in particular of the electronic and structural parameters that influence T_c . We now understand why T_c of one copper oxide is higher than T_c of another one. T_c of conventional superconductors is rather a trivial problem. It is basically understandable in the framework of the Migdal-Eliashberg theory developed from the original Bardeen-Cooper-Schrieffer (BCS) theory, even though the theoretical calculations do not necessarily reproduce T_c of real material precisely. On the other hand, T_c 's of most of the high- T_c superconductors show a broad distribution within each family due to unusual sensitivity to electron concentration,

lattice disorder in the lattice, and so on. This, in turn, will give an experiment-based strategy for enhancing T_c in the known high- T_c families. Also, we have learned from various different high- T_c families what the common ingredients are among these families, which will provide a guide for searching out new high- T_c superconductors. Thus, it is now possible to develop a new approach to the problem of T_c on the basis of the results from the long and extensive study of the copper oxides and the lessons learned from a plethora of different high- T_c families. This is a main objective of this book.

This book has been written aiming to provide non-specialist readers with an in-depth overview of the past, present, and future of high-temperature superconductivity. Specialist readers will be given up-dated information on the research forefront of the study of various high- T_c families and some hints on the possibility of enhancing T_c and on finding new high- T_c materials. A message that the author would like to pass to researchers of the younger generation and graduate-course students is not to give up the challenges to the problems of high-temperature superconductivity.

Tokyo

Shin-ichi Uchida

Acknowledgements

The author of this book started his research of superconductivity in 1984 motivated by the unusual oxide superconductor $\text{BaPb}_x\text{Bi}_{1-x}\text{O}_3$. Since 1986, the high- T_c copper oxides have continued to be the main subject of his laboratory, and from 2008 iron arsenides/selenides were added as a research target. He was involved in the discovery of some copper oxide superconductors and borocarbides. Many parts of this book are based on the experimental results that are due to the dedicated persistent efforts by the former students, H. Sato, T. Ito, T. Ido, S. Ishibashi, Y. Nakamura, K. Takenaka, K. Tamasaku, T. Noda, K. Fujita, M. Ishikado, H. Hobou, Y. Hirata, S. Ishida, M. Nakajima, T. Liang, L. Liu and many others. In particular, the author would like to acknowledge long-standing experimental collaboration with J.C. Seamus Davis, H. Eisaki, A. Fujimori, C.-Q. Jin, K.M. Kojima, Z.-X. Shen, S. Tajima, H. Takagi, Y. Tokura, J.M. Tranquada, and Y.J. Uemura. He has been inspired also by the discussions with many theorists, particularly, with T.P. Devereaux, D.-H. Lee, S. Maekawa, and N. Nagaosa.

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Chapter 1

Introduction

Abstract Triggered by the discovery of high-transition-temperature (high- T_c) superconducting copper oxides in 1986, seven different material families have been found to show superconductivity at temperatures higher than 23 K, the record high- T_c value before 1986. Six of them have T_c 's not reaching 40 K, but the copper oxides and the iron compounds are distinct from others in their outstandingly high T_c values, 135 K and 55 K, respectively and unconventional Cooper pairs. Most of them do not obey the Matthias rules which gave a guiding principle for finding new superconducting materials with high T_c . Instead, several features emerge in common with most of the high- T_c families. In this chapter, are raised basic questions; what makes T_c high in each family and why copper oxides and iron compounds are so special with central concern on a possibility of enhancing T_c .

The discovery of high temperature superconducting copper oxides by Bednorz and Müller [1] in 1986 opened up a new era of superconductivity. Since then, eight (nine) different families of materials have continually been discovered and joined the group of high temperature superconductors (HTSCs) with their superconducting critical temperature (T_c) exceeding 23 K recorded in 1973 for A15 intermetallic compound Nb_3Ge [2]. The HTSC families are in the order of the discovery year indicated in parentheses; (1) layered copper oxides built up of the CuO_2 planes (discovered in 1986), (2) bismuth oxides, $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$, with perovskite structure (1988) [3], (3) fullerenes composed of C_{60} molecules (1991) [4], (4) borocarbides, $\text{YPd}_2\text{B}_2\text{C}$ (1994) [5], (5) transition-metal chloronitrides, HfNCl (1998) [6], (6) magnesium diborides, MgB_2 (2001) [7], (7) elemental calcium (Ca) metal under high pressure (2006) [8], (8) iron arsenides/selenides (2008) [9]. The T_c -histogram is shown in Fig. 1.1 for these eight families. Picene ($\text{C}_{22}\text{H}_{14}$), a member of the polycyclic aromatic hydrocarbons, was found to show superconductivity at 18 K in 2009 [10]. Afterward, $T_c \sim 30$ K was reported for its relative, but superconductivity has not been fully confirmed yet. From heavy fermions, a representative family of strongly interacting electrons, PuCoGa_5 achieved $T_c = 18$ K [11]. These are from surprisingly different families of materials, so high temperature superconductivity is now ubiquitous and possibility of finding a new HTSC in a different family of

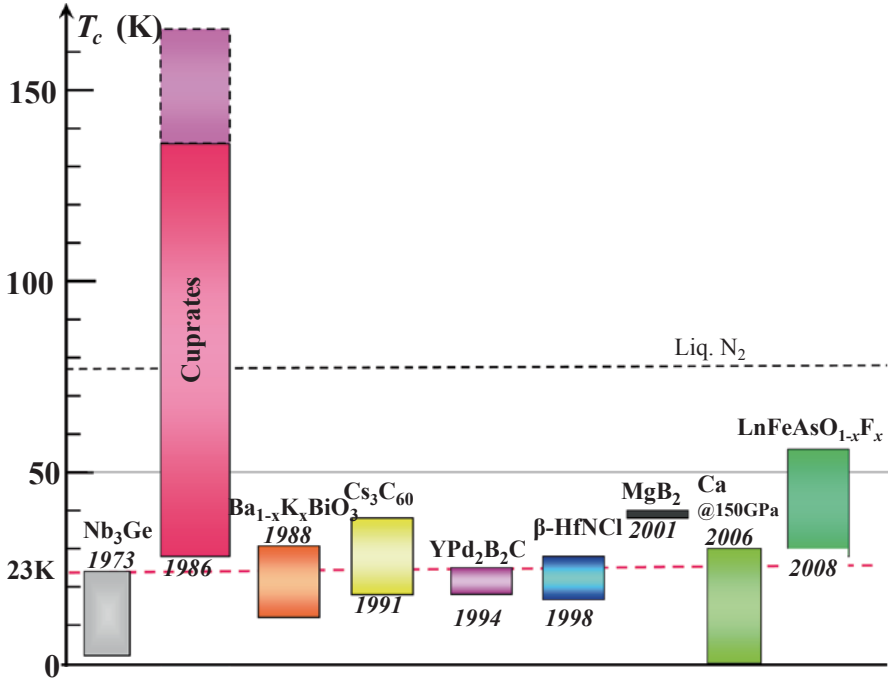


Fig. 1.1 T_c histograms. Distribution of T_c and the maximum value of T_c for each family of high- T_c superconducting materials discovered since 1986. Representative material and the year of discovery are indicated

materials is high. Ubiquitous high- T_c superconductivity has changed a landscape of physics and chemistry of superconductivity.

Before 1986 a guiding principle for finding new superconducting materials with high T_c was the so-called Matthias rules [12] such as

- #1: find cubic crystals,
- #2: find d -electron metals,
- #3: find metals with the average number of valence electrons, preferably odd numbers 3, 5, and 7,
- #4: exclude metals showing or in close vicinity of magnetism,
- #5: exclude metals near a metal-insulator transition such as oxide materials.

These rules successfully lead to the finding of the A15- Nb_3Ge . The Matthias rules apply to metals with high electron density or high electron density of state at the Fermi level which are favorable for high T_c in the framework of the Bardeen-Cooper-Schrieffer (BCS)—Migdal-Eliashberg theory. Interestingly, the newly discovered high- T_c materials are in most cases completely outside the Matthias rules.

Despite the discovery of a number of HTSCs in the past 28 years, the rise of T_c has stopped for over 20 years, since the highest T_c value of 135 K at ambient pressure [13] (164 K at pressure of 30 GPa [14]) was recorded for the Hg-based copper oxide in 1993. The period of this “silence” is longest in the history of superconductivity

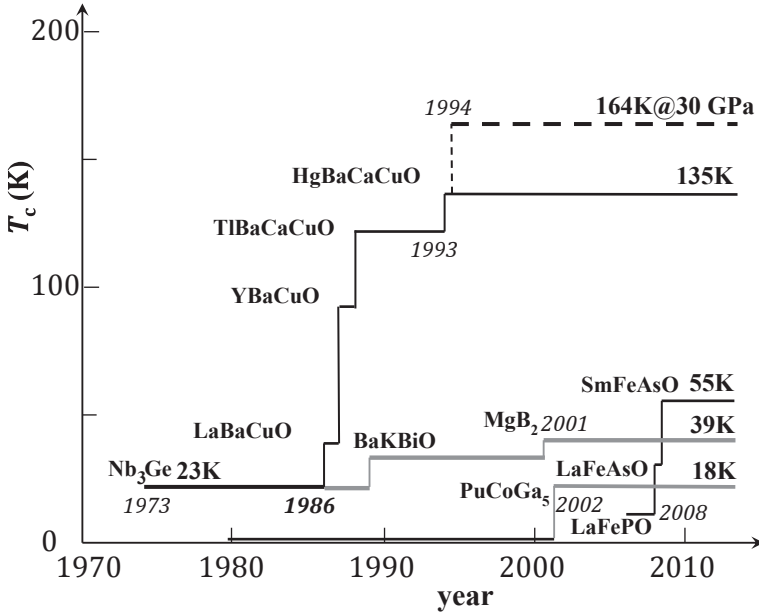


Fig. 1.2 History of T_c (T_c vs year) for four representative classes of superconductors, cuprates, iron-based compounds, superconductors with phonon-mediated pairing, and heavy-fermion superconductors

(see the curves T_c —year shown in Fig. 1.2). The second longest silence was 13 years from 1973, the year of the discovery of Nb_3Ge , to 1986. Therefore, to break the silence and to find a material with higher T_c is one of the most challenging problems in material sciences.

Among eight (nine) families of HTSCs so far discovered, six (seven) are superconductors with $T_c^{\max}$ lower than 40 K. In most of them the electron-electron attractive interaction mediated by phonons is thought to be a major pairing interaction. In particular, MgB_2 with the highest T_c (=39K) among the six (seven) is obviously a phonon-mediated superconductor as conventional superconductors, and its high T_c value is understood in the framework of the (BCS) Migdal-Eliashberg theory. For others, a usual application of the Migdal-Eliashberg theory is difficult to explain high T_c values and additional effects, such as electronic correlations, which may enhance the electron-phonon coupling seems to be at work.

The copper oxides and the iron compounds are distinct from others in their outstandingly high T_c values, $T_c^{\max}=135\text{K}$ for the former and 55 K for the latter [15], and unique in their material diversity. In both families T_c is material dependent despite having the common structural units. Also, common with these two systems is superconductivity with unconventional pairing symmetry and emergent by doping into parent compounds showing an antiferromagnetic order. Both evidence an important role of repulsive electron-electron interaction (electronic correlation) in

the formation of Cooper pairs. Although the mechanisms of Cooper pair formation in both systems are still under hot debate, the understanding of the two systems have well advanced thanks to the intense and persistent experimental and theoretical efforts. Also, on the basis of more than 28 years accumulation of a huge number of experimental data and improvement of the crystal quality we can specify factors (material parameters) that influence T_c and hence are sources of diverse T_c values in each family. Now it is ready to address the basic questions on the high- T_c values in these families;

- i. Why the two families are distinct from others,
- ii. Which factors are most influential on T_c ,
- iii. How each factor affects the electronic state in the normal state and the superconducting properties,
- iv. Whether or how one can find a possibility to enhance T_c .

The Matthias rules no more apply to the new HTSCs. Many of them have *layer* structures. Most are in close vicinity of metal-insulator phase transition boundary, thereby having *low carrier density* and *low superfluid density*. In addition, most families contain *light elements* (B, C, N, or O) which take part in *strong chemical bond*. Notably, *strong electronic correlations* play a dominant role in the formation of Cooper pairs in the copper oxides and the iron compounds with the highest T_c 's among all. Electronic correlations also play a role in enhancing electron-phonon interaction and hence T_c in many of the families. Certainly, these features constitute a new paradigm in the physics and chemistry of superconductivity and provide an experiment-based strategy for finding new high- T_c superconducting materials.

This book presents “physics of T_c ” of new high- T_c superconductors. Starting from an overview of HTSCs with possible phonon-mediated superconductivity in Chap. 2, major emphases are put on the factors which influence T_c and give rise to diverse T_c values for the two unconventional high- T_c superconducting materials, the copper oxides (Chap. 3) and for the iron-based high- T_c superconductors (Chapter 4). In each chapter, a possibility of enhancing T_c or a possible route toward higher T_c are discussed. In Chap. 5 are summarized necessary ingredients for high- T_c superconductivity learned by the lessons from the study of variety of HTSCs. Finally, with a particular emphasis on the role of electronic correlations played in HTSC, is proposed new possible high- T_c superconducting materials that would hopefully follow the cuprates and iron-based compounds.

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Chapter 2

Overview of Superconducting Materials with T_c Higher than 23 K

Abstract Among the eight families of high- T_c superconductors, magnesium diboride (MgB_2), borocarbide ($\text{YPd}_2\text{B}_2\text{C}$), and calcium (Ca) at high pressures are thought to be conventional superconductors with phonon-mediated pairing. $T_c = 39$ K for a simple metal MgB_2 is surprising in view of the old-known ceiling of 30 K of the electron-phonon mechanism. Several circumstances in MgB_2 appear to optimize the phonon-mediated pairing and to up-shift the old ceiling of T_c . These give a hint on further optimization or further enhancement of T_c . In doped bismuthates (BaBiO_3), fullerenes (C_{60}), and chloronitrides (HfNCl), dominant pairing interaction is also supposed to be electron-phonon coupling. These superconductors are proximate to insulating phases. Because of this, the electron (carrier) density is significantly low as compared to that in simple metals, suggestive of contribution from electron-electron interactions which may act to strengthen electron-phonon coupling. One other family, from organic compounds, is going to join the latter group. Copper oxides and iron arsenides/selenides, as well as heavy fermions compounds, are distinct from others, and obviously belong to unconventional superconductors with dominant electron-electron interactions.

2.1 Introduction

Among the eight families of high- T_c superconductors (HTSCs), superconductivity in $\text{PdY}_2\text{B}_2\text{C}$, MgB_2 , and elemental Ca in the high-pressure phase is discussed in the context of superconductivity with the phonon-mediated pairing interaction. Superconductivity in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ (BKBO), doped C_{60} and $\beta\text{-HfNCl}$ are also supposed to be phonon-mediated, but the estimated T_c values are significantly lower than those of real materials. As these three are in proximity to some insulating phases, it is plausible that contributions from electron-electron interactions (electronic correlations) enhance the electron-phonon coupling. A possible high- T_c organic superconductor, doped polycyclic-aromatic-hydrocarbon, might join the second group. All these families, except Ca, have light elements, B, C, N, or O and strong covalent bonds, so that large energy prefactor Ω_θ (phonon frequency) and strong electron-phonon coupling λ in a simplified formula, $k_B T_c \sim \hbar \Omega_\theta e^{-1/\lambda}$, are presumably important factors for high T_c 's.

Although there is uncertainty in evaluating the parameter for screened/renormalized Coulomb interaction, usually parameterized by μ^* , the calculation of T_c in the framework of the Migdal-Eliashberg theory successfully reproduces $T_c = 39$ K of MgB_2 , the highest T_c so far achieved in obviously weakly correlated systems. $T_c = 39$ K for a simple metal MgB_2 is surprising in view of the old-known ceiling of 30 K of the electron-phonon mechanism. Several circumstances appear to be optimized in MgB_2 to allow for very strong electron-phonon coupling without inducing lattice instability.

Copper oxides and iron arsenides/selenides, as well as PuCoGa_5 with $T_c = 18$ K derived from heavy fermions compounds, are distinct from others, and obviously belong to unconventional superconductors with dominant electronic correlations.

2.2 Materials with Phonon-Mediated Pairing

For superconductors with phonons as pairing glue, T_c is understood or the T_c value is calculated in the well-established framework of the Migdal-Eliashberg theory. Two important parameters that determine T_c are the electron-phonon coupling strength λ and the phonon frequency Ω_0 . Large Ω_0 and strong λ are favorable for high T_c , while the phonon energy $\hbar\Omega_0$ needs to be considerably smaller than the Fermi energy E_F of the electronic system, $\hbar\Omega_0 \ll E_F$ (the Migdal (retardation) condition). The Migdal condition is necessary for the bare Coulomb repulsive interactions (μ) between electrons to be significantly renormalized (decreased);

$$\mu^* = \mu / [1 + \mu \ln (E_F / \hbar\Omega_0)].$$

The coupling strength λ is usually expressed by

$$\lambda = N(E_F) \langle I^2 \rangle / M \langle \omega^2 \rangle = N(E_F) V_{ph},$$

with $\langle I^2 \rangle$ being the mean-square electron-phonon matrix element averaged over the Fermi surface, $N(E_F)$ the electron density of states at the Fermi energy, M the ion mass, $\langle \omega^2 \rangle$ the averaged square phonon frequency, and V_{ph} , the effective electron-phonon interaction. In a crude approximation, that is a guide for extracting important parameters for T_c , $\langle \omega^2 \rangle \sim K/M$ (K , stiffness of the lattice) and T_c is approximated by the McMillan formula, $k_B T_c \sim \hbar\Omega_0 e^{-1/(\lambda - \mu^*)}$. More rigorously, T_c is expressed by the McMillan-Allen-Dynes formula [1]. In the strong coupling limit (large λ), the formula has an asymptotic form, $T_c \sim \lambda^{1/2}$, and T_c continues to increase, if other parameters are kept unchanged.

These equations suggest that larger $N(E_F)$, $\langle I^2 \rangle$, and Ω_0 are favorable for higher T_c values. Some of the old Matthias rules, #1: cubic crystals #2: d -electron metals, and #3: special average number of valence electrons, are guides to a search for materials with larger $N(E_F)$. Also, metals composed of light elements (small M) with stiff lattice (large K), hence large Ω_0 , were candidates for high- T_c SC. Since V_{ph} is

independent of M and $\Omega_0 \sim 1/M^{1/2}$, it was expected that materials composed of light elements would have a large Ω_0 and a substantial λ . Metallic hydrogen (H) was supposed to be the limiting case as predicted in 1968 [2], but realization of HTSC in metallic hydrogen remains challenging.

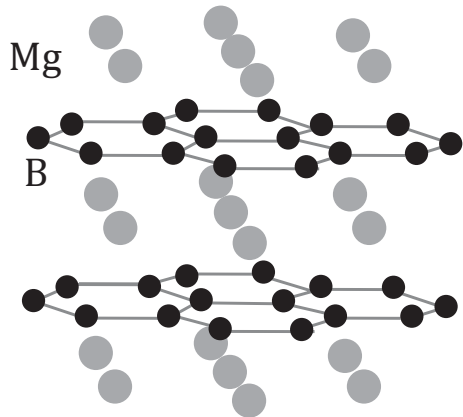
However, there were discussions on the T_c ceiling for SC with phonon mediated pairing:

1. The magnitude of T_c is bound by the inequalities, $k_B T_c \ll \hbar \Omega_0 \ll E_F$, so it was thought that T_c could not be high.
2. Large $N(E_F)$ is a characteristic of narrow band metals which implies a small E_F . This tends to make the renormalization of repulsive interaction weaker. Materials with a pronounced peak in $N(E)$ at E_F which was expected by the Matthias rule #3, have tendency for electronic and structural instabilities and their T_c would be sensitive to disorder or impurities.
3. The old idea, which is not necessarily correct, is that Ω_0 and λ are not independent parameter; when Ω_0 is large, λ cannot be large, since the formula for λ contains Ω_0^2 in its denominator.
4. T_c for SC in the strong coupling regime is thought to monotonically increase following the Allen-Dynes formula, $T_c \sim \lambda^{1/2}$. However, even so, too strong electron-phonon coupling induces a structural instability which gives a ceiling.

2.3 High- T_c Superconductivity in MgB_2

In this regard, MgB_2 with $T_c = 39$ K is a surprising material [3]. As shown in Fig. 2.1, the crystal structure consists of a stack of hexagonal honeycomb Mg layer sandwiched by hexagonal B layers above and below. It is a sort of fully intercalated graphite structure. The B-B bond is a strong covalent bond arising from the sp^2 hybridization, and hence the corresponding bond-stretching phonon modes have high frequencies ($\Omega_0 \sim 1000 \text{ cm}^{-1}$) [4]. MgB_2 is obviously a simple metal in the normal

Fig. 2.1 Crystal structure of MgB_2



state and phonon-mediated SC is evidenced, for example, by the boron isotope effect (for $^{10}\text{B} \rightarrow ^{11}\text{B}$ isotope substitution T_c decreases by 1 K [5]). MgB_2 is basically a weakly correlated (*s*)*p*-band metal with large Fermi energy $E_F \sim$ several eV which is much larger than the highest energy phonon (~ 0.1 eV), so that SC is understood within the framework of the Migdal-Eliashberg theory. Indeed, the calculation of T_c based on the density-functional theory (DFT) and linear-response theory (LRT) in the local-density approximation (LDA) successfully reproduces $T_c = 40$ K [6], though the renormalized Coulomb repulsion μ^* is adjusted to $\mu^* = 0.09\text{--}0.13$ which are used for conventional superconductors.

The crucial ingredients for the high- T_c value in MgB_2 are thought to be the followings:

1. Layer structure: $N(E_F)$ maintains a substantial magnitude even when E_F is located near the band edge, since the electronic density of states is nearly constant against energy in two dimensions.
2. Strong sp^2 bonding: Layer structure favors sp^2 hybridization/bonding. The sp^2 bond is much stronger than *d-d* bond, and even stronger than sp^3 .
3. Light element B: Combined with the strong sp^2 bond leads to very large Ω_0 .
4. Very strong electron-phonon coupling without instability: There is a cylindrical FS (so-called σ -FS) with character of strong bonding orbitals (E_F crosses the sp^2 hybridized bands) which couples strongly to the B-B bond stretching phonon modes. The calculated deformation potential Σ_D , a change of electronic band energy due to lattice distortion by a unit length ($\text{\AA}$) corresponding to a specific phonon mode, is $\Sigma_D = 13 \text{ eV} / \text{\AA} (\langle I^2 \rangle \propto \Sigma_{D^2})$. If the electronic system very strongly couples with a particular phonon mode at momentum Q , the frequency of this phonon is strongly renormalized and softened, and the lattice becomes unstable. In the case of MgB_2 the relevant FS is circular associated with 2D parabolic bands, so there is no nesting Fermi surface nor a special Q . The electron-phonon coupling is very strong ($\lambda \sim 0.82$) for phonons in the two bond-stretching branches. This gives rise to nearly constant Ω -renormalization over a range of Q 's with Ω remaining large, and thereby the material avoids a structural instability.
5. Band degeneracy $n_B = 2$: MgB_2 is a multiband/multiple FS system. There are two almost identical but separated σ -FSs which are relevant to the strong coupling with phonons in the two bond-stretching mode branches exist in the 1st BZ. In this case λ is further enhanced by a factor of $n_B^2 = 4$ [7]. These seem to conspire to optimize the phonon-mediated superconductivity in MgB_2 .

2.4 Other Electron-Phonon Superconductors with Fairly High T_c

2.4.1 Doped Bismuthate $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$

$\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ (BKBO) shows superconductivity at $T_c \sim 30$ K [8, 9]. The parent compound BaBiO_3 is a distorted perovskite oxide (see Fig. 2.2a), and a three-

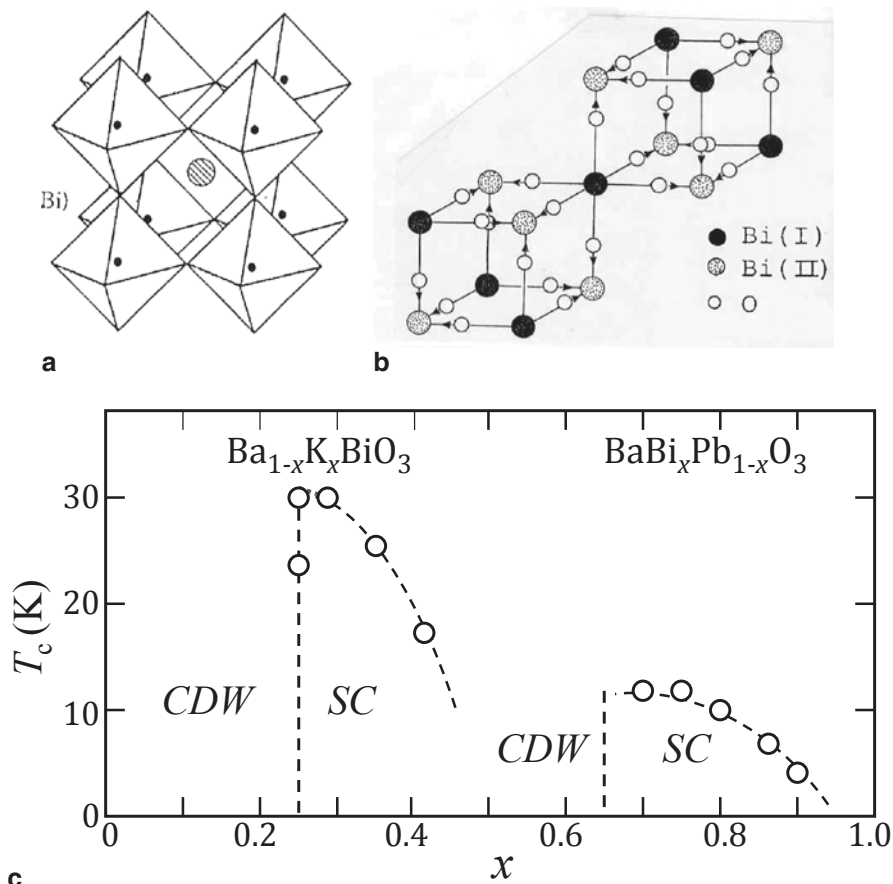


Fig. 2.2 **a** Idealized perovskite structure of BaBiO_3 . Actual structure is distorted due to breathing-mode distortion and rigid rotation of BiO_6 octahedra. **b** Breathing-mode distortions in the CDW state of BaBiO_3 which make the compound insulating with inequivalent neighboring Bi atoms [10]. **c** Temperature (T)-doping (x) phase diagram of doped BaBiO_3 , $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ and $\text{BaPb}_x\text{Bi}_{1-x}\text{O}_3$. The superconducting region is bounded by a half-dome in both cases. Most of the remaining region is CDW state which is so robust that the CDW transition temperature is too high to be chased

dimensional charge-density-wave (CDW) insulator with a CDW gap of 2 eV [10]. CDW is supposedly an array of alternating Bi^{3+} ($6s^2$ -lone pair) and Bi^{5+} (closed shell ion). In reality, only little charge difference on the Bi sites is observed, but the oxygen sites are distorted, the breathing-mode distortion—the O atoms expanding around a Bi atom and shrinking around the neighboring Bi atom as sketched in Fig. 2.2b. The CDW order is quite stable and never melts up to temperature 1000 K. It melts by substituting (doping) K for Ba ($x \sim 0.3$) or Pb for Bi ($\text{BaPb}_x\text{Bi}_{1-x}\text{O}_3$, $x \sim 0.6$), giving way to superconductivity. The phase diagram is displayed in

Fig. 2.2c. The CDW order occupies a wide region of the phase diagram and is quite stable. As a consequence of the robust CDW, strong CDW fluctuations either static or dynamical, remain viable even in the SC regime [11].

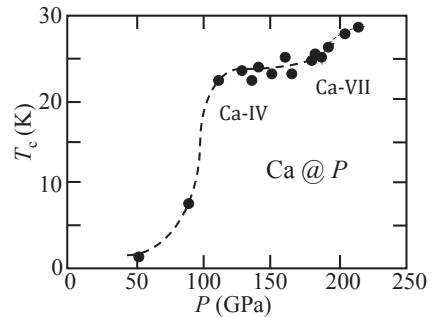
The electron-phonon coupling estimated by the DFT and LRT in the local-density approximation (LDA) is $\lambda=0.34$ [12] which is well below the value required to account for SC with $T_c \sim 30$ K. This failure indicates some correlations beyond LDA need to be incorporated, since the LDA tends to underestimate λ due to over-screening. This is particularly the case with materials in the vicinity of a metal-insulator transition. SC in the doped bismuthates is realized in the metallic side of the CDW insulator-metal transition and T_c is high in close vicinity of the transition. An attempt to go beyond LDA shows that λ is enhanced by a factor of 3 by taking into account of nonlocal electronic correlation effect arising from a poor screening [13]. The value of $\mu^* \sim 0.1$ is estimated by first-principle calculations. Using the enhanced λ , the renormalized Ω , and μ^* , T_c is calculated to be 30 K from the modified McMillan equation.

2.4.2 Elemental Superconductors at High Pressures

In the last 15 years a number of elements have been found to be SC with fairly high T_c values under pressures (P) of 30–50 GPa or higher. These include sulphur (S) ($T_c = 17$ K) [14], lithium (Li) ($T_c = 20$ K) [15], yttrium (Y) ($T_c = 20$ K) [16], and calcium (Ca) ($T_c = 29$ K) [17, 18]. As in the case of MgB_2 , for these elemental SCs the LDA-based calculations appear to be successful in deriving large λ and estimating high T_c . Li is an s -electron metal and is not expected to have large electron-phonon coupling λ despite its light atomic mass. In fact, T_c of Li at ambient pressure is only 100 μK . The enormous increase of T_c at high pressures is ascribed to the transformation from an s -band metal to an s - p metal [7] in which the covalent character is possibly added to the bonding and thus Li may possess necessary ingredients for high T_c in common with MgB_2 .

Ca in the high- P phases have distinctly higher T_c and joins the group of HTS. As plotted in Fig. 2.3, T_c rapidly rises in the P range between 50 and 100 GPa, reaching

Fig. 2.3 T_c of calcium plotted as a function of pressure (the data points are from [17, 18])



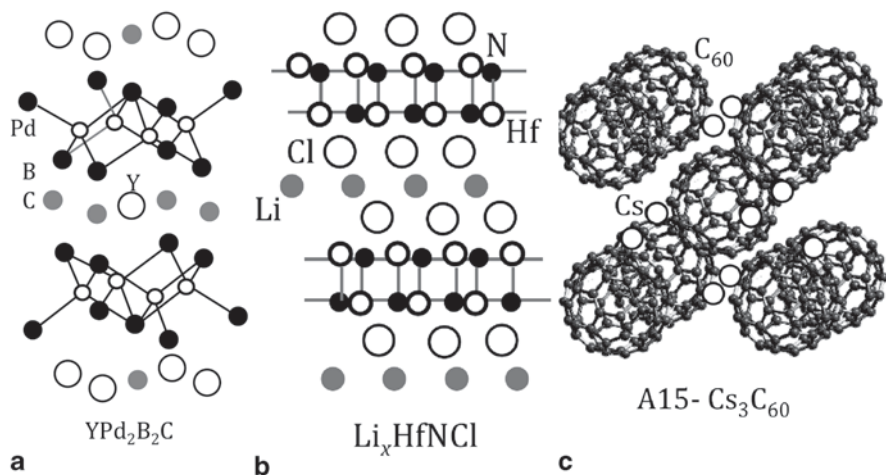


Fig. 2.4 **a** Crystal structure of $\text{YPd}_2\text{B}_2\text{C}$. **b** Crystal structure of $\beta\text{-HfNCl}$. It becomes a superconductor at $T_c = 26$ K upon electron doping. **c** A15 type crystal structure of Cs_3C_{60} . $T_c = 38$ K is achieved upon applying pressure [29]

25 K at $P = 160$ GPa in the Ca IV structural phase [17]. With further increase of P , T_c gradually rises to 29 K at $P = 220$ GPa [18] where Ca is in the distinct Ca VII phase with so-called “host-guest” structure [19]. It is surprising that Ca is not a light mass element. It is unlikely that Ca under pressure is a strongly correlated electronic system with some magnetic state nearby because of its proximity to the $3d$ transition-metal elements. Instead, as the Ca IV and VII phases are structures with high-density of Ca atoms which is by a factor of 4–5 higher than that at ambient pressure, hardened phonons and/or a $3d$ orbitals mixing may strengthen electronic correlations and enhance the electron-phonon coupling as in the case of the doped bismuthates.

2.4.3 Borocarbide $\text{YPd}_2\text{B}_2\text{C}$

Among the family of borocarbides, $\text{YPd}_2\text{B}_2\text{C}$ has the highest $T_c = 23$ K [20]. Since single crystals are not available, its physical properties and material parameters have not been studied yet. Instead, most extensively studied compounds are the Ni borocarbides, representatively $\text{YNi}_2\text{B}_2\text{C}$ ($T_c = 15$ K). The basic building block of the layer structure, displayed in Fig. 2.4a, is a B-C-B trimer (double dumbbell) linked to YNi_2 layers. The Ni-B configuration is the same as that of Fe-As (Se) in the Fe-based high- T_c superconductors (see Chap. 4). The strong B-C-B bonds and light masses give rise to high-frequency optical phonon modes (~ 1000 cm^{-1}) well separated from the low-lying phonons. The high-frequency phonons are considered

to provide a majority of electron-phonon coupling strength as in the case of MgB_2 [21]. However, some low-frequency modes show a marked change, either softening or line-broadening, upon cooling down to above T_c [22], which is a signature of strong electron-phonon coupling, not arising from FS nesting nor from phonon anharmonicity. Nevertheless, given that there is no insulating phase nearby and that 4d-Pd compound has higher T_c than 3d-Ni compound, superconductivity of this family is understood most likely by the type of phonon-mediated pairing without need for electronic pairing interactions nor correlation-induced enhancement of the electron-phonon coupling.

2.4.4 Electron Doped $\beta\text{-HfNCl}$

Transition-metal chloronitrides MNX ($\text{M}=\text{Ti, Zr, and Hf}$, $\text{N}=\text{nitrogen}$, $\text{X}=\text{Cl, Br, and I}$) form a fairly large family of superconductors. These materials are basically insulating, but electron doping makes them superconductors. T_c is 16 K for electron doped ZrNCl ($\beta\text{-Li}_x\text{ZrNCl}$) [23] and the highest $T_c=26$ K was recorded in 1998 for $\beta\text{-Li}_x(\text{THF})_y\text{HfNCl}$ (THF stands for tetrahydrofuran) [24]. The crystal structure, shown in Fig. 2.4b, consists of (grapheme-like) honeycomb double sheets of alternating Hf and N. Each Hf (N) atom is bonded with three N (Hf) atoms within a layer. Layers of Cl on either side of this double sheet form an insulating block with charge neutral $(\text{HfNCl})_2$ units. The neutral $(\text{HfNCl})_2$ blocks are coupled each other via a weak van der Waals force along the c axis.

The chloronitrides have some features in common with MgB_2 , such as layer structure and light element N. However, the LDA-based calculation yield the electron-phonon coupling $\lambda \sim 0.5$ and $\omega_m (\sim \sqrt{\langle \omega^2 \rangle}) \sim 36$ meV, giving $T_c \sim 6$ K for the electron doped ZrNCl assuming $\mu^*=0.1$ [25]. The calculated low T_c indicates either that an electronic pairing mechanism may be in operation or that electronic correlations (beyond LDA) may enhance the electron-phonon coupling as suggested for doped bismuthates. In fact, the doped MNCl's are metals with low carrier density in the normal state, and thus the screening effect is expected to be weak. An *ab initio* analysis using a DFT for SC non-empirically calculates both electron-phonon (λ) and electron-electron (μ^*) interactions. The calculated λ is larger than 0.5 obtained by the LDA based calculation, but the screened/renormalized Coulomb interaction parameter μ^* is found to be larger by a factor of about 2 than the commonly used empirical values (0.09–0.13). Because of the large μ^* values, the resulting T_c values are low, below 10 K both for doped ZrNCl and HfNCl [26]. On the other hand, the calculations beyond LDA as is adapted to the doped bismuthates yield correlation-enhanced electron-phonon coupling $\lambda \sim 1$, giving T_c 's comparable with the experimental values, but they assume $\mu^*=0.1$ [13]. The discrepancy between experiment and theory may be a signature for unconventional superconductivity. This remains open for future experiments and theories.

2.4.5 Doped Fullerides (C_{60}) and Polycyclic-Aromatic-Hydrocarbons

Superconductivity of doped (alkaline ions (A) intercalated) fullerides (A_3C_{60}) was discovered in 1991 [27]. Within a year T_c rose from 18 to 33 K by using larger alkaline ions as dopants [28]. In these fullerides C_{60} molecules build up a cubic fcc lattice. Since Cs has largest ionic radius, T_c for Cs_3C_{60} was expected to be higher. In fact, superconducting Cs_3C_{60} with $T_c=38$ K was synthesized in 2008 [29]. However, its crystal structure is not fcc but A15, a bcc packing of C_{60} with Cs-Cs pairs on the faces of the cubes (see Fig. 2.4c), and it is insulating at ambient pressure. Application of hydrostatic pressure transforms A15- Cs_3C_{60} from insulator to superconductor at $P\sim 4$ kbar. The maximum $T_c=38$ K is achieved at $P\sim 7$ kbar.

Organic molecular SCs are one of the oldest “exotic” superconductors. The first discovered in 1980 was the one-dimensional (TMTSF)PF₆ showing SC with $T_c=0.9$ K under pressure of 12 kbar [30]. After several years T_c of organic SCs increased in the class of the organic charge transfer solids up to 13 K for the κ -(ET)₂Cu[N(CN)₂]Cl salt under pressure [31], but its increase stopped for more than 10 years before jumping up to 18 K in 2009. The newly discovered SC is a picene ($C_{22}H_{14}$) which shows superconductivity at $T_c=18$ K at ambient pressure when doped (intercalated) with potassium [32]. The picene is composed of a hydrocarbon molecule with *five* benzene rings arranged in an “armchair” form and a member of a family of polycyclic aromatic hydrocarbons (PAH) (see Fig. 2.5). The K-doped phenanthrene ($C_{14}H_{10}$) with *three* benzene rings is also a superconductor with $T_c=5$ K [33]. It is natural to expect a higher T_c for PAH with *seven* benzene rings. Recently, $T_c\sim 30$ K has been reported for K-doped dibenzopentacene ($C_{30}H_{18}$) [34]. However, the zero-resistance has not been confirmed yet.

A15- Cs_3C_{60} as well as doped PAHs is narrow band metals. High electronic density of state at the Fermi energy $N(E_F)$ and high phonon frequencies involving light C and H atoms may favor high T_c . Moreover, since they are in the proximity to an insulator-metal transition, the correlation-induced enhancement of the electron-phonon coupling may also be at work. On the other hand, E_F should be small and comparable with phonon energy $\hbar\Omega_0$, so they might be in the regime outside the Migdal-Eliashberg theory. A15- Cs_3C_{60} is also an insulator at ambient pressure. The large inter C_{60} separation results in a reduction of the overlap between neighboring C_{60} molecules which produces a narrow band. The insulating states of both A15- Cs_3C_{60} and undoped PAHs are likely Mott insulators due to electronic correlation U larger than the bandwidth W . The application of pressure would drive an insulator-metal transition by increasing the bandwidth. In this regard, superconductivity in doped C_{60} and PAH systems are marginal between phonon-mediated and electronic pairing.

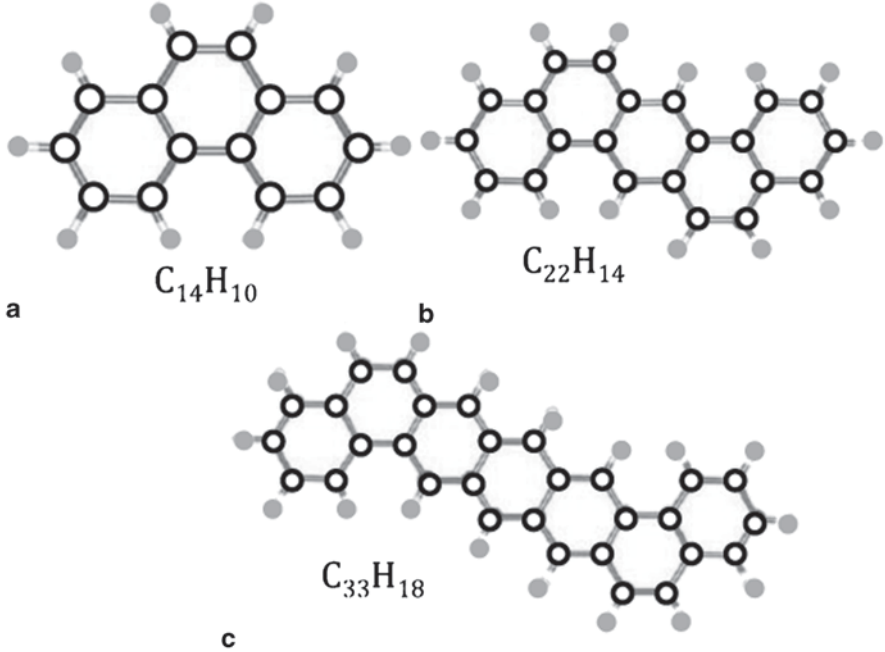


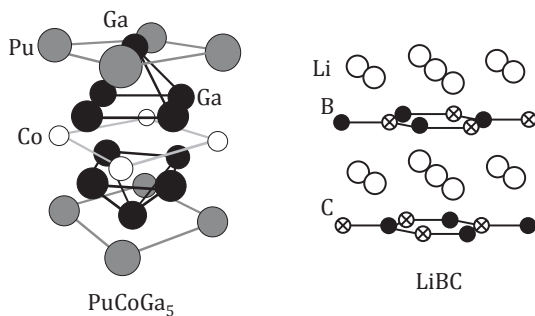
Fig. 2.5 Structural units of polycyclic aromatic hydrocarbons with 3 ($C_{14}H_{10}$), 5 ($C_{22}H_{14}$), and 7 ($C_{30}H_{18}$) benzene rings. Picene with 5 rings becomes a superconductor with $T_c = 18$ K upon electron doping [32]

2.5 Materials with Unconventional Pairing

Dominant pairing interaction, either electron-phonon or electron-electron, is yet to be determined for β -HfNCl, A_3C_{60} , and doped picene. On the other hand, the cuprates, heavy fermions compounds, iron pnictides/chalcogenides, and possibly some class of the organic superconductors are obviously superconductors with Cooper pairs formed by electronic pairing interactions derived from purely repulsive Coulomb interactions. This is evidenced by the unconventional SC pairing with sign-changing/anisotropic order parameter (SC gap). The d -wave gap is established for the cuprates with the maximum $T_c^{\max} = 135$ K at ambient pressure, and the gap symmetry for most of iron-based superconductors with $T_c^{\max} = 55$ K is either $s_{\pm}$ or nodal s (or d -wave) depending on the material and doping level. T_c 's and their physics will be discussed in details in the next two Chapters.

The heavy-fermions (HF) superconductors, first discovered for $CeCu_2Si_2$ in 1980 [35], are one of the representative strongly correlated electron systems. Their T_c 's are basically very low, $T_c < 1$ K. Exceptionally, one of the HF families, the 115 family ($CeMIn_5$ and $PuMGa_5$ where $M = Co, Ir, \text{ or } Rh$), show unusually high T_c .

Fig. 2.6 **a** Crystal structure of PuCoGa_5 . **b** Crystal structure of LiBC with potential higher T_c than MgB_2 [41]



$T_c = 18$ K was recorded for PuCoGa_5 in 2002 [36]. A schematic crystal structure of 115 is shown in Fig. 2.6a. The 115 materials are remarkably similar to the cuprates in the layer structure and the d -wave pairing symmetry or the SC gap with nodes [37]. In particular, the nearest-neighbor spin-spin interaction J for PuCoGa_5 is as large as ~ 400 K [38], distinctly larger than $J \sim 70$ K for CeCoIn_5 with $T_c = 2.6$ K and orders of magnitude larger than J of other HFs. Note that the corresponding spin superexchange interaction J in the cuprates is typically ~ 1500 K. In view of typical $T_c \sim 90$ K, it seems that T_c scales with J as expected from the spin-fluctuation theory in which the energy scale of spin fluctuation J plays a role of Ω_0 in the phonon-mediated SCs. From this fact, a guide for discovering higher T_c in strongly correlated systems is proposed [38]:

- Antiferromagnetic materials which can be metallic by tuning doping and/or pressure.
- The normal-state is characterized by two-dimensional spin and charge dynamics.
- Containing local spin moments whose nearest neighbor interaction J is comparable to or larger than J in the cuprates.

However, the spin fluctuation mechanism is not a unique one to explain the T_c of PuCoGa_5 . In fact, the electrons in PuCoGa_5 are no more heavy with the electronic specific heat coefficient $\gamma \sim 77$ mJ/mol.K² by an order of magnitude smaller than γ (~ 1000 mJ/mol.K²) of CeCoIn_5 . Small γ value is linked to the large exchange interaction J . On the other hand, Pu is a valence-skipping element like Bi and Tl, so the mechanism of valence (charge) fluctuation is also possible [39]. Note that even for the cuprates, T_c does not necessarily scale with J . Despite the large variation of T_c across the cuprate family, 25–135 K, the value of J changes only between 1100 and 1500 K. T_c^{max} is known to even anticorrelate with J in the $\text{LnBa}_2\text{Cu}_3\text{O}_7$ (Ln, rare earth element) family [40]. As will be shown and discussed in the next chapter, the cuprate- T_c is influenced by many factors.

2.6 Possibility of Higher T_c in Electron-Phonon Superconductors

Elemental superconductors at high pressures continue to be a candidate for achieving higher T_c . Metallic hydrogen, supposed to be realized at very high pressure of ~ 1000 GPa, is the limiting case. It would be a high- T_c superconductor with possible T_c value of 100 K or even higher [2]. At present, hydrogen at pressure of ~ 600 GPa is not metallic due to a strong tendency for dimerization (H_2), but the prediction remains unretract.

Though fully confirmed yet, T_c of the K-doped PAH is rising with increase of the number (N) of benzene rings; $T_c = 5$ K for $N=3$ (phenanthrene), 18 K for $N=5$ (picene), and possibly 30 K for $N=7$ (dibenzopentacene). If T_c continues to rise with N , then higher T_c may be realized in doped PAHs with $N=9$ and more.

Given that T_c was raised to the level of 40 K in MgB_2 , there is no theoretical reasoning that T_c will never exceed 40 K in the phonon-SCs. Since T_c of MgB_2 is well explained by the calculation based on the DFT (LRT) in LDA within the framework of the Migdal-Eliashberg theory, a practical approach toward higher T_c is to search for or to design materials having similar features to those of MgB_2 and having the electronic and phonon parameters more favorable for the T_c -enhancement. As was discussed in 2.3, the following circumstances appear to optimize the phonon-mechanism of superconductivity in MgB_2 , (i) layer structure, (ii) light elements with strong covalent bonds between them, (iii) high frequency phonon modes corresponding to the modulations of the bond length between light elements (bond stretching mode), (iv) FS with character of strong bonding orbitals (σ -FS), and (v) band degeneracy.

To further optimize the circumstances in MgB_2 , candidate higher T_c compounds should have much stronger electron-phonon coupling λ and higher bond stretching mode frequency Ω_0 than those of MgB_2 . Note that stronger electron-phonon coupling λ tends to decrease Ω_0 , but it is possible that the larger value of λ more than compensates the decrease in Ω_0 . An experimental attempt along this guideline was the elemental substitution for MgB_2 . Al substitution for Mg results in a decrease in T_c , and Be for Mg leads to collapse of the MgB_2 structure. Substitution of monovalent atoms for Mg is theoretically expected to increase T_c , but it has been unsuccessful to date.

A theoretically predicted higher T_c compound is Li_xBC [41]. As is shown in Fig. 2.6b, $LiBC$ has a hexagonal lattice structure with alternating Li and B-C layers. It is derived from MgB_2 by substituting Li for Mg and BC for B_2 . In a hexagonal BC layer each hexagon is composed of alternating three B and three C atoms, and the layers are B-C alternating also along the stacking direction. $LiBC$ is isovalent to MgB_2 —one less valence electron Li substituted for Mg is compensated by one more electron C substitution for B. Since the nearest neighbor B-C bonds are strongly covalent (sp^2) and Li is also a light element, the frequencies of the most phonon branches are very high.

LiBC is, however, insulating because of the alternating array of B and C in a layer [42]. It can be made metallic by reducing the Li content, Li_xBC ($x < 1$). The reduction of the Li content corresponds to “hole” doping, and results in the appearance of the σ -FS. As in the case of MgB_2 , the electrons on the σ -FS are strongly coupled to the B-C bond-stretching mode. The calculations of the electronic yield the corresponding deformation potential $\Sigma_D = 18.5 \text{ eV/\AA}$, considerably larger than $13 \text{ eV/\AA}$ in MgB_2 . The calculated frequency of the B-C bond-stretching mode is also higher by about 20% than the corresponding B-B stretching mode frequency in MgB_2 due to the shorter in-plane lattice constant. These results indicate that T_c of Li_xBC could be significantly higher than 40 K. A crude and overoptimistic estimate of T_c gives a value close to 100 K. Unfortunately, attempts to realize this high T_c have been unsuccessful due to difficulty in reducing the Li content [43].

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Chapter 3

Copper Oxide Superconductors

Abstract The copper oxides (cuprates) stand out in their high T_c values, 135 K, and are only family that achieved T_c exceeding 100 K. Thanks to the enormous research efforts over 28 years, understanding of the cuprates has remarkably advanced, though some important issues remain under hot debate. A consensus which has been achieved is that primarily repulsive electron-electron interactions lead to superconductivity with such high T_c as well as to unconventional d -wave pairing. Superconductivity emerges upon doping into the Mott insulating CuO_2 planes. The temperature-doping phase diagram of the cuprates is extremely complex with several orders or incipient orders showing up. Among the known orders, the pseudogap order encompasses a wide doping-temperature region and appears to be home to the superconducting order and its fluctuation at very high temperatures. In contrast to these generic features, T_c values of the cuprates are strongly material dependent. A few parameters, such as disorder and multilayer, have been identified that control the wide-spread T_c . T_c is actually enhanced in some cuprates by reducing disorder in the crystal, and there is a possibility of T_c enhancement to 150 K or even higher by optimizing multilayer structure.

3.1 Introduction

Among the eight families of high- T_c superconductors, the copper oxides (cuprates) stand out in their high T_c values, and are only family that achieved T_c well above the liquid nitrogen temperature. High- T_c superconductivity (HTS) in the cuprates was discovered by Bednorz and Müller in 1986 [1]. Even after intensive research efforts over 28 years unraveling the mechanism of HTS and searching for higher T_c continue to be two grand challenges in condensed matter sciences. However, the understanding of the high- T_c cuprates has substantially advanced. A consensus that has been achieved is that primarily repulsive electron-electron interactions lead to superconductivity with unprecedentedly high T_c as well as unconventional Cooper pairs. The common structural unit, CuO_2 plane, is an insulator driven by strong

electron-electron repulsive interaction (a Mott insulator). Unconventional superconductivity emerges upon doping into the insulating CuO_2 plane.

Another consensus is that characterization of the “normal” state, in particular, the pseudogap regime above T_c and the “strange metal” regime at elevated temperatures in the phase diagram, is indispensable for unraveling the mechanism. Recent progress is the discovery of a “plethora of orders” with broken-symmetry and their fluctuations that manifest in the pseudogap regime. Also, by improvement in the crystal quality, a few important parameters that control T_c are identified for the hole-doped cuprates, such as doping, disorder in the crystal, multilayer structure, and lattice parameters. In this chapter, starting from (1) a historical review, are discussed (2) necessary ingredients for high T_c extracted from the unique features of the cuprates, (3) the current understanding of the doping-temperature phase diagram and relationship of various emergent orders with the superconducting order, (4) factors that influence T_c values and thereby make T_c strongly material dependent, and (5) possibility of enhancing T_c and a few examples of T_c enhancement by optimizing some of the influential factors.

3.2 A brief history of high- T_c cuprates

The cuprate high- T_c superconductor was first discovered by Bednorz and Müller in early 1986. In December 1986, the structure and chemical composition were identified as $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ (LBCO) with K_2NiF_4 (layered perovskite or “214”) structure shown in Fig. 3.1a [2]. T_c^{max} of LBCO was 30 K, but by simply replacing Ba by Sr, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO), T_c went up to ~ 40 K [3, 4]. Remarkable features of these cuprates were (i) the undoped (parent) compound La_2CuO_4 is a Mott insulator due to strong inter-electron repulsive interactions [5] (the LDA band structure calculation predicted a metal with a half-filled conduction band), and (ii) superconductivity emerges by doping holes into this parent compound. Notably, these cuprates were not new materials but already known oxides by chemists. It was unlucky enough that the chemists who studied them did not measure resistivity below the liquid nitrogen temperature (77 K) [6].

Right after the identification of the structure and chemical compositions, many researchers tried to replace La by other rare earth elements. T_c actually rose up to ~ 90 K for a compound composed of Y, Ba, Cu, and O during the period between December 1986 and January 1987 [7]. They aimed to apply chemical pressure by replacing La by Y with smaller ionic radius. This was really an epoch-making discovery of superconductor with T_c exceeding the liquid nitrogen temperature. The crystal structure of this liquid-nitrogen superconductor was found to be really new [8], $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ (YBCO) with so-called “123” structure, composed of double CuO_2 planes ($\text{CuO}_2\text{--Y--CuO}_2$ unit), Ba_2O_2 blocks, and incomplete CuO_{1-y} chain blocks shown in Fig. 3.1b. The fully oxygen reduced compound $\text{YBa}_2\text{Cu}_3\text{O}_6$

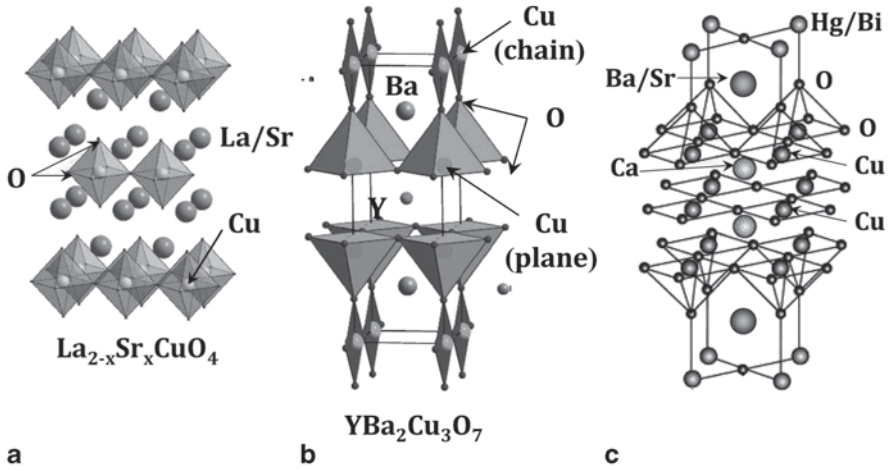


Fig. 3.1 Crystal structures (schematic) of two representative high- T_c cuprates, **a** $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and **b** $\text{YBa}_2\text{Cu}_3\text{O}_7$. Structural unit for trilayer cuprates is shown in **c** which was first discovered for $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$, and the highest T_c value 135 K was recorded for $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ with the same structural unit

is a Mott insulator, and hole doping is made by adding oxygen atoms to the CuO chains.

The third breakthrough was brought about in early 1988 [9]. T_c exceeded 100 K in another new cuprate structure, $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ (Bi2223), with trilayer CuO_2 – Ca – CuO_2 – Ca – CuO_2 unit. In this compound $\text{Bi}_2\text{O}_{2+\delta}$ blocks are charge reservoir layers and excess oxygen atoms O_δ provide holes to the CuO_2 planes. The fundamental part of its crystal structure is displayed in Fig. 3.1c. The Bi-based cuprates are the first multilayer “homologous series”, with chemical formula $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}$ [Bi22($n-1$) n] including single layer ($n=1$) $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+\delta}$ (Bi2201) and bilayer ($n=2$) $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi2201) are its close relatives. Soon after this discovery, another homologous series $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}$ [Tl22($n-1$) n] was discovered by replacing Bi and Sr by Tl and Ba, respectively [10]. $T_c^{\text{max}} = 125$ K was achieved for Tl2223.

It was straightforward to find another homologous series by replacing Bi or Tl by other heavy elements such as Pb or Hg. In 1993, Hg-homologous series, $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ [Hg12($n-1$) n], was successfully synthesized. Again, the HgO_δ blocks are charge reservoir and excess oxygen atoms (O_δ) supply holes to the CuO_2 planes. $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ ($n=3$) recorded the highest T_c value, 135 K, at ambient pressure [11]. T_c of the same compound increased to 164 K at pressure higher than 20 GPa [12]. Striking feature of the Hg-based cuprate is that the multilayers up to $n=8$ or larger were synthesized [13, 14]. T_c increases with n up to $n=3$ and then decreases for n larger than 4 which turned out to be generic for multilayer cuprates.

3.3 Uniqueness of the Cuprates

3.3.1 Characteristics of the CuO_2 Plane

High-temperature superconductivity with T_c well exceeding the liquid-nitrogen temperature (77 K) is found only in a class of materials whose basic structural unit is the surprisingly simple CuO_2 plane, layers of Cu and O arranged in a square lattice (see Fig. 3.2a). The neighboring CuO_2 planes are separated by so-called “charge reservoir” layers/blocks. Representative charge reservoir blocks are seen in Fig. 3.1a–c. Roles of the charge reservoir layers are: (i) To supply carriers to the CuO_2 planes by chemical substitution and/or by adding or reducing oxygen atoms, (ii) to neutralize the negatively charged CuO_2 planes, $[\text{Cu}^{2+}\text{O}_2^{2-}]^{2-}$ by forming an alternating stack with positively charged layers, and (iii) to stabilize the cuprate crystal structure by inserting layers consisting of cations with large ionic radii. Typical examples for (i) is the $\text{La}_{2-x}\text{Sr}_x\text{O}_2$ layers in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) and $\text{Bi}_2\text{O}_{2+\delta}$ layers in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi2212). La_2O_2 layers, $[\text{La}^{3+}_2\text{O}_2^{2-}]^{2+}$, play all the three roles in LSCO. Major role of the $\text{Y}^{3+}(\text{Ca}^{2+})$ layers in YBCO (Bi2212) is (ii) and that of the neutral Ba_2O_2 (Sr_2O_2) layers is (iii).

The undoped CuO_2 plane is a “Mott” or charge transfer (CT) insulator due to the strong Coulomb repulsion ($U \sim 6-8$ eV) between electrons on the $3d$ orbitals of Cu atoms. As schematically depicted in Fig. 3.2b, the energy gap is actually created between occupied $\text{O}2p$ band and empty $\text{Cu}3d$ band (the upper Hubbard band), so it is called as a charge-transfer (CT) gap E_{CT} . A Cu^{2+} ion has 9 electrons in the $3d$ orbitals and it is four-fold coordinated in a CuO_2 square lattice. As a consequence, the uppermost $3d$ orbital is $3d_{x^2-y^2}$ and occupied by a single electron (hole) as depicted in Fig. 3.2c. This lone electron (hole) is localized on Cu due to strong Coulomb repulsion, leaving a magnetic moment associated with the $S=1/2$ spin quantum number. The Cu spins align antiferromagnetically on the CuO_2 plane in the undoped cuprate due to superexchange interaction J between neighboring Cu spins via an intervening O atom. The singly occupied Cu $3d_{x^2-y^2}$ level form a single band by the hybridization with the $\text{O}2p_x$ and $\text{O}2p_y$ states which would be half-full, if the Coulomb repulsion were not strong. Since Cu is at the end of the $3d$ transition metal series in the periodic table, the energies of $\text{Cu}3d$ states are incidentally close to those of the $\text{O}2p$ states as schematically shown in Fig. 3.3. This makes the CT energy gap small, $E_{\text{CT}}=1.5-2.0$ eV, compared with that in other transition-metal oxide. In particular, the wavefunction of $3d_{x^2-y^2}$ has large overlap with that of $\text{O}2p_x$ and $\text{O}2p_y$ (see Fig. 3.2b). The overlap integral or hopping matrix element t_{pd} (or t) is large, $\sim 0.3-0.4$ eV, leading to strong hybridization between the two.

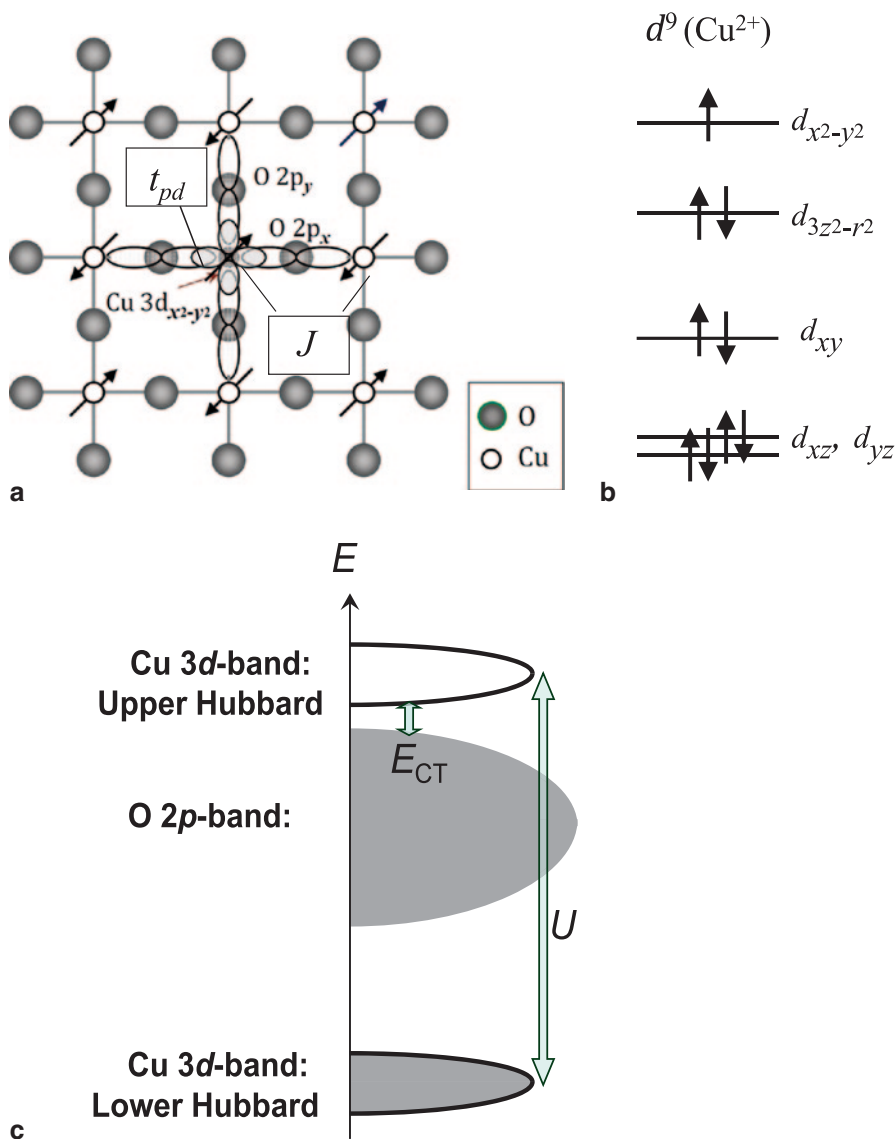
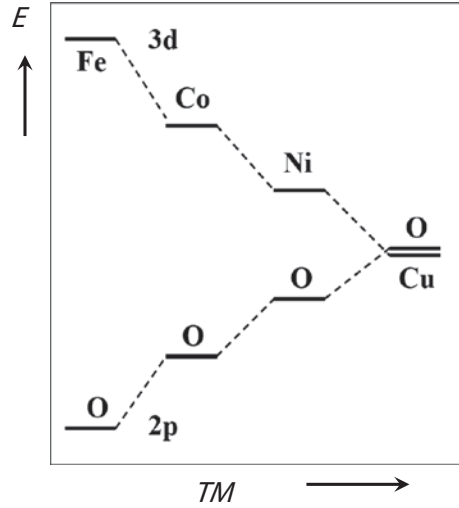


Fig. 3.2 Basic structural and electronic structure of the cuprates: **a** Structure of CuO_2 plane showing relevant $Cu3d_{x^2-y^2}$ and $O2p\sigma$ ($\sigma=x$ or y) orbitals, both being strongly hybridized. **b** Electron filling of $3d$ orbitals of the $Cu^{2+}(d^9)$ state. **c** Schematic energy scheme of the insulating undoped cuprate showing a strong electronic correlation (U) on a Cu atom and a charge-transfer (CT) energy gap between $O2p$ and $Cu3d$ upper Hubbard band

Fig. 3.3 Schematic energy diagram of the energy level of transition-metal(TM)3d orbitals and that of O2p orbitals for various TM oxides in the order of the atomic number of TM element



3.3.2 Necessary Ingredients for High T_c

The unique features of the cuprates and widely anticipated necessary conditions for high T_c are thus summarized as

1. layer structure,
2. strong electronic correlations,
3. a single band,
4. $S=1/2$ spin state,
5. accidental degeneracy between Cu3d and O2p energies.

No other materials so far known have all these features simultaneously. The perovskite copper oxide, LaCuO_3 and the linear chain cuprate, Sr_2CuO_3 shown in Fig. 3.4, satisfy (2)–(5), but the crystal structure is three-dimensional for the former and one-dimensional for the latter. In reality, LaCuO_3 is a non-superconducting metal. Sr_2CuO_3 is a Mott/CT insulator and difficult to dope carriers, but the doped CuO chains in $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ (YBCO) do not show superconductivity by themselves. A counter-example is Sr_2VO_4 which crystallizes in the same layered K_2NiF_4 structure. In this compound the V^{4+} ion has only one electron in the 3d orbitals ($3d^1$), so that the spin state is $S=1/2$. It is a Mott insulator due to strong electronic correlations. In this regard, it is an “electron” version of La_2CuO_4 ($3d^9$). Therefore, the conditions from (1), (2), and (4) are fulfilled in this compound. However, the lowest 3d levels, d_{xz} and d_{yz} , are degenerate in energy in a tetragonal lattice which makes the vanadate a multiband system. In addition, since V is near the other end of the 3d transition metal series, the V3d energy levels are significantly lower than the O2p levels. Probably because of these two differences, the vanadate remains insulating even when it is doped [15].

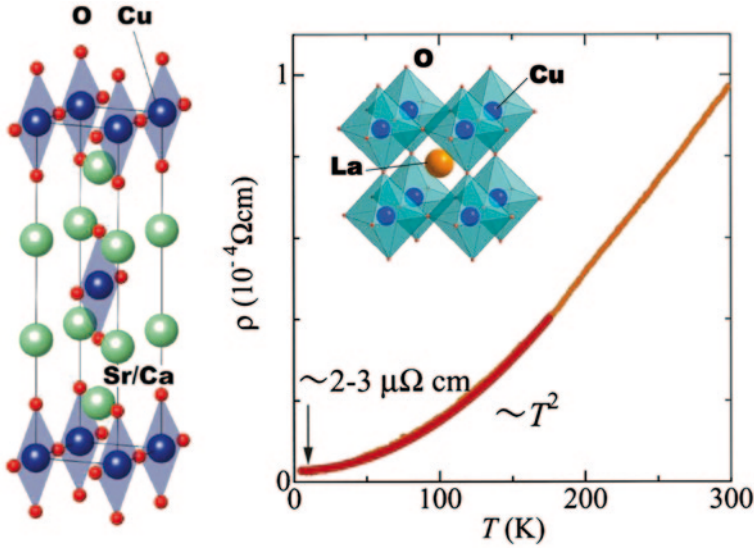


Fig. 3.4 Crystal structure of the one-dimensional cuprate Sr_2CuO_3 (a) and three-dimensional (perovskite) LaCuO_3 (b). Sr_2CuO_3 is a Mott (CT) insulator, whereas LaCuO_3 is a good metal with low resistivity as shown in (c) measured for a polycrystalline sample

Another interesting case is $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ near $x=1$. This system has the same layer structure as that of LSCO. At $x=1$ the formal ionic state of Ni is Ni^{3+} with $3d^7$ filling. Ni^{3+} state has two spin states, $S=3/2$ high-spin state and $S=1/2$ low-spin state. From the measurement of magnetic susceptibility the low-spin $S=1/2$ with localized spin only on the $3d_{x^2-y^2}$ orbital is more likely in LaSrNiO_4 . Moreover, the energy difference between $\text{Ni}3d$ and $\text{O}2p$ levels is very small in the Ni^{3+} state in contrast to the Ni^{2+} state where the $3d$ levels are significantly lower than the $\text{O}2p$ levels. Then, it seems that LaSrNiO_4 has all the features in common with the cuprates. Nevertheless, it does not show any signature of superconductivity, though metallic [16]. The reason might be that the condition (3), a single band, is not fully satisfied. The d^7 configuration of Ni^{3+} necessarily requires the energy band derived from the $3d_{z^2}$ orbital involved in the electronic states near E_F .

Physical consequences of these features are two-fold:

The large overlap integral t_{pd} and the closeness of $3d$ and $2p$ levels, *i.e.*, small CT gap, give rise to strong covalent nature of the Cu-O bond as well as to the unusually large spin superexchange interaction $J \sim t_{pd}^4 / E_{\text{CT}}^3 \sim 0.15$ eV. The strong covalent bond makes the phonon frequency corresponding to the modulations of the Cu-O bond length (or bond angle) fairly high ($\hbar\Omega_0 \sim 0.07$ eV). The large energy scales of the charge (t_{pd}), spin (J), and phonon (Ω_0) related excitations are probably sources of strong pairing interactions and hence high T_c .

The layer structure leads to their highly two-dimensional (2D) character of the electronic state, and $S=1/2$, the minimal spin quantum number, makes the spin fluctuation maximal. Because of these two, the otherwise very stable AF order (due to large

J) becomes fragile against doping and raising temperature. Finally, the strong correlations favor unconventional pairing with nodes in the superconducting (SC) gap.

3.4 Temperature-Doping Phase Diagram

A generic phase diagram of the hole doped cuprates is very complex. Multiple orders recently discovered by advanced spectroscopies are found to be superposed on the ‘standard’ phase diagram in which antiferromagnetic (AF), superconducting (SC), overdoped ‘Fermi liquid’ (FL), and pseudogap (PG) phases evolving with increasing the density of doped holes (p) and temperature (T).

It turns out that various ordering phenomena (broken symmetries) take place in the PG region, or more rigorously, in the PG region are observed various types of fluctuating orders including the SC fluctuations. At high temperatures, there is a “strange” metal regime in which the in-plane (current flowing along the CuO_2 planes) resistivity continues to increase linearly with T without a tendency for saturation.

3.4.1 Unconventional Superconductivity

As regards the SC phase, there are many differences from conventional SCs:

1. T_c is unprecedentedly high.
2. The SC gap (order parameter), $\Delta(\mathbf{k})$, has an unconventional d -wave symmetry [17], strongly momentum ($\mathbf{k}$) dependent, $2\Delta(k) = \Delta_0 [\cos(k_x a) - \cos(k_y a)]$, a being the in-plane lattice constant. It changes sign on the Fermi surface (FS) and hence vanishing at some $\mathbf{k}$'s (gap nodes). The gap nodes are along the Brillouin-zone diagonal, and the gap magnitude is maximum (called as “antinodes”) at the zone edges, $(\pm\pi, 0)$ and $(0, \pm\pi)$ as schematically depicted in Fig. 3.5.
3. The SC transition temperature T_c as a function of hole doping p , $T_c(p)$, shows non-monotonic variation with p , consisting of a dome, starting to rise from $p_{\min}$, reaching a maximum at so-called “optimal” doping p^{opt} , and then dropping to zero at $p_{\max}$. On the other hand, the amplitude of $\Delta(\mathbf{k})$ is only weakly dependent on p (see Fig. 3.6a), so there appears no direct link between T_c and Δ_0 for conventional s -wave SC $\Delta \sim 2k_B T_c$.
4. The superfluid density or SC phase stiffness ρ_s ($\sim n_s/m^*$, n_s and m^* being Cooper pair density and carrier effective mass, respectively) is by orders of magnitude smaller than that in conventional superconductors. T_c increases linearly with ρ_s in the underdoped region [18] (see Fig. 3.6b).
5. SC shows highly unusual response to disorder or impurities [19].

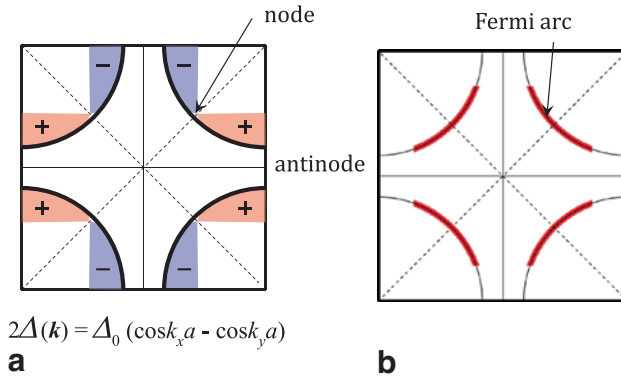


Fig. 3.5 **a** Fermi surface (schematic) in the first Brillouin zone for optimally doped cuprate. Superposed on the Fermi surface is shown the d -wave superconducting gap, both magnitude and sign. The gap nodes are along the zone-diagonal and the gap magnitude is maximal at the zone edges (antinodes). **b** The gapless region around the node defines the Fermi arc in the pseudogap regime above T_c . The arc appears to be reconstructed into electron pockets once charge order sets in, as revealed by quantum oscillation studies

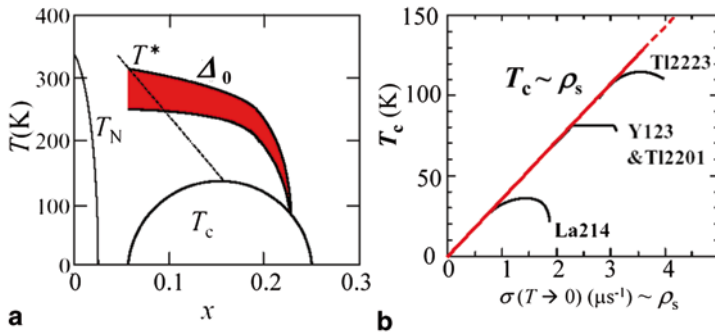


Fig. 3.6 Schematic doping dependence of **a** the superconducting gap magnitude Δ_0 . **b** T_c plotted against the superfluid density ρ_s which is proportional to the muon relaxation rate σ extrapolated to $T=0$ K and related to the magnetic penetration depth [18]. The large error bars in Δ_0 in the underdoped region is due to coexisting pseudogap in the gap excitation spectrum

3.4.2 Phase Diagram and Pseudogap Regime

The currently established temperature (T)—doping (p) phase diagram, sketched in Fig. 3.7, is very complicated and contains various orders (broken symmetries). The observed orders and the characteristic electronic feature in the six doping regions in the order of increasing hole density p :

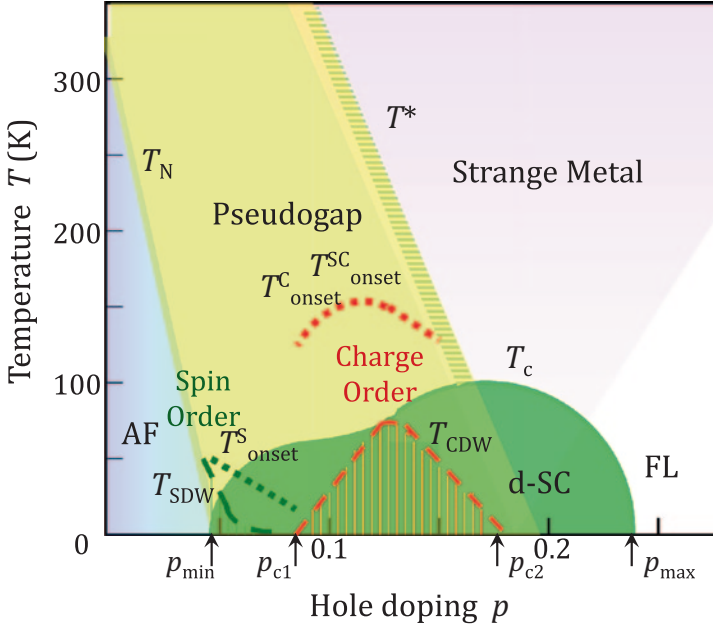


Fig. 3.7 Generic temperature (T)–doping (p) phase diagram of the cuprates. Various orders and their fluctuations are observed in the underdoped regime. “Onset” marks where precursor order or fluctuations become apparent

3.4.2.1 Long-Range AF Order ($0 \leq p < 0.02$)

Local $S=1/2$ spin magnetic moments on Cu atoms align antiferromagnetically in the CuO_2 plane (the Néel order with ordering wavevector $\mathbf{Q}=(\pi, \pi)$ in the unit of $1/a$) by the huge superexchange interaction J between neighboring Cu spins. The Néel order sets on at $T=T_N$ (~ 300 K for the parent compound) in a second order phase transition. This phase is essentially Mott insulating and the insulating gap is a $\text{Cu}3d\text{--O}2p$ charge-transfer (CT) gap, not arising from the AF order. This phase does not allow for the presence of d -wave Cooper pairs or coexistence with the SC phase [20]

3.4.2.2 Incommensurate Spin Order ($0.02 < p < \sim 0.08$)

This region is called as “heavily underdoped region”. The long-range AF order is fragile against doping and temperature due to thermal and quantum mechanical fluctuations. After the commensurate Néel order collapses upon doping holes, spin order (SO) persists as an incommensurate spin order (or spin-density-wave (SDW) order). In contrast to the Néel order in the region (1), the incommensurate spin order freezes gradually with lowering temperature [21]. The onset temperature of the

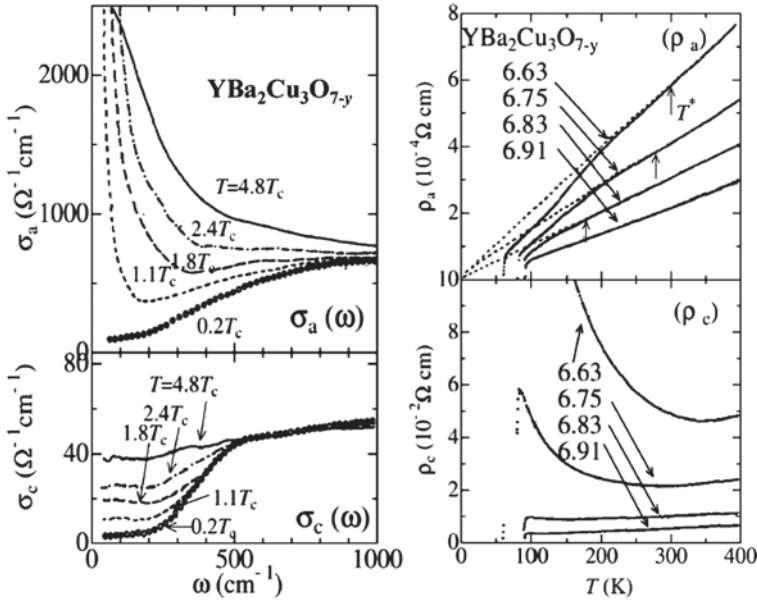


Fig. 3.8 Doping evolution of the temperature dependent in-plane and c -axis resistivity measured for $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$. Temperature evolution of optical conductivity spectra for polarization parallel and perpendicular to the planes is shown for a typical underdoped cuprate

incommensurate spin correlation is low $T_{\text{onset}}^{\text{S}} < 50$ K. The spin correlation length is short but finite at all temperatures showing slow dynamics with a wide distribution of the relaxation rates, characterized as a spin-glass.

In this phase some materials (e.g., LSCO) are insulating while others (e.g., YBCO) are superconducting. Probably, disorder effect would manifest in the former, and in either cases SC shows up or an insulator-superconductor transition takes place when the resistance of the CuO_2 sheet or CuO_2 bilayer sheet is near $h/4e^2$, the 2D universal resistance. Signatures of SC fluctuations such as the large Nernst effect are observed even for non-SC compounds. Notably, a large gap, a pseudogap (PG, see 3.4.2.4), opens in the *antinodal* region where the SC gap is maximal. Around the SC gap nodes (in the *nodal* region) gapless quasiparticles exist in a region of the Fermi surface centered at node—Fermi arcs—observed by the angle-resolved-photoemission-spectroscopy (ARPES) experiments. Obviously, the antinodal gap or pseudogap has nothing to do with the SDW order.

3.4.2.3 Incommensurate Charge Order ($0.08 < p < \sim 0.18$)

This region, so-called “moderately underdoped region”, has been identified recently and is characterized by charge order (CO). CO was first discovered in the La-based cuprates with the K_2NiF_4 structure [22], $\text{La}_{2-x-y}\text{Nd}_y\text{Sr}_x\text{CuO}_4$ and $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ (LBCO) at $x \sim 1/8$ as stripe order. As displayed in Fig. 3.8, various forms of charge

order or charge-density-wave (CDW) have been found depending on the degree of disorder and underlying lattice; checkerboard in YBCO (Hg1201) and Bi2201 [23–26], stripe (LBCO), disordered smectic electron liquid crystal (Bi2212) [27], and bond order with d -wave form factor [28]. The spin order disappears in YBCO, but coexists in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ (LBCO). The stripe charge order is a fairly long-range order, and is accompanied by the spin order in the La-based cuprates. To the contrary, in YBCO the spin order disappears in the doping range between $p_{c1} \sim 0.08$ and $p_{c2} \sim 0.16$ where the charge order is observed [29, 30]. Charge excitations in this regime continue to be gapless, while spin excitations are gapped. The x-ray scattering experiments find an onset of static and short-range CO (or CDW correlations) at $T_{\text{onset}}^{\text{CO}} = 100\text{--}160$ K, possibly due to the pinning of fluctuating CO by defects.

The CO is not destructive for d -wave superconductivity (d -SC), but is apparently “intertwined”—CO weakens below T_c , but in turn its persistence weakens the interlayer SC phase coherence. Application of a high magnetic field (~ 20 Tesla) weakens the d -SC order, and a field-induced transition to a long-range CO state is observed at $T_{\text{CO}} (< 60 \text{ K})$ by NMR [31]. The doping dependence of T_{CO} forms a sub-dome within the T_c -dome terminating at $p_{c1} \sim 0.08$ and $p_{c2} \sim 0.16\text{--}0.18$ [32]. Notably, quantum oscillations associated with an *electron* Fermi surface pocket are observed when the magnetic field is intense enough to suppress the zero-resistance state [33]. A problem is how the *hole* Fermi arc at low fields is converted to the *electron* pockets at high fields. A scenario of Fermi surface reconstruction due to CO is proposed, as the doping region of CO coincides with that where the quantum oscillations are observed [34, 35].

3.4.2.4 Pseudogap Regime ($T < T^*$ and $\sim 0.02 < p < \sim 0.18$)

It is the most mysterious regime in the phase diagram, and the understanding its origin and nature is considered to be a key to resolve the high- T_c mechanism: The pseudogap (PG) regime covers a wide T - p area of the phase diagram in which various spectroscopies indicate a suppression of low energy electronic excitations below the pseudogap temperature T^* . There remains puzzles in this regime, but it is a playground for various types of “fluctuating” (short-range) order, SDW, CDW as well as d -SC fluctuations. As described above, the incommensurate spin and charge fluctuations/short-range order develop within the PG regime ($T_{\text{onset}}^{\text{S}}$ and $T_{\text{onset}}^{\text{C}}$ are significantly lower than the PG temperature T^*). In other words, the PG state is unstable against these orders at low temperatures.

Other than the spectroscopic gap opening, various properties show a rather dramatic change at T^* . For example, as is shown in Fig. 3.9, the c -axis (directed perpendicular to the CuO_2 planes) resistivity shows an upturn below T^* like an insulator, whereas the in-plane resistivity drops at T^* associated with a drop in the carrier scattering rate [36]. The ARPES revealed an anisotropic nature of PG in momentum space [37]. The magnitude of PG is maximal in the *antinodal* region (in the vicinity of the Brillouin-zone edges, $\mathbf{k} = (\pi, 0)$ and $(0, \pi)$). On the other hand, gapless excitations are observed on a “Fermi arc” centered around the nodes (see

Fig. 3.9 T - p phase diagram (schematic) showing the regions of superconducting fluctuations and superconducting state in the overdoped region in the right-hand side of the $T^*(p)$ line

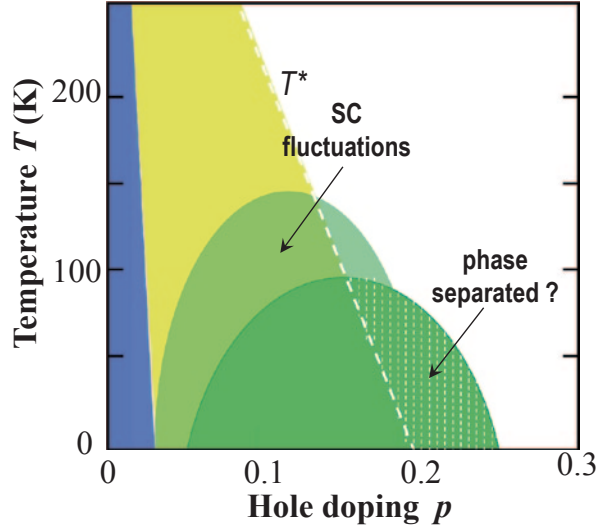


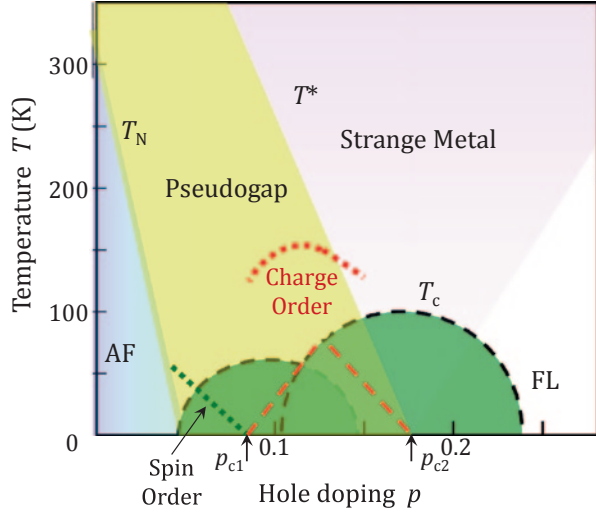
Fig. 3.5b). In this regard, PG has a d -wave-like anisotropy in the momentum space as the SC gap does. This anisotropy is reflected in the resistivity anisotropy; the in-plane resistivity dominated by the nodal region of the FS, and the c -axis resistivity by the antinodal region.

Quasiparticles (QPs) in the antinodal region are completely incoherent—the spectral function does not show a discernible peak with a depletion of spectral weight at low energies. Nevertheless, the antinodal region is not only most important for pairing, but also is the place where the charge order (and possibly other orders) is supposed to get born [38].

PG and d -SC coexist in quite a non-trivial manner. Given that there is no evidence that the SC gap energy scale is diminished by the presence of PG, it is likely that PG is also home to the SC pairing correlation. In fact, for a range of temperature above T_c up to $T_{\text{onset}}^{\text{SC}} (< T^*)$ a fairly large diamagnetism and sizeable fluctuation conductivity are observed in the PG regime [39] (see Fig. 3.10). Another evidence for local phase coherence is that the interlayer Josephson plasma resonance within a bilayer in YBCO [40] persists up to $T \sim T_{\text{onset}}^{\text{SC}}$ (see the discussion in 3.5.3 in this chapter). $T_{\text{onset}}^{\text{SC}}$ is comparable with the onset temperature of the charge fluctuations, $T_{\text{onset}}^{\text{C}}$, and both show similar doping dependence. Hence, PG is not necessarily a competing order of d -SC, but appears to be home to various orders including SC. Note that the maximum T_c value of 164 K achieved at high pressure is also comparable to these two temperature scales.

It continues to be a matter of debate whether the T^* line indicates a phase transition or a crossover. There are experimental observations that are suggestive of broken symmetries associated with the “PG phase”. Spin-flip neutron scattering experiments on underdoped YBCO, $\text{HgBa}_2\text{CuO}_{4+\delta}$, Hg1201 , and Bi2212 indicate intra-unit cell time-reversal symmetry breaking ($q=0$ antiferromagnetic order)

Fig. 3.10 Putative quantum critical points (QCPs), p_{c1} and p_{c2} inside the superconducting dome. In the case of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$, incommensurate spin order terminates and charge order appears at p_{c1} . At p_{c2} both charge order and the pseudogap $T^*(p)$ line terminate. Two superconducting T_c domes supposedly develop from these two QCPs



[41], supposedly arising from counter-circulating orbital current inside the unit cell [42]. Scanning Tunneling Spectroscopy (STS) also suggests a rotational symmetry breaking inside the unit cell ($q=0$ ‘nematic’ order) [43]. This nematicity is ascribed to electronic inequivalence of the two oxygen atoms (O_x and O_y) in the unit cell. Not only has the experimental indication of symmetry breaking, the ultrasound velocity also appeared to show a signature of a thermodynamic transition at T^* [44]. However, these experimental results and their interpretations have been a matter of debate. Furthermore, it appears difficult for the $q=0$ order to create such a large gap which might be rather linked to some local/fluctuating pairs. Thus, the origin of the PG has been identified yet.

3.4.2.5 Single d -wave Superconducting Phase ($\sim 0.18 < p < \sim 0.25$)

In this “slightly overdoped region” CO and other orders are not seen, but SC survives maintaining fairly high T_c . Existence of this region is based on the assumption that the PG- T^* line terminates at ~ 0.18 inside the SC dome (see Fig. 3.9). The T^2 component in the in-plane resistivity, characteristic of the heavily overdoped (non-SC) region, gradually dominates, and the SC gap magnitude gets smaller with increasing p in this region. Inelastic neutron scattering (INS) experiments indicate a dramatic suppression of spectral weight near the AF wavevector $\mathbf{Q}=(\pi, \pi)$ [45]. In the context of the spin-fluctuation mediated pairing model, this implies a fading out of pairing glue leading to a decrease in T_c . However, quite curiously the superfluid density also starts to decrease [46]. A hypothetical argument on the origin of the decreased superfluid density is that it arises from a mixing of non-SC phase spilled over from the FL phase far beyond $p \sim 0.18$. If this phase were not a single phase but spatially phase separated, then a *single-phase uniform d -SC state might be unstable in the cuprates*.

3.4.2.6 ‘Fermi Liquid’ Phase ($\sim 0.25 < p$)

In the “heavily overdoped region”, a large FS, consistent with the result of band calculations, is observed by both ARPES and quantum oscillations measurements [47]. Most of the properties in this region are normal except for that the spin wave, characteristic of localized spins, is robustly present without changing its dispersion in the AF ordered phase [48].

3.4.3 Quantum Critical Points and “Strange” Metal

3.4.3.1 Putative Quantum Critical Points Inside the T_c Dome

As the correlation lengths of all these fluctuating orders in the PG regime get longer, it is reasonable to expect presence of one or more quantum critical points (QCPs) at which continuous phase transitions take place at zero-temperature. The two termination points in the $T_c(p)$ “dome”, $p = p_{\min} \sim 0.05$ and $p_{\max} \sim 0.25$ are possible QCPs. A two-dimensional superconductor to insulator transition appears to take place at $p_{\min}$, while it is debatable if $p_{\max}$ is a real critical point as mentioned in 3.4.2.5. Both are too sensitive to disorder to explore the nature of transitions and associated changes of symmetry.

It is known that magnetic order, incommensurate SO/SDW order or spin-glass order, in the heavily underdoped region of YBCO disappears in the moderately underdoped region where magnetic excitations have a spin gap and no magnetic order is seen in most of the cuprates. This is suggestive of existence of some form of “magnetic QCP” at $p_{c1} \sim 0.08$ between $p_{\min}$ and p^{opt} , $p_{\min} < p_{c1} < p^{\text{opt}}$, inside the superconducting dome. Further, the PG- $T^*(p)$ line seems to penetrate the $T_c(p)$ dome and to extrapolate to another critical point $p_{c2} \sim 0.18$ with $p^{\text{opt}} < p_{c2} < p_{\max}$. Remember that p_{c1} and p_{c2} are close to the termination points of the long-range CO under strong magnetic field and/or zero-field CO correlations observable in the x-ray experiments. Then, the second QCP would be a “charge QCP” associated with the broken translational symmetry of the CO. It is also possible that, if PG is a phase associated with some broken symmetry, the nature of the second QCP would be tied up with the character of PG. However, experimental effort to unambiguously identify the presence of the two QCPs is limited by the onset of SC at fairly high temperature.

Supportive evidence for QCPs at p_{c1} and p_{c2} has recently been presented by quantum oscillation experiments on YBCO which show that observation of the quantum oscillations is confined to the range $p_{c1} < p < p_{c2}$, and that the effective mass, m^* , deduced from the T dependence of the oscillations indicates that m^* tend to diverge as p approaches these limiting values [34, 35]. In fact, in the presence of a sufficiently high magnetic field, the superconducting dome appear to split into two domes—one centered at $p \sim p_{c1}$ and the second at $p \sim p_{c2}$ (the two-dome feature is reminiscent of the phase diagram for the stripe ordered LBCO in which T_c is radically suppressed at around $p = 1/8$ [49]). It is, however, possible that the QCPs detected in quantum

oscillations under high magnetic fields do not exist at low magnetic fields, that is, evolution of the phase diagram with magnetic field would be discontinuous, since it is difficult to imagine a continuous evolution from the Fermi arc at zero field to the Fermi surface pockets at high fields.

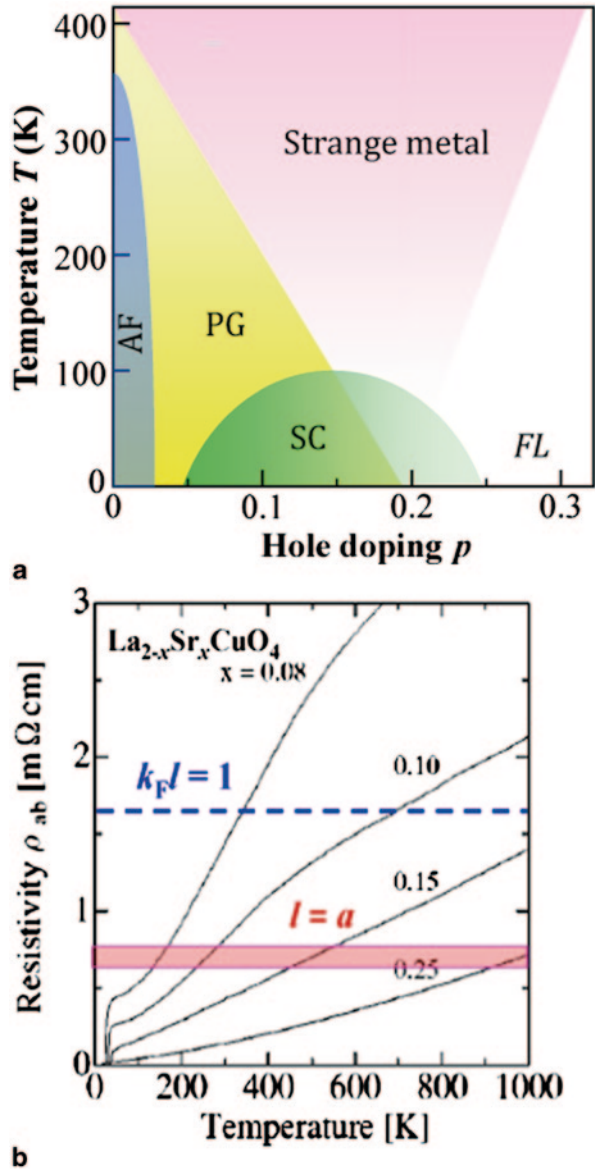
3.4.3.2 “Strange” Metal Regime ($T > T^*$)

The cuprate near optimal doping are “bad metals” in which it is difficult to discern well-defined quasiparticles at high temperatures above T^* . Although the normal state resistivity shows a “metallic” T dependence (i.e., it increases with increasing temperature, typically linear in T), its magnitude is too large to be interpreted in terms of propagating quasiparticles—the Boltzmann transport theory. The large magnitude implies a quasi-particle mean-free path (l) comparable to or shorter than the de-Broglie wavelength, $k_F l < 1$ (de Broglie wavelength $\lambda_F = 1/k_F$ where k_F is the Fermi momentum) and the in-plane lattice constant a , $l < a$ (this seems to violate the Heisenberg uncertainty principle $\Delta x \Delta p > \hbar$). As is shown in Fig. 3.11a for LSCO, the T -linear resistivity persists from above T_c up to as high a temperature as measured without showing saturation of the resistivity [50] typically observed in the normal metallic state of A15 superconductors. In this temperature region, the coherent Drude spectral weight almost vanishes in the optical conductivity and the low-energy spectral weight even decreases with elevating temperature which is found to be transferred to high-energy region comparable with the CT gap energy scale of the undoped cuprates [51]. The failure of the ordinary physics of good metals to account for this behavior has provided strong motivation for theoretical investigations. The origin of this behavior is, however, still a subject of much debate, but is of obvious importance since PG and/or FL appear to get born upon cooling from this regime.

In the QCP scenario, the strange metal regime, emphasized in Fig. 3.11b as well as the high- T_c superconductivity itself is controlled by the two or more QCPs discussed in 3.4.3.1. The strange metal would be a consequence of quantum critical fluctuations associated with the QCPs which might also serve as pairing glue for SC. Contrary to this “bottom up” scenario, a “top down” scenario has long been proposed [52] in which the strange metal regime is considered to be home to PG and overdoped FL and from PG various orders, including SC, emerges with lowering temperature.

A conclusion that can be inferred from the cuprate phase diagram is that the basic interactions between electrons are strong and repulsive. The repulsive nature of the interactions is inferred from the existence of AF phases in proximity to and even overlapping with the SC phase, and from the persistence of local spin magnetic moment over almost entire range of the phase diagram. The unconventional d -wave SC pairing arises also from dominant repulsive interactions. This is essentially different from the HTSCs discussed in the previous chapter, and is similar to the Fe-based superconductors as will be seen in the next chapter.

Fig. 3.11 **a** Schematic phase diagram emphasizing the strange metal regime at high temperatures. **b** Typical temperature dependent in-plane resistivity measured for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ showing no resistivity saturation [51] in the strange metal regime. The resistivity continues to increase to high temperatures, even though its magnitude well exceeds the critical values, $k_F l = 1$ and $l = a$, for conventional metallic charge transport



(*) **Footnote: Electron-doped cuprates** Representative electron-doped cuprates are $\text{T}'\text{-Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ ($T_c^{\text{max}} = 25$ K) [53] and so-called infinite-layer $\text{Sr}_{1-x}\text{La}_x\text{CuO}_2$ ($T_c^{\text{max}} = 40$ K), both having no apical-O atoms [54]. The electron-doped cuprates appear to belong to a class different from the hole-doped cuprates with distinctly higher T_c values although the superconductivity is conceived to be unconventional in both cases. Because of its difficulty in controlling the chemical

compositions, in particular, the oxygen content, many things remain unclear yet. Even the phase diagram is currently under debate. In the old well-known phase diagram, the AF phase is robust, while the SC phase soon disappears with increasing doping. Recent finding is that the SC phase extends (the AF phase shrinks) toward the undoped point for oxygen controlled bulk crystals, and even the undoped ($x=0$) compound is metallic and superconducting below ~ 20 K for thin films [55]. We have at present no hint on whether the lower T_c is a property inherent to the electron-doped cuprates due to different mechanism of superconductivity or whether T_c could go up to the level of the hole-doped cuprates if, e.g., disorder in the charge reservoir block next to the CuO_2 plane is removed and/or if a new electron-doped cuprate were discovered with charge reservoir block distant from the CuO_2 plane.

3.5 Material Dependence of T_c and Factors that Influence T_c

The maximum T_c so far attained at ambient pressure is 135 K for Hg-based trilayer cuprate $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$, and T_c of the same compound goes up as high as 164 K under high pressure. The cuprate family consists of a large variety of materials with CuO_2 plane as an only common structural ingredient, but T_c is strongly material dependent, ranging from ~ 25 to 135 K at ambient pressure. After 28 years experimental and theoretical efforts, several important parameters that control T_c are identified for the hole-doped cuprates. these are, (a) doping level p , (b) number of CuO_2 planes (n) in a unit cell, (c) presence of competing orders, such as stripe and/or charge order, (d) disorder inside and outside the CuO_2 plane, (e) positions of apical-oxygen atoms, (f) ionic radius of cations, such as rare-earth (Ln), and (g) oxygen isotope substitution ($^{16}\text{O} \rightarrow ^{18}\text{O}$).

3.5.1 Doping Effect

Quite distinct from conventional superconductors, doping, chemical substitution of constituent atoms or adding/removing oxygen atoms, is the primary parameter controlling T_c . How the doping controls T_c is now getting clear. Starting from optimal doping at which T_c is maximum, underdoping (decreasing p) reduces the superfluid density (ρ_s)—a measure of the phase stiffness of superconducting order parameter. Underdoping simultaneously weakens the interlayer Josephson coupling strength, making the SC state more two-dimensional, as indicated by the red-shift of the Josephson plasma frequency shown in Fig. 3.12a. Both small ρ_s and weakened interlayer coupling result in strong superconducting phase fluctuations, and thereby T_c is suppressed.

Possibly, these are connected to various ordering phenomena inherent to the underdoped regime. The competing order tends to reduce ρ_s as well as to decouple

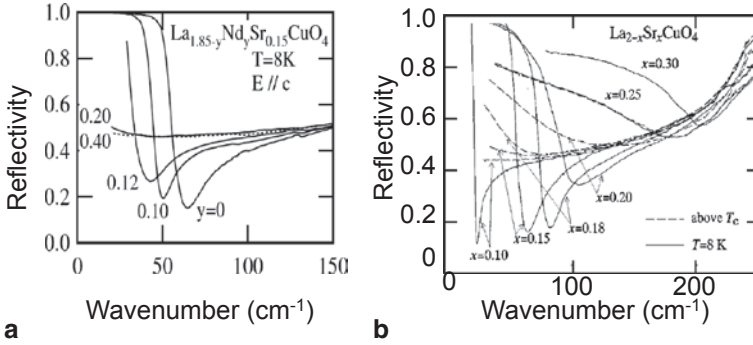


Fig. 3.12 Plasma edge in the c -axis reflectivity spectrum which emerges upon entering the superconducting state below T_c associated with Josephson coupling between CuO_2 planes. The plasma edge—Josephson plasma—frequency shows a *red* shift with **a** decreasing Sr content in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [68] and **b** as the stripe order gets stronger with increase of Nd content in $\text{La}_{1.85-y}\text{Nd}_y\text{Sr}_{0.15}\text{CuO}_4$ [56], indicating an interlayer phase decoupling

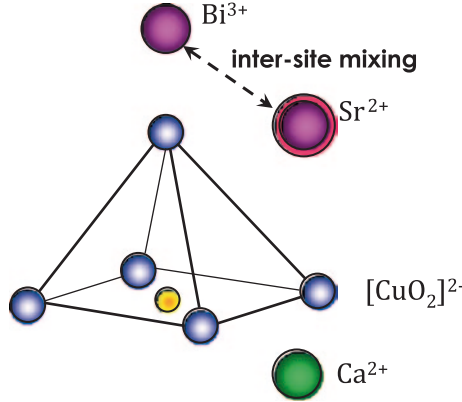
the planes making the superconducting state more two-dimensional and suppressing T_c , as is typically the case with the stripe order in $\text{La}_{2-x-y}\text{Nd}_y\text{Sr}_x\text{CuO}_4$ [56] (see Fig. 3.12b) and in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ [57]. On the other hand, there is evidence that overdoping (increasing p) weakens the pairing interaction supposedly mediated by antiferromagnetic fluctuations, although ρ_s also decreases with overdoping. It progressively turns out that a change of ρ_s and/or interlayer coupling is more or less related to a balance between superconducting and competing orders. This is radically different from that in conventional superconductors and seems to be difficult to understand in the framework of the Migdal–Eliashberg theory in which most relevant parameter controlling T_c is the superconducting gap magnitude or the electron-boson coupling strength λ .

The ^{18}O isotope substitution reduces T_c in the underdoped regime. This appears to be the ‘normal’ isotope effect in conventional superconductors, since the ^{18}O substitution decreases the frequencies of the oxygen phonon modes. However, it turns out that the major isotope effect in the cuprates is to decrease ρ_s and the reduction of T_c appears to be a consequence of the decrease of ρ_s in the underdoped regime [58]. The isotope substitution also decreases ρ_s near optimal doping, but T_c does not change at all (null isotope effect), as T_c is almost independent of ρ_s in this region (see Fig. 3.6b).

3.5.2 Disorder Effect

An important problem concerning T_c is what makes maximum value of T_c^{opt} so different (25–135 K) among different cuprate materials with optimal doping, despite that the normal state is a ‘strange metal’ showing universal linear in temperature (T) resistivity with almost the same carrier scattering rate. To the best of the current

Fig. 3.13 An example of disorder in the apical-oxygen block showing a Bi atom occupying the Sr site, Bi-Sr site mixing, in the Bi-based high- T_c cuprates. This type of disorder, arising from substitution of cations with different ionic charge and ionic radius for the A-site cations neighboring the apical-O atoms, is most influential on T_c in any other cuprate



understanding, major causes of the diverse T_c^{opt} are the number of CuO_2 planes n (multilayer effect), disorder in the charge reservoir blocks, and the apical oxygen position/distance.

Disorder in the charge reservoir block, specifically that introduced by cation substitution with different ionic charge and radius in the layer (we call this as *apical-O block* as it contains apical oxygen atoms) next to the CuO_2 plane is found most influential—the disorder associated with substitution of Zn or Ni for the in-plane Cu is most detrimental for d -SC or T_c , if it is intentionally introduced. Such disorder is the most plausible reason for the distinctly lower T_c^{opt} values in many of the single-layer cuprates, such as $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO, $T_c^{\text{opt}}=40$ K), $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{CuO}_{6+\delta}$ (Bi2201, $T_c^{\text{opt}}=35$ K), $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$ (CNCOC, $T_c^{\text{opt}}=29$ K), and $T^*-\text{La}_{1-x}\text{LnSr}_x\text{CuO}_4$ ($T_c^{\text{opt}}=25$ K) [59] as disordered layers exist on both sides, below and above a CuO_2 plane in the single-layer compounds [60]. These values should be compared with $T_c^{\text{opt}}=98$ K for $\text{HgBa}_2\text{CuO}_{4+\delta}$ (Hg1201) and $T_c^{\text{opt}}\sim 90$ K for $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ (Tl2201) where disorder is in the charge reservoir layers well separated from the CuO_2 plane. Disorder effect is weaker (by a factor of two) in the bilayer cuprates, since the disordered apical-O block exists only in one side. It is further weakened in the trilayer systems because there is a plane (inner CuO_2 plane) isolated from the apical-O blocks. This is evidenced by the narrower distribution of T_c^{opt} , $T_c^{\text{opt}}=65\text{--}127$ K across bilayer cuprates and $T_c^{\text{opt}}=115\text{--}135$ K across trilayer cuprates.

The crystals of Bi-based cuprates, which are most extensively studied by ARPES and STS owing their stable and clean surfaces, contain a large amount of disorder in the SrO blocks arising from $\text{Sr}^{2+}\text{--Bi}^{3+}$ intersite mixing (shown in Fig. 3.13) which is difficult to remove completely. This disorder is a major source of the observed electronic inhomogeneity and substantially affects the p - T phase diagram [61].

The disorder in the charge reservoir block next to CuO_2 plane results in a huge reduction in T_c^{opt} , $\Delta T_c^{\text{opt}}/\Delta T_c^{\text{opt}}$ appears as large as ~ 50 K for single-layer cuprates estimated from the comparison between Bi2201 ($T_c^{\text{opt}}\sim 35$ K) and isostructural Tl2201 ($T_c^{\text{opt}}\sim 90$ K). For bilayer cuprates $\Delta T_c^{\text{opt}}\sim 30$ K ($\text{La}_{2-x}\text{Sr}_x\text{CaCuO}_6$ ($T_c^{\text{opt}}\sim 60$ K) vs

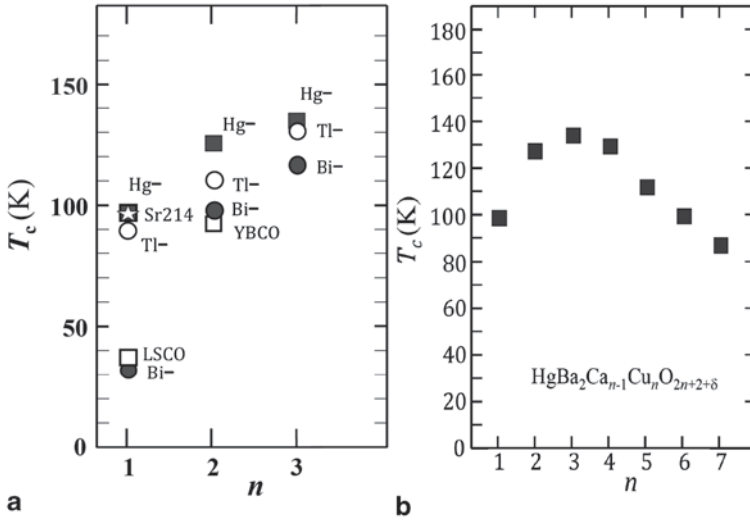


Fig. 3.14 **a** Plot of the T_c^{opt} values for various single-, bi-, and tri-layer cuprates attained after reducing disorder. **b** T_c^{opt} vs number (n) of CuO_2 planes in a unit cell for a multilayer homologous series $\text{Hg}12(n-1)n$ [13, 14]

YBCO ($T_c^{\text{opt}}=93$ K)). In this case, again, the suppression of T_c appears to take place along with the reduction of ρ_s . It remains open whether or not the T_c reduction is explained by the Abrikosov–Gorkov pair-breaking mechanism due to ‘normal’ impurities in a d -wave superconductor [62].

As will be described in 3.6.1, reduction of disorder in the apical-O blocks actually leads to sizeable enhancement of T_c^{opt} in some of the cuprate materials; T_c^{opt} of the trilayer Tl1223, in which a major source of disorder is thought to be Tl-Ba intersite mixing, is enhanced to 133 K [63], close to the highest T_c record in Hg1223, and T_c^{opt} of the bilayer Bi2212 is improved to 98 K [64]. In one of the single-layer cuprates, $\text{Sr}_2\text{CuO}_{3+\delta}$, with the same “214” structure as that of LSCO, T_c^{opt} reaches 98 K when dopant atoms get ordered [65], sharing the T_c record with Hg1201. These “optimized” T_c values are summarized in Fig. 3.14a for single-, bi-, and tri-layer cuprates.

3.5.3 Multilayer Effect

The number of CuO_2 planes, n , in a unit cell is one of the old-known factors influencing T_c values as the history of high- T_c indicates. Even after reducing disorder, the multilayer effect is surely seen in Fig. 3.14a, T_c values being significantly higher for bilayer and trilayer cuprates than for single-layer cuprates. As plotted in Fig. 3.14b for the multilayer homologous series $[\text{Hg}12(n-1)n]$ [13, 14], T_c^{opt} rises with increasing n up to 3 but turns to decrease for $n \geq 4$ [14]. A problem to be explained

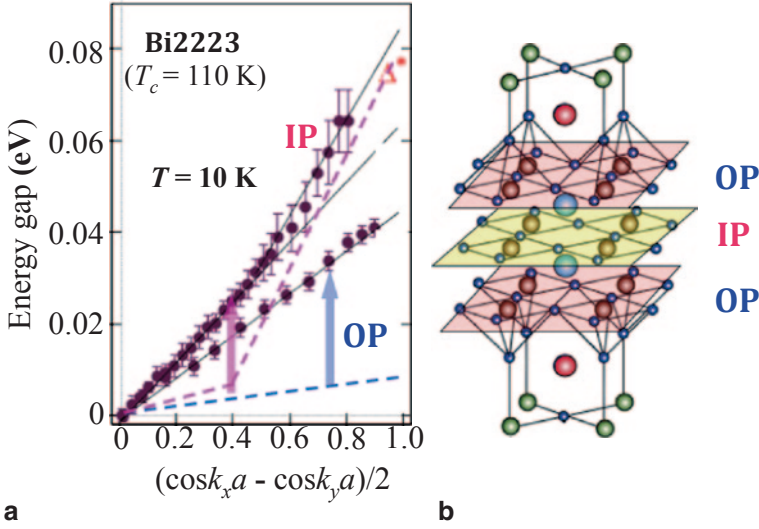


Fig. 3.15 **a** Enhanced superconducting energy gaps in the trilayer $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ observed by ARPES [67]. The gap magnitudes in both inner (IP) and outer planes (OP) (shown in **b**) are plotted as a function of momentum starting from the nodes toward antinodes. They are enormously enhanced as compared to the values for the bilayer Bi2212 with nearly the same doping levels

is why T_c decreases for n larger than 4. This certainly arises from the charge imbalance, difference in the hole density between outer CuO_2 planes (OP) and inner planes (IP) [66]. The hole density in IPs tends to be smaller as they have no apical-O atoms and are sandwiched on both sides by Ca^{2+} layers, making an electro-positive circumstance for holes to enter.

The ARPES measurement on the trilayer Bi2223 with $T_c = 110 \text{ K}$ tells us what is going on in the multilayer system [67]. The ARPES confirms the result of the preceding NMR experiments in that two OPs are in fact overdoped, whereas IP is heavily underdoped. The hole density estimated from the Fermi surface (FS) area is $p \sim 0.23$ in OP and $p \sim 0.07$ in IP. When these values are mapped on the phase diagram of the bilayer Bi2212, T_c 's of OP and IP should be well below 50 K. To the contrary, the SC gap of OP follows the d -wave momentum dependence over the entire FS without showing PG feature near antinodes and the d -wave gap magnitude is $\Delta_0 = 43 \text{ meV}$ by a factor of 4 or more enhanced with respect to the estimated value for Bi2212 with $p = 0.23$ (indicated in Fig. 3.15). The SC gap of IP shows a PG feature on approaching the antinodal region of FS, but the feature is considerably weakened as compared to that in Bi2212 with $p \sim 0.07$. The SC gap magnitude obtained by extrapolating to the antinode $\Delta_0 = 60 \text{ meV}$ is again much or even more enhanced. Certainly, a multilayer effect is at work in Bi2223 which simultaneously enhances the pairing interactions in both OP and IP via a coupling between them.

The c -axis optical spectrum gives a hint on this problem. The measurement of the c -axis optical response allows one to directly measure the interlayer Josephson coupling [68]. The coupling strength is proportional to the square of the frequency

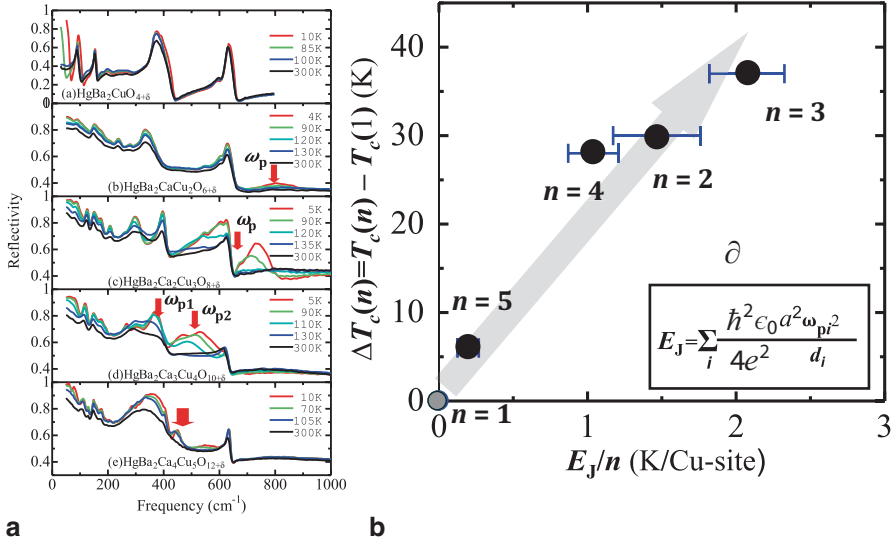


Fig 3.16 **a** Optical spectra of multilayer $\text{Hg}12(n-1)n$ from $n=1$ to 5 measured at various temperatures [71]. The optical Josephson plasma modes (indicated by arrows) are seen to develop below T_c . **b** Enhancement of T_c in the multilayer with respect to T_c of single-layer, $\Delta T_c = T_c(n) - T_c(1)$ plotted against the Josephson coupling energy per plane E_J/n estimated from the frequencies of the Josephson plasma modes observed for $\text{Hg}12(n-1)n$ with $n=2-5$

of the Josephson plasma mode showing up below T_c as a reflectivity edge in the c -axis polarized infrared optical spectrum. The multilayer cuprate which contains more than two CuO_2 planes in a unit cell is an alternating array of more than one kind of Josephson junctions—a bilayer cuprate is a stack of a stronger junction within a bilayer and a weaker junction between bilayers. In such structure additional modes, called ‘optical’ Josephson plasma modes [69], appear like the optical phonon modes in a crystal with more than two inequivalent atoms in a unit cell. In a typical bilayer system YBCO this optical mode is observed at fairly high frequency, 400–500 cm⁻¹ (50–60 meV) [70], reflecting stronger coupling between closely spaced CuO_2 planes within a bilayer.

A systematic study of the Josephson plasma modes was carried out for the Hg-based multilayer system, $\text{Hg}12(n-1)n$ [71]. The result, shown in Fig. 3.16a, revealed how the interlayer Josephson coupling strength within a multilayer varies with n . In Hg-based multilayer cuprates the frequency ω of the optical Josephson plasma mode is distinctly high, $\omega_0 \sim 800$ cm⁻¹ for $n=2$, indicating a strong interlayer coupling within bilayer, strongest among the known bilayer cuprates. The highest frequency of this mode appears to correlate with the highest transition temperature $T_c = 127$ K for $\text{Hg}1212$. On the other hand, the frequencies of the optical plasma modes tend to decrease for $n > 2$ which is apparently related to a slow down and a subsequent decrease in T_c .

Various scenarios have so far been proposed to account for the multilayer enhancement of the pairing interactions. The interlayer tunneling (ILT) theory [72] is

one of the proposals which try to explain the rise of T_c with increasing n . The tunneling of Cooper pairs in a CuO_2 plane between the planes via Josephson coupling gains kinetic energy along the c -axis (perpendicular to the planes) which promotes the pair formation within the plane. In this model T_c is an increasing function of n . However, a serious problem with this ILT model was found for single-layer cuprates in which the strength of interlayer Josephson coupling estimated from the Josephson-plasma frequency is too weak to account for the superconducting condensation energy [73]. However, the interlayer pair hopping within a multilayer (intra-multilayer tunneling) remains a possible scenario to explain the enhancement of T_c^{opt} . The systematic evolution of the optical Josephson plasma modes with n [71] appears to support the multilayer scenario [74]. In this scenario T_c is an increasing function of n with C being a constant;

$$T_c(n) = T_c(1) + C(1 - 1/n).$$

A remarkable correlation is found between ΔT_c ($T_c(n) - T_c(1)$) and intra-multilayer Josephson coupling energy E_J which is estimated from the Josephson plasma frequencies observed for $\text{Hg}12(n-1)n$. The correlation strongly suggests that the interlayer tunneling within a multilayer may be at work to contribute to the enhancement of T_c , whatever the pairing mechanism, which determines $T_c(1)$, is in a CuO_2 plane. As seen in Fig. 3.16a, E_J and T_c decrease for n greater than 3. The decrease appears to be related to the pronounced doping imbalance between IP and OP which weakens the Josephson coupling strength within a multilayer. This seems to happen even in the trilayer material as inferred from the lower frequency of the optical Josephson plasma mode in $\text{Hg}1223$ than that for the bilayer $\text{Hg}1212$ – the reason for the increase of E_J for $n=3$ with respect to $n=2$ is that the trilayer structure has two near neighbor junctions.

An alternative scenario was proposed by considering nonlocal Coulomb interaction arising from poor screening along the c axis [75], and the same relation between T_c and n was derived. From a similar viewpoint, a possible contribution of phonon-mediated pairing in the multilayer cuprates is considered in [76]. In the case of, e.g., trilayer $\text{Bi}2223$, the OP has SrO on one side and Ca^{2+} on the other, and the IP is sandwiched by Ca on both sides. So, IP has mirror symmetry, whereas the symmetry is broken in OP (see Fig. 3.15b). The broken symmetry establishes a local electric field. The local field exists in the OP and does not in the IP. It enhances the electron-phonon coupling in the OP, specifically to the c -axis phonons. This phonon coupling may provide an additional pairing channel to the d -wave pairing in each CuO_2 plane, and thereby enhances T_c with respect to the single-layer system.

3.5.4 Lattice Effect

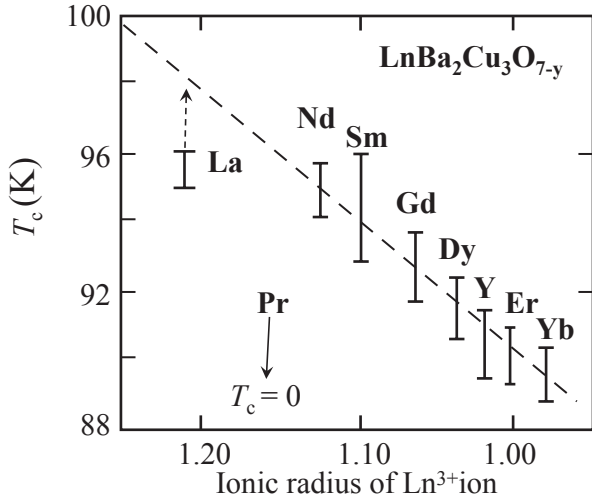
There are some known correlations between T_c^{opt} and lattice parameters. Well known is that T_c^{opt} is higher for the material with longer apical-oxygen distance from the neighboring CuO_2 plane or equivalently with flatter CuO_2 plane [77]. For single-layer systems the wide distribution of the values of T_c^{opt} arises from the disorder effect as was discussed in 3.5.2. On the other hand, among the bilayer cuprates, one notices that T_c^{opt} of the cleaner YBCO is relatively low as compared with T_c^{opt} (=98 K, see 3.6.1.1) of highly disordered Bi2212, and much lower than 110 K for Tl2212 and 127 K for Hg1212. The low T_c^{opt} for YBCO was ascribed to the warped (not flat) CuO_2 planes. A plausible parameter that gives rise to this difference in T_c^{opt} as well as to the flatness of the CuO_2 plane is the distance of apical oxygen (apical-O) from the CuO_2 plane. The apical-O distances (d) are $d=2.30$ Å for YBCO, 2.43 Å for Bi2212, 2.70 Å for Tl2212, and 2.80 Å for Hg1212, just in the order of increasing T_c^{opt} . Note that this is also in the order of increasing optical Josephson plasma frequency in the bilayer cuprates [71].

It is argued in [77] that the longer apical-O distance enhances the longer-range hopping of electrons which changes the Fermi surface with larger curvature unfavorable for the formation of competing orders such as CDW and SDW. A theoretical analysis based on the local (point charge) model of the cuprates find a correlation between T_c and Madelung energy difference between in-plane and apical O sites [78]. It is argued that the longer apical-O distance results in a larger Madelung energy difference and hence favors higher T_c by stabilizing local spin singlets.

The enhancement of T_c under pressure [12] and the transient redistribution of interlayer coupling strength by short-pulsed light excitations [79] are thought to be intimately related to the change of lattice parameters. In the multilayer cuprates, the inner CuO_2 planes (IPs) are more apart from the apical-O atoms, which might explain the observed stronger pairing interaction in IPs. To understand the microscopic origin of this effect on T_c^{opt} theoretical investigations in the Migdal–Eliashberg framework appear helpful. One of the hints from such study is that contribution of out-of-plane orbitals, $\text{Cu}3d_{z^2}$ and $\text{Cu}4s$, to the states on the Fermi surface may work to reduce the pairing interactions, so that longer apical-O distance would be favorable for higher T_c [80].

It is also known empirically that in some families T_c^{opt} tends to be higher for materials consisting of cations with bigger ionic radius. For the $\text{LnBa}_2\text{Cu}_3\text{O}_{7-y}$ system T_c^{opt} is lower for Ln with smaller ionic radius, *i.e.*, larger atomic number, known as “lanthanoid contraction” [81]. As plotted in Fig. 3.17, $T_c^{\text{opt}}=96$ K for Ln=Nd, and 89 K for Ln=Yb. The ionic radius of Y^{3+} is similar to that of Dy^{3+} or Er^{3+} , just on the relationship between T_c^{opt} and ionic radius of rare earth element. This trend may also be a consequence of the difference in the apical-O distance, since a larger ionic radius of Ln tends to make the apical-O distance longer in $\text{LnBa}_2\text{Cu}_3\text{O}_{7-y}$. However, the same trend is seen also in the electron doped cuprates, $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_4$ without apical O atoms— $T_c^{\text{opt}}\sim 30$ K for Ln=Pr (La) and almost 0 K for Ln=Gd. The mechanism/reason of this T_c^{opt} degradation has never been addressed up to now.

Fig. 3.17 T_c^{opt} of $\text{LnBa}_2\text{Cu}_3\text{O}_7$ (Ln123) for different rare-earth elements Ln in the order of increasing atomic number or decreasing radius of Ln^{3+} ionic state. Pr123 is not a superconductor due to a circumstance arising from the special Pr ionic state, and T_c^{opt} of La123 is relatively low because of the disorder in the BaO block due to La-Ba intersite mixing



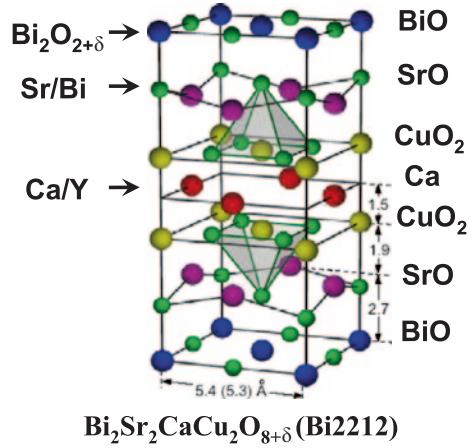
3.6 Possibility of Enhancing T_c

After the maximum value of $T_c = 135$ K was recorded in 1993, T_c has stopped rising for more than 21 years. This does not imply that we should give up the effort to obtain higher T_c values. There is a possibility or hope of enhancing the cuprate T_c in view of the following observations; (i) the superconducting gap magnitude is typically 40–50 meV which corresponds to the mean-field $T_c^{\text{MF}} \sim 200$ K or higher, (ii) the SC fluctuations or Cooper pair without phase coherence seem to exist at temperatures as high as 200 K, and (iii) $T_c = 164$ K was actually attained by applying high pressure to the Hg1223 cuprate [12]. To the best of the current understanding, major causes of the diverse T_c^{opt} are the number of CuO_2 planes n (multilayer effect), disorder in the charge reservoir blocks, and the apical oxygen position/distance. These, in turn, show the way to further increase T_c .

3.6.1 Increasing T_c by Reducing Disorder

In this sub-section two cases are shown that demonstrate T_c enhancement/improvement by reducing disorder outside the CuO_2 plane. One is bilayer Bi-based cuprate, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$, and the other is single-layer $\text{Sr}_2\text{CuO}_{3+\delta}$ with the same K_2NiF_4 crystal structure as that of the first high- T_c cuprate La_2CuO_4 . In both cases T_c is actually enhanced by reducing most harmful disorder in the former and by ordering dopant atoms in the latter.

Fig. 3.18 Three disorder sites in the bilayer Bi2212



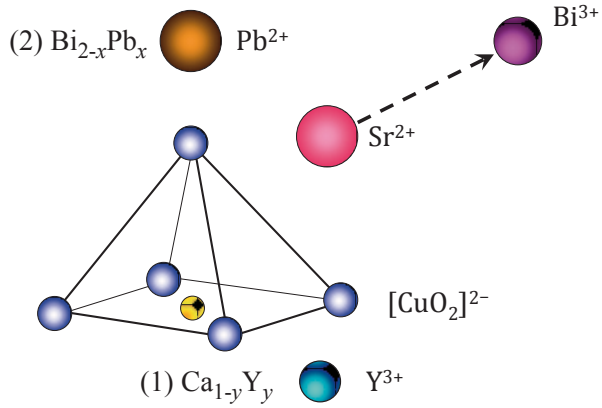
3.6.1.1 Reducing Disorder in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$

The effect of disorder is quantitatively examined [62], specifically in the single-layer Bi-based cuprate (Bi2201) in which disorder is intentionally introduced at the Sr site by partial substitution of various rare-earth elements (Ln), $\text{Bi}_2\text{Sr}_{2-x}\text{Ln}_x\text{CuO}_{6+\delta}$ (Ln-Bi2201). The result indicates that this type of disorder has a substantial influence on T_c , and hence that Bi-based cuprates with highly disordered crystal structures provide sufficient room for increasing T_c .

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi2212) is composed of three building blocks other than two CuO_2 planes: Bi_2O_2 block, SrO block, and Ca block (see Fig. 3.18). These three blocks are charge reservoirs, and, at the same time, sources of disorder. Excess oxygen atoms (δ) are hole dopants and randomly distributed in the BiO block. The BiO blocks are also disturbed by the so-called structural supermodulations. The Ca^{2+} ions are in the plane sandwiched by two CuO_2 planes forming a bilayer, and are easily substituted by rare-earth (Y or Ln) ions. In as-grown crystals of Bi2212 the SrO blocks are highly disordered due to Bi-Sr intersite mixing— Bi^{3+} ions tend to invade the Sr sites. This is because (i) the CuO_2 bilayer is negatively charged, $[\text{CuO}_2\text{—Ca—CuO}_2]^{2-}$ and so more electro-positive Bi^{3+} ions are allocated to occupy the neighboring Sr^{2+} sites, and (ii) the SrO block composed of relatively small Sr^{2+} ions as compared with Ba^{2+} has smaller tolerance factor and hence is vulnerable to the intrusion of different cations to stabilize the structure. In fact, typical Bi2212 crystals contain a fairly large amount of Bi at the Sr sites, and the actual chemical formula is $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{CaCu}_2\text{O}_{8+\delta}$ with $x=0.10\text{--}0.20$. Usually, increasing/decreasing disorder in the charge reservoir block changes doping level and hence affecting T_c . However, in Bi2212 doping level can be controlled also by an operation to other building blocks. In this regard Bi2212 is a good playground for investigating the effect of disorder in each block on T_c and for the effort of increasing T_c .

As pointed out in [60] in their paper in 2004, and also in view of the systematic investigation of disorder effect on Bi2201 [62] disorder in the SrO block is most

Fig. 3.19 Two steps for reducing the Bi-Sr intersite mixing; (1) partial Y substitution for Ca and (2) partial Pb substitution for Bi [64]. Both are expected to purge Bi atoms occupying the Sr sites



influential on T_c . Hence, the Bi/Sr site mixing (depicted in Fig. 3.19) is considered to be most detrimental for T_c in Bi2212, since Bi^{3+} ion has different ionic charge from Sr^{2+} and its ionic radius is considerably smaller than that of Sr^{2+} . On the other hand, disorder in other two blocks, BiO and Ca, has very small effect. The small effect of disorder in the BiO block, due to both excess oxygen atoms and supermodulation, is conceivable, since it is well apart from the CuO_2 planes. In fact, it has been long known that YBCO is one of the cleanest systems, although there is rather strong disorder in the charge reservoir CuO chain layers where oxygen vacancies/defects exist. T_c is almost unchanged when disorder in the CuO chains is removed by ordering oxygen/oxygen-deficiency in the chains achieved by post-annealing at relatively low temperatures. Interestingly, though not widely anticipated, the disorder in the Ca block has negligible influence on T_c , even though the location of the Ca site is close to the CuO_2 planes. Residual resistivity is a measure of the scattering strength of charge carriers due to impurities and/or defects and hence a good measure of the strength of disorder. It is experimentally confirmed that for Bi2212 disorder in the Ca as well as BiO blocks does not produce appreciable residual resistivity, whereas disorder in the SrO block, either Ln or Bi partially substituted for Sr does small but finite residual resistivity [62]. Therefore, an effective way to increase T_c for Bi2212 is to reduce the disorder, specifically the Bi-Sr site mixing, in the SrO block.

The best way to reduce this type of disorder in Bi2212 would be replacement of Sr by Ba, but Ba tends to form impurity phases such as BaBiO_3 . Then, a practical way is to minimize the disorder in the SrO block at the expense disorder in other two blocks, Bi_2O_2 and Ca layers, which has a minimal effect on T_c . This was actually done in [64] in two steps as sketched in Fig. 3.19. The first step is to partially substitute Y for Ca, $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{Ca}_{1-y}\text{Y}_y\text{Cu}_2\text{O}_{8+\delta(\text{opt})}$. The Y^{3+} substitution for Ca^{2+} decreases the hole density p in the CuO_2 planes, so it should be compensated by increasing and adjusting the excess oxygen content δ to yield maximum T_c (this, in turn, limits the amount of Y-substitution to $y < 0.10$). The reason for why the Y-substitution reduces the Bi-Sr site mixing is supposed to be that introduction of Y^{3+}

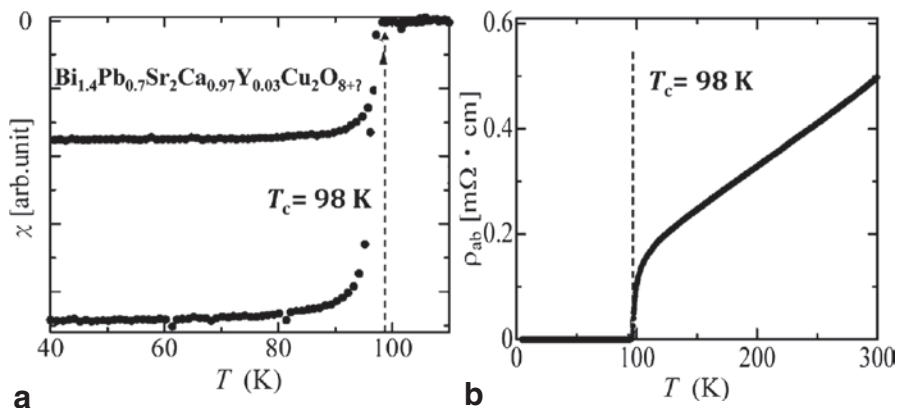


Fig. 3.20 Temperature dependences of **a** the in-plane resistivity and **b** magnetic susceptibility for “optimized” Bi2212 ($\text{Bi}_{1.4}\text{Pb}_{0.7}\text{Sr}_2\text{Ca}_{0.97}\text{Y}_{0.03}\text{Cu}_2\text{O}_{8+\delta}$) showing a superconducting transition at 98 K [64]

makes $[\text{CuO}_2\text{--Ca--CuO}_2]^{2-}$ bilayer more electropositive which would purge Bi^{3+} ions from the SrO blocks.

The second step is to partially substitute Pb for Bi. The Pb substitution is known to relax the supermodulation of the BiO block, but this does not affect T_c as described above. An expected effect of Pb substitution is to decrease the total amount of Bi which reduces the possibility of Bi intruding the SrO block. The ionic valence of Pb is expected to be Pb^{2+} , so Pb substitution for Bi increases the hole density. This compensates, to some extent, the decrease of p due to the Y substitution for Ca, making the optimization of p by adjusting δ easier. Some of Pb may also occupy the Sr site (Pb/Sr-site mixing). Fortunately, the ionic state of Pb (Pb^{2+}) is identical to that of Sr, and the ionic radius of Pb^{2+} is nearly equal to that of Sr^{2+} . Therefore, the Pb-Sr site mixing is harmless for T_c . After this ‘two-step optimization’, the maximum $T_c = 98$ K was achieved for $\text{Bi}_{2-w}\text{Pb}_w\text{Sr}_2\text{Ca}_{1-y}\text{Y}_y\text{Cu}_2\text{O}_{8+\delta}$ (nominal) with $w = 0.60\text{--}0.65$ and $y = 0.03\text{--}0.05$ as shown in Fig. 3.20.

Note that the first process cannot apply to the single-layer Bi2201 without Ca block in its structure. In order to increase T_c in Bi2201, the La substitution for Sr is usually adopted. La^{3+} has least mismatch in the ionic radius with that of Sr^{2+} , and may play a role in reducing the Bi/Sr-site mixing to some extent. However, disorder due to the charge mismatch remains between Sr^{2+} and La^{3+} which continues to produce relatively stronger disorder, which is the reason for its lowest T_c (~ 30 K) even after optimization as compared with $T_c \sim 90$ K realized in the isostructural $\text{Tl}_{1-x}\text{Ba}_x\text{CuO}_{6+\delta}$ (Tl2201).

Although the maximum T_c of 98 K was achieved for Bi2212 which is comparable with (or a bit higher than) that of much cleaner YBCO, a question remains why it is lower by 10–30 K than the maximum T_c of its close relatives such as Tl2212 (~ 110 K) and Hg1212 (~ 127 K). It is possible that Bi atoms are not completely

removed from the SrO blocks. It is also inferable that other factors might be responsible for the T_c difference among these bilayer cuprates.

3.6.1.2 Dopant Oxygen Ordering in $\text{Sr}_2\text{CuO}_{3+\delta}$

Single-layer cuprates comprise two groups in T_c . Hg1201 and Tl2201 having T_c^{opt} exceeding 90 K, belong to a high T_c group, while LSCO (LBCO), Bi2201 and $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$ with T_c^{opt} at highest 40 K form a low T_c group. Obviously, the difference between the two groups is in the location of dopant atoms and/or disordered block. For the low- T_c group disorder is in the block next to the CuO_2 plane, that is, in the block containing the apical-O atoms (apical-O block) which is highly disordered due to randomly distributed substituent/dopant atoms (e.g. Sr in the case of LSCO) with different ionic charges from those of host cations (e.g. La in LSCO). Since doping into this block is essential for inducing SC in these single-layer cuprates, there is no way to remarkably increase T_c by reducing disorder. Ordering of randomly located doping cations is practically impossible, as these cations (Sr, Bi and Na) have very low diffusion constants in the crystals.

As was discussed in 3.5.2 and 3.6.1.1, the apical-O atom forming a CuO_3 pyramid or a CuO_6 octahedron is known to have an impact on the electronic structure. Hence, disorder in the apical-O sites is expected to have substantial effect on T_c . However, for almost all the hole-doped cuprates, apical-O sites are fully occupied. The stoichiometric Sr_2CuO_3 (see Fig. 3.4) is a well-known cuprate with Cu-O chains aligning along the crystalline a -axis and is an insulator. Introduction of extra O atoms, $\text{Sr}_2\text{CuO}_{3+\delta}$, and application of high pressure (~ 6 GPa) convert the structure to a layered K_2NiF_4 structure. The $\text{Sr}_2\text{CuO}_{3+\delta}$ compound can be synthesized only under high pressure or in the form of thin films grown on a certain substrate. It is a unique cuprate with the K_2NiF_4 structure in that the apical sites are partially occupied; $(1+\delta)$ apical sites are occupied and $(1-\delta)$ sites are empty, and that the extra apical-O atoms (δ) themselves play a role of hole dopants.

It was first synthesized by Hiroi et al. [82] and was found to show superconductivity at 70 K. After this discovery the quality of the $\text{Sr}_2\text{CuO}_{3+\delta}$ superconductors was improved and T_c was enhanced to well above 90 K by post annealing (shown in Fig. 3.21) [65]. The annealing effect is dramatic as shown in the inset. When it is annealed at temperatures higher than 300°C, superconductivity is completely destroyed. The 90 K class superconductivity is realized only by low-temperature (in the range between 200 and 250°C) annealing. T_c rises to 98 K after optimization [83] which is highest among the known single-layer cuprates.

Although no direct evidence exists as yet because of difficulty in synthesizing a large amount of single-phase samples, it is highly probable that ordering of dopant apical-O atoms is essential in realizing high- T_c superconductivity in this cuprate, as the diffusion constant of O is large. Satellite spots observed by the electron diffraction experiment suggest that they correspond to some periodic distortions of Sr or Cu sublattices associated with an ordering of the apical-O atoms [65]. The annealing temperature below 250°C is low enough not to cause a change of oxygen

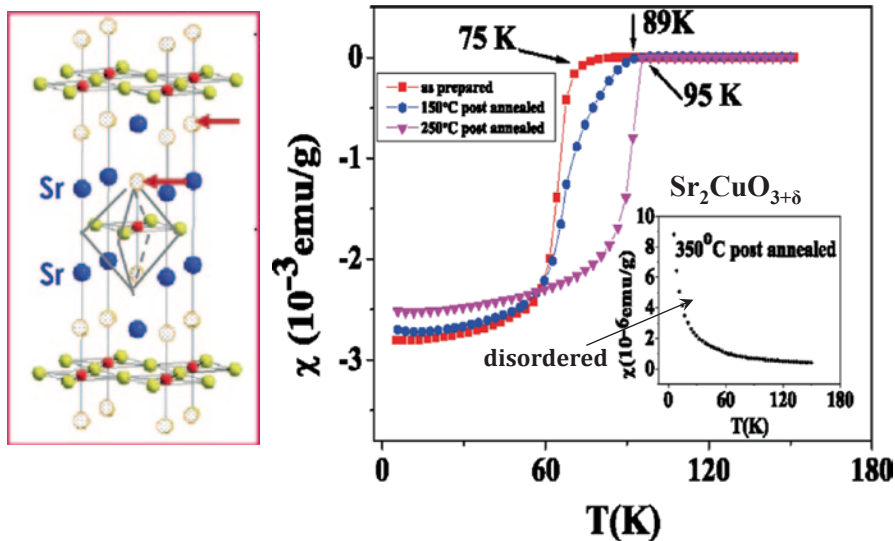


Fig. 3.21 **a** The “214” structure of $\text{Sr}_2\text{CuO}_{3+\delta}$ which is transformed at high pressures from the Sr_2CuO_3 chain structure. In this structure the apical sites of CuO_6 octahedra are not fully occupied by oxygen atoms. **b** $\text{Sr}_2\text{CuO}_{3+\delta}$ becomes a superconductor with T_c exceeding 95 K after annealing at low temperatures which promotes ordering of apical-O atoms [65]

content. If apical-O atoms order, then the compound is regarded as a regular array of three different CuO_4 plaquettes with apical-O on both sides, on one side, and without apical-O.

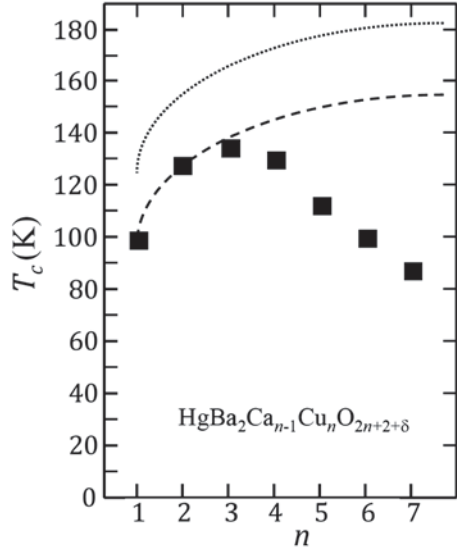
The reason for the high T_c value comparable with that of Hg1201 is not clear yet. Geballe and Marezio [84] suggest a possibility that this compound might be a very heavily hole doped cuprate, presumably $\delta \sim 0.2$ ($p \sim 0.4$) and the highest T_c may be realized in the second T_c dome. The content of the extra apical-O atoms δ , i.e., the hole-doping level, is difficult to estimate even at present. Another possibility is that the average apical-O distance would be large, if one supposes an “infinite” apical-O distance for the CuO_4 plaquettes without apical-O. It is empirically suggested that the longer apical-O distance favors higher T_c (see 3.5.4).

$\text{Sr}_2\text{CuO}_{3+\delta}$ is likely the first case demonstrating that the ordering of dopant atoms reduces disorder and thereby enhances T_c to well above liquid nitrogen temperature. Dopant order, if applicable to other cuprate materials, is one of effective ways to increase the cuprate- T_c .

3.6.2 Optimizing Multilayer Structure

As was described in 3.5.3, the multilayer effect surely exists that enhances T_c with respect to T_c of single-layer cuprates. Also, considering the fact that the maximum T_c (135 K at ambient pressure and 164 K at high pressure) is actually achieved in

Fig. 3.22 T_c vs n plot (the same as that in Fig. 3.15b). The *dashed curve* indicates the interlayer-tunneling model for the situation of all equivalent CuO_2 planes assuming that the interlayer Josephson coupling strength within a multilayer recovers to the level in the bilayer material [74]. When the pairing interaction within a plane is strengthened by about ΔT_c ($n=1$)=30 K, as might be the case under high pressure, further enhancement of T_c is like that shown by the *dotted curve*



trilayer Hg1223, it is natural to expect that higher T_c in the cuprates would be realized in the multilayer structure. The ARPES experiment on Bi2223 unambiguously shows that the SC gap magnitude and therefore pairing interaction is enhanced in the trilayer with respect to single and bilayer materials. For further enhancement of T_c in the multilayer cuprates, a challenging problem to be attacked is to improve the circumstances that degrade T_c for n larger than 4. This is thought to arise from the charge imbalance, difference in the hole density between outer CuO_2 planes (OP) and inner planes (IP). The hole density in IPs tends to be smaller as they have no apical-O atoms and are sandwiched on both sides by Ca^{2+} layers, making an electro-positive circumstance for holes to enter. If the position of the apical-O atoms were far away from OP, then the circumstance of OP would be similar to that of IP and the charge imbalance would be diminished.

The correlation between ΔT_c and intra-multilayer Josephson coupling energy E_J strongly suggests that the interlayer tunneling within a multilayer may contribute to the enhancement of T_c in the multilayer. As was seen in Fig. 3.16b, E_J (and hence T_c) decreases for n greater than 3. The decrease of ΔT_c appears to originate from the doping imbalance between IP and OP which weakens the Josephson coupling strength within a multilayer. Then, it could be guessed, if the Josephson coupling strength were recovered to the level of that in the ($n=2$) bilayer system by, for example, reducing the doping imbalance, T_c would go up further. Quantitative estimate is possible, assuming that all the CuO_2 planes become equivalent, so that the Josephson coupling between the neighboring planes within a multilayer maintains the strength of the bilayer Hg1212. This corresponds to the assumption of the interlayer tunneling (ILT) model [74]. T_c is enhanced for $n \geq 3$, and the “optimized” T_c increases with n following the equation, $T_c(n) = T_c(1) + C(1 - 1/n)$, as indicated by the dashed curve in Fig. 3.22 (with $T_c(1)=98$ K and $C=60$ K derived from the

T_c^{opt} values for $n=1$ and 2). Estimated T_c values are ~ 150 K for $n \geq 5$, but it is significantly lower than 164 K achieved in the real trilayer ($n=3$) cuprate at pressure of 30 GPa.

Suppose, for example, that pressure were to make the apical-O distance from outer-plane (OP) longer, and then it would reduce the circumstantial difference between IP and OP and thereby enhance Josephson coupling strength between planes involving IP. It should be noted that the high-pressure experiment on $\text{Hg}12(n-1)n$ with $n=1$ to 3 [12] actually shows that T_c 's of all the multilayers, even the single layer, increase by ~ 30 K in the high pressure limit. This is suggestive of an additional effect of pressure which enhances the pairing interaction in each plane or increases $T_c(1)$ in the ILT model via, e.g., lattice effect discussed in 3.5.4. Alternatively, pressure might quench the superconducting fluctuations by increasing the phase stiffness ρ_s and/or by strengthening the interlayer Josephson coupling. When the value of $T_c(1)$ is reset to 130 K, the ILT model yields the $T_c(n)$ curve as indicated by the dotted line in Fig. 3.22. These two effects of pressure may explain the record high $T_c=164$ K at 30 GPa. From this perspective, an accessible way to achieve $T_c > 150$ K at ambient pressure would be to quench the high-pressure structure either by applying chemical pressure or by fabricating thin films of the multilayer cuprate on a suitable substrate material.

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Chapter 4

Iron-Based Superconductors

Abstract The iron-based superconductors (Fe-SCs) comprise a big family having the highest $T_c = 55$ K. In this family, an indispensable element is the typical magnetic element Fe, and except for the layer structure the characteristic electronic parameters are largely different from those in the cuprates. The discovery of this family, therefore, evidences that there are more than one route to finding high- T_c materials with T_c higher than 50 K. The parent compounds are antiferromagnetic metals, and both chemical substitution (doping) and application of pressure induce superconductivity. Like the cuprates, Fe-SCs show unconventional pairing, suggesting that strong electronic correlations play a major role in the pair formation. The strong correlations and high T_c have a root in the unique characteristics of the common building block composed of Fe and As (Se) layers in which an unusual antiferromagnetic state is also formed. T_c is material dependent, but the maximum T_c reaches around 50 K in most of sub-families after optimization, and never exceeds 55 K. For further enhancement of T_c , it may be needed to prepare an additional pairing channel by fabricating a novel structure.

4.1 Introduction

$T_c = 26$ K superconductivity in iron-based superconductors (Fe-SC) was discovered in 2008 [1] for $\text{LaFeAsO}_{1-x}\text{F}_x$. T_c values went up to 43 K by application of pressure to the same compound, and then as high as 55 K by replacement of La by other rare earth element, $\text{SmFeAsO}_{1-x}\text{F}_x$ [2]. This was quite unexpected in that the superconductors contain, as an indispensable element, one of the typical magnetic elements Fe (the elemental Fe metal is known to be a superconductor under high pressure), and the maximum T_c value exceeding 50 K has never been achieved in materials other than the cuprates.

Except for the layered crystal structures, the electronic parameters of Fe-SCs are quite different from those of the cuprates; (i) spin quantum number associated with Fe is larger than 1/2, (ii) they are multi-band system with multiple Fermi surface pockets, both electrons and holes, and (iii) on-site Coulomb repulsive energy U

and the spin-superexchange energy J are considerably smaller. Therefore, Fe-SCs opened a new avenue of quest for higher T_c superconductors. Like the cuprates, superconductivity (SC) emerges upon “doping” into the parent compounds which are antiferromagnetic (AF) metals at low temperatures. SC can also be induced by applying pressure to the parent compounds, unlike the cuprates. The phase diagram with AF and SC as two major phases is generic and resembles those in other superconducting materials with strongly correlated electrons, such as the cuprates and the heavy fermion compounds. Strong correlations are tied to superconductivity having unconventional pairing symmetry with sign-changing SC order parameter. In fact, unconventional pairing symmetries have been confirmed for Fe-SCs.

The strong correlations and high T_c have a root in the unique characteristics of the common building block composed of Fe and As (Se) layers. Like the cuprates T_c is material dependent, but the maximum T_c reaches around 50 K in most of sub-families after optimization, and never exceeds 55 K. For further enhancement of T_c , it may be needed to prepare an additional pairing channel by fabricating a novel structure.

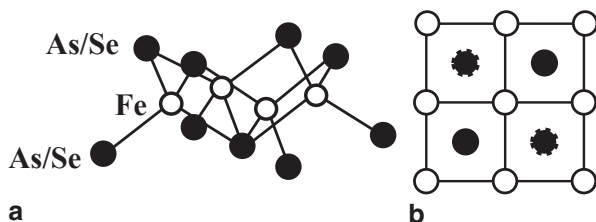
In this chapter, in parallel to that for the cuprates, the T_c -physics of Fe-SCs is extended in the following sequence, (1) material dependence of T_c and parameters that influence T_c , (2) uniqueness of Fe-As or Fe-Se combination, (3) phase diagram with unusual AF and unconventional SC phases, (4) roles of doping and electronic correlations in SC, and (5) possibility of enhancing T_c .

4.2 Material Dependence of T_c and Parameters that Influence T_c

4.2.1 Material Dependence of T_c

It turned out that, like the high- T_c cuprates, the iron-based superconductors comprise a large families of iron arsenides (FeAs) and iron selenides (FeSe) having a common structural unit, FeAs or FeSe block in which a Fe atom is coordinated by As/Se distorted tetrahedron, shown in Fig. 4.1. In this unit Fe atoms form a tetragonal lattice layer sandwiched by a layer of As (Se) atoms above and below it. Fe and As/Se atoms are bonded with strong covalent bond. The structure of

Fig. 4.1 **a** Common structural unit of iron arsenide and selenide high- T_c superconductors. **b** Its top view



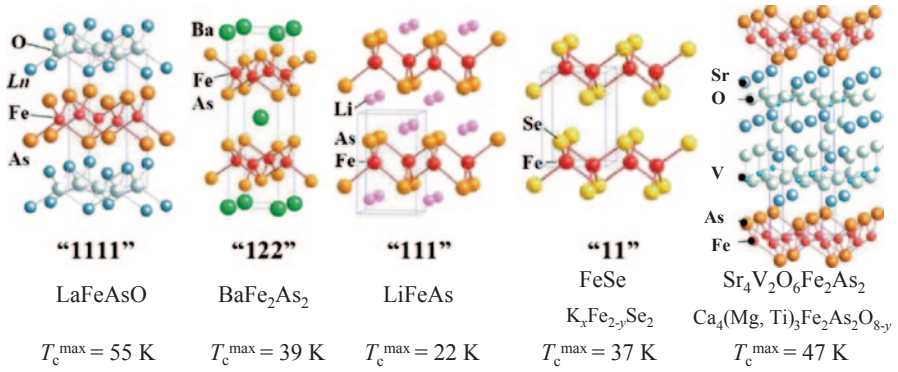


Fig. 4.2 Crystal structures of five representative sub-families of iron-based superconductors. The maximum T_c value so far achieved for a member of each sub-family is indicated

this FeAs/FeSe block is a familiar one already seen in the $T_c = 23$ K borocarbide, $\text{YPd}_2\text{B}_2\text{C}$, as well as the first discovered heavy fermion superconductor CeCu_2Si_2 , and provides a playground of superconductivity with second highest T_c among the known superconductors. Again, like the cuprates, several families of Fe-SCs have been discovered, showing strong material dependence of T_c . Representative sub-families are (1) LnFeAsO (abbreviated by 1111), (2) BaFe_2As_2 (122) [3], (3) LiFeAs (111) [4], (4) $\text{Fe}(\text{Se}, \text{Te})$ (11) [5] and $\text{K}_x\text{Fe}_{2-y}\text{Se}_2$ [6], and (5) $\text{Sr}_4\text{V}_2\text{O}_6\text{Fe}_2\text{As}_2$ (42622) [7]. The crystal structure and its maximum T_c value for each sub-family are shown in Fig. 4.2. The first two compounds, LnFeAsO and BaFe_2As_2 , and FeTe are not superconductors but metals showing an antiferromagnetic order below a temperature T_N , accompanied ($T_N = T_s$) or preceded ($T_N < T_s$) by a tetragonal-orthorhombic structural phase transition at T_s . Hereafter the low-temperature phase is called as antiferromagnetic-orthorhombic (AFO) phase with respect to the high-temperature paramagnetic-tetragonal (PT) phase. T_s range between 60 and 200 K. They are called as “parent” compounds, in analogy to that in the cuprates, and are made superconductors by chemical substitution or oxygen reduction (in the case of 1111)—“doping” and by external pressure (in the case of 122). The other two, 111 and 42622, are “self-doped” superconductors. The normal state (above T_c) of the SC region is in most cases paramagnetic and tetragonal in structure. The α -PbO type FeSe is a superconductor in its own with low $T_c = 8$ K, but T_c is enhanced to ~ 35 K by alkaline atom (K or Rb) doping into a modified Fe-deficient compound, $\text{K}_x\text{Fe}_{2-y}\text{Se}_2$. The maximum T_c value, $T_c^{\max}$ ranges from 8 K (for 11), 22 K (for 111), 39 K (for 122) to 55 K (for 1111) across the Fe-SC family. Also, in each family $T_c^{\max}$ significantly varies, e.g., between 26 K ($\text{LaFeAsO}_{1-x}\text{F}_x$) and 55 K ($\text{SmFeAsO}_{1-x}\text{F}_x$) for 1111, depending on the constituent elements other than Fe and As (Se) and degree of disorder.

4.2.2 Parameters that Influence T_c

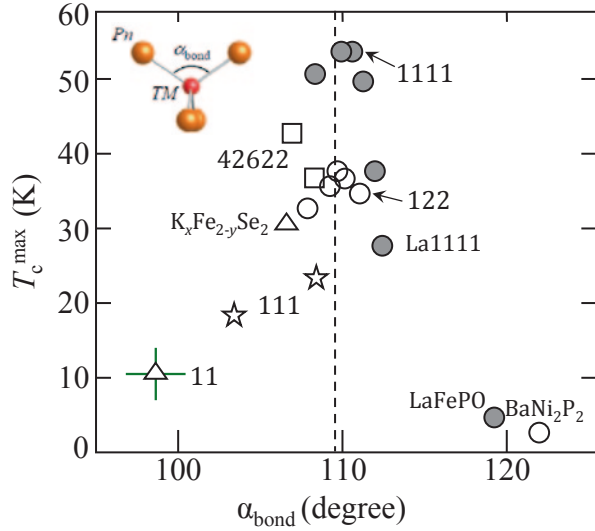
The key parameter is again **doping** that induces SC and hence controls T_c , but somewhat in a different ways from that in the cuprates. As in the case of the cuprates, the major doping process is chemical substitution for constituent cations or oxygen reduction. For 1111, e.g., LaFeAsO, the electron doping is made by various processes, (i) F-substitution for O, LaFeAsO_{1-x}F_x, (ii) O-reduction, LaFeAsO_{1-y}, and (iii) hydrogen (H⁻) substitution for O, LaFeAsO_{1-x}H_x. For 112, BaFe₂As₂, both electron and hole dopings are possible, e.g., Ba(Fe_{1-x}Co_x)₂As₂ for the former and Ba_{1-x}K_xFe₂As₂ for the latter. In this case, even “isovalent” doping, either BaFe₂(As_{1-x}P_x)₂ or Ba(Fe_{1-x}Ru_x)₂As₂, induces superconductivity. As will be discussed in 4.5, a major effect of doping is not necessarily changing the carrier density. Doping tunes the lattice parameters and the strength of electronic correlations as well. Differences from the cuprates are also (i) the parent compounds, e.g., BaFe₂As₂, are metals, and (ii) even doping, chemical substitution, into the active Fe-As (Se) layer induces SC. The parent compounds of the cuprates are Mott (or charge-transfer) insulators, and only one type of carriers can be doped to induce superconductivity. Moreover, direct chemical substitution, such as Zn or Ni for Cu, in the CuO₂ plane can never drive SC but easily destroys SC.

Disorder, to some but lesser extent than in the cuprates, affects T_c . The maximum T_c value, $T_c^{\max}$, is significantly lower for materials doped into the active FeAs blocks than $T_c^{\max}$ achieved by doping into layers outside the FeAs block. For BaFe₂As₂, $T_c^{\max}$ decreases in the order of Ba_{1-x}K_xFe₂As₂ ($T_c^{\max}=39$ K), BaFe₂(As_{1-x}P_x)₂ ($T_c^{\max}=32$ K), and Ba(Fe_{1-x}Co_x)₂As₂ ($T_c^{\max}=25$ K). This site-dependent disorder effect is similar to that in the cuprates, but a crucial difference is that even a substitution of other transition-metal element for Fe is not so destructive of SC. The low $T_c^{\max}=18\text{--}22$ K for 111 materials, LiFeAs and NaFeAs, are ascribed to disorder in the layers of alkali-metal ions (Li or Na) which are incidentally located close to the As planes, while the disorder site located far away from the FeAs block is one of the reasons for the highest T_c in 1111.

Competing order, which is widely agreed on, is the AFO order alone. It competes with SC in that SC emerges when AFO is suppressed both by doping and by applying pressure. However, in some materials, the AFO phase is sharply separated from the SC phase, and both coexist in others. Notably, T_c is always maximal near the boundary of AFO and SC phases, and tends to decrease as one moves away from the AFO phase. Role of the AF order is apparently different from that in the cuprates.

The crystal structure seems more influential on T_c than doping, and there are actually correlations between T_c and some structural parameters. Just after the discovery, a correlation was found between T_c and the **Pn-TM-Pn bond angle** α_{bond} (Pn and TM stand for pnictogen and transition-metal element, respectively) [8]. They found that T_c as a function of α_{bond} is peaked at 109.5° which corresponds to the ideal (undistorted) TM-Pn₄ tetrahedron (see Fig. 4.3). This is particularly the case with the iron arsenides with highest T_c such as $T_c=50$ K-class 1111 and Ba_{1-x}K_xFe₂As₂.

Fig. 4.3 T_c vs Pn-TM-Pn bond angle (defined in the inset) plotted for various TM pnictides (simplified from that in Ref. [8]). The angle, 109.5° , of the ideal tetrahedron is indicated by the dashed line

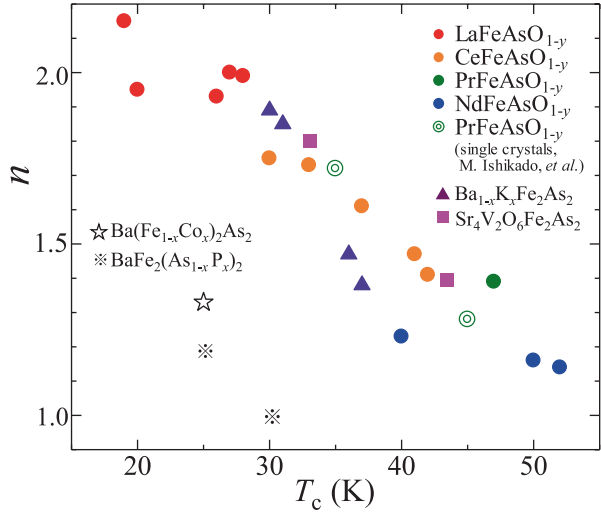


The lower T_c ($=26$ K) for $\text{LaFeAsO}_{1-x}\text{F}_x$ than that (55 K) for $\text{SmFeAsO}_{1-x}\text{F}_x$ is ascribable to the larger bond angle. However, no unique correlation is found across the sub-families— CsFe_2As_2 with $T_c = 2.6$ K is a known exception having α_{bond} close to 109.5° . It is theoretically an open question why the ideal tetrahedral configuration favors higher T_c .

A closely related but alternative structure parameter is the distance of pnictogen (chalcogen) atom from the adjacent Fe layer (so called **pnictogen height** or anion height h_p). T_c was found to have a peak around $h_p \sim 1.38$ Å [9]. The theoretical calculations based on the spin-fluctuation-mediated pairing scenario show that the FS nesting condition and the appearance of an extra hole pocket are sensitively affected by a change of the pnictogen height [10]. They argue that large h_p favors nodeless sign reversing (s_{+-}) pairing rather than nodal (e.g. d -wave) pairing and thereby favors high T_c owing to the robustness of SC against impurities. The pnictogen height is reminiscent of the apical-O distance of the cuprates. However, the former would have more direct relevance to the electronic state (affecting the nearest neighbor hopping t) of iron pnictides as the FePn block is an active layer, while the apical-O is outside the active CuO_2 plane (affecting the long distance hopping, t'). Again, at present it is not clear whether the above theoretical explanation is generically applicable across different TM pnictides and Fe selenides sub-families.

In conventional superconductors T_c is more or less correlated with the magnitude of resistivity in the normal state, since the electron-phonon interaction is responsible for both SC and scattering of carriers. By contrast, the optimally doped cuprates show universal **T -linear resistivity** in the normal state irrespective of the T_c^{opt} values. Fe-SCs show both features. Like the cuprates, the resistivity for the compound that is “optimally doped”, tends to be dominated by a linear-in- T term regardless of its T_c value [11]. On the other hand, as plotted in Fig. 4.4 mainly for

Fig. 4.4 $T_c^{\max}$ plotted against the exponent of the temperature dependent resistivity ($\rho \sim T^n$) for various iron arsenides [12]



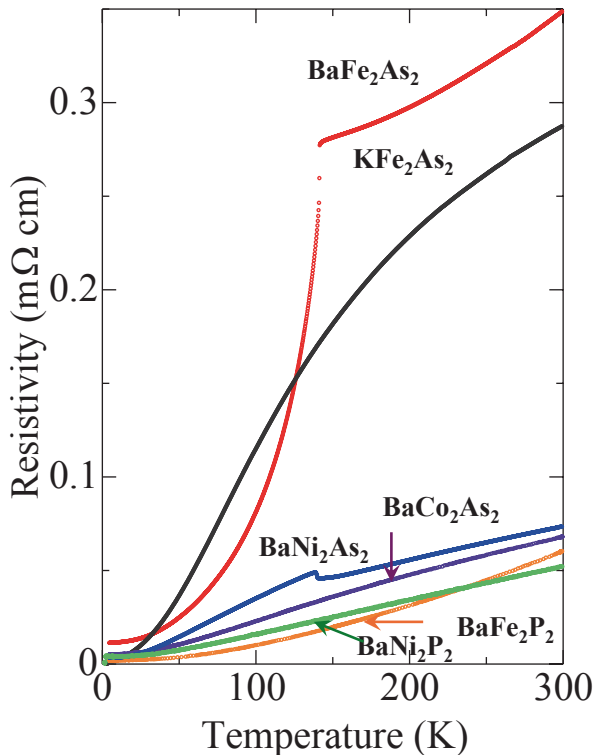
the 1111 family, the compounds with 50 K-class, e.g., $\text{NdFeAsO}_{1-x}\text{F}_x$, show T -linear resistivity, whereas the low- T_c members, e.g., $\text{LaFeAsO}_{1-x}\text{F}_x$, show T^2 dependence, typical of a Fermi liquid, indicating that stronger electron scattering favors higher T_c [12]. The correlation between electron scattering strength and $T_c^{\max}$ suggests that scattering from some (bosonic) excitations which gives rise to the T -linear resistivity is relevant to stronger pairing interaction in Fe-SCs. This is similar to conventional superconductors of the electron-phonon mechanism, but is in contrast to the cuprates in which the T -linear resistivity is generic for optimally doped materials irrespective their T_c values.

4.3 Uniqueness of Iron Arsenides/Selenides

4.3.1 Unique Fe-As(Se) Combination

So far hundreds of transition-metal (TM) pnictide and chalcogenide compounds with similar structures have been synthesized. To date, only iron-arsenides and selenides show superconductivity with T_c well above 20 K. One of the unique features of the iron arsenides/selenides is that they show the AFO order in their “undoped” and sometimes in the “heavily doped” regimes, indicating that the electrons in the Fe 3d orbitals or a part of them are on the verge of localization. Another unique feature is that the normal-state resistivity is distinctly high (typically 200–400 $\mu\Omega$ cm at room temperature) among other metallic TM pnictides, as displayed in Fig. 4.5 for various TM pnictides with the same 122 structure. The high resistivity is indicative of either low carrier density or strong carrier scattering or both.

Fig. 4.5 Temperature dependent in-plane resistivity measured for various transition-metal pnictides with the same “122” structure



Fe-SCs are, in common with the cuprates, combinations between 3d-TM and anions with filled *s/p* orbitals. The basic physics is, however, is entirely different. The main electronic bands around the Fermi level are basically Fe 3d-derived bands with all five 3d orbitals involved. Every Fe atom is tetragonally coordinated by As (Se) atoms, and the Fe layer in which the Fe atoms form a simple square lattice is sandwiched between two As slabs. Because of this, the hybridization between Fe and As is not strong and also the electronegativity of As ion (As^{3-}) is much smaller than that for O^{2-} . However, this does not mean that As (Se) atoms are irrelevant. The heavy As (Se) 4*p* orbitals are much spread in space as compared with the $\text{O}2p$ orbitals and highly polarizable which are affected sensitively by extra charges in their vicinity. The unique electronic properties, the fragile AF spin order, itinerant electrons, superconductivity, are probably, in part, ascribable to the large As (Se) polarizability [13].

4.3.2 Unique Electronic State

The electronic structure of Fe-SC (specifically iron arsenides) in the normal state, i.e., in the paramagnetic-tetragonal (PT) phase, is well described by the band structure derived from Fe 3d- orbitals. Fermi surface (FS) consists of two or three

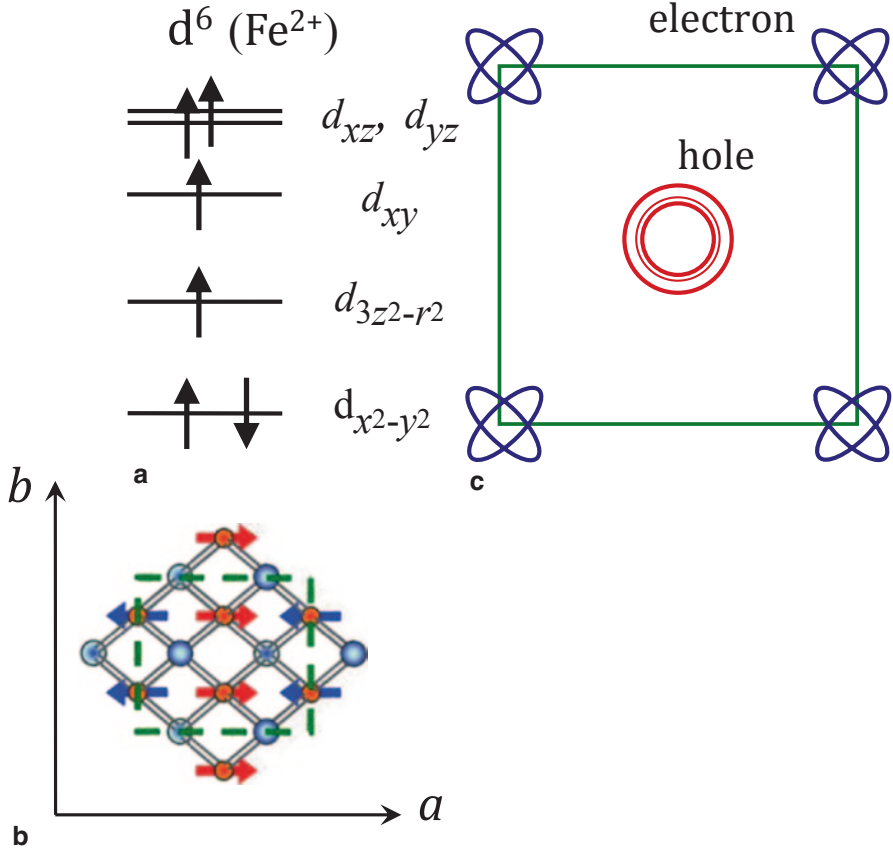


Fig. 4.6 **a** Electron filling of the 3d orbitals in the Fe^{2+} state. **b** Magneto-structural ordered state with collinear AF spin order and orthorhombic lattice distortions. **c** Schematic picture of Fermi surface typical of iron arsenides in the high-temperature tetragonal phase

hole pockets around the Brillouin zone (BZ) center and two electron pockets centered at $(0, \pm\pi)$ and $(\pm\pi, 0)$ zone boundary [14] (schematic sketch of FS is shown in Fig. 4.6). To be strict, the presence of two inequivalent As sites (above and below the Fe lattice layer, sketched in Fig. 4.1b) makes the BZ folded to contain two Fe atoms in a unit cell and put the electron FS pockets at the BZ corners $(\pm\pi, \pm\pi)$. These FS pockets have quasi-2D cylindrical shapes. Some of them are warped along the c axis (cylindrical direction), so that the electronic properties are not two-dimensional but anisotropic 3D metallic. The calculated band structures, mainly by LDA, qualitatively agree with the experiments such as ARPES and quantum oscillations.

4.4 Phase Diagram and Competing Order

4.4.1 Temperature-Doping Phase Diagram

There are two classes of materials showing distinct temperature (T)-doping (x) phase diagram. As schematically shown in Figs. 4.7a and b, in one class, $\text{LnFeAsO}_{1-x}\text{F}_x$ ($\text{Ln}=\text{La}$ and Nd) and $\text{Sr}(\text{Ca})\text{Fe}_2\text{As}_2$, the AFO and SC phases are sharply separated by a first-order like phase transition and do not overlap [15]. $\text{SmFeAsO}_{1-x}\text{F}_x$ [16] and the doped BaFe_2As_2 systems belong to the second class in which both phases overlap and coexist over a range of doping. Whether AFO and SC are phase-separated or uniformly coexist is still a matter of debate. Also material dependent are the two transition temperatures that characterize the AFO phase, the tetragonal-orthorhombic structural transition at T_s and the paramagnetic-antiferromagnetic transition at T_N . T_s coincides with T_N in 122 compounds, whereas T_s is higher than

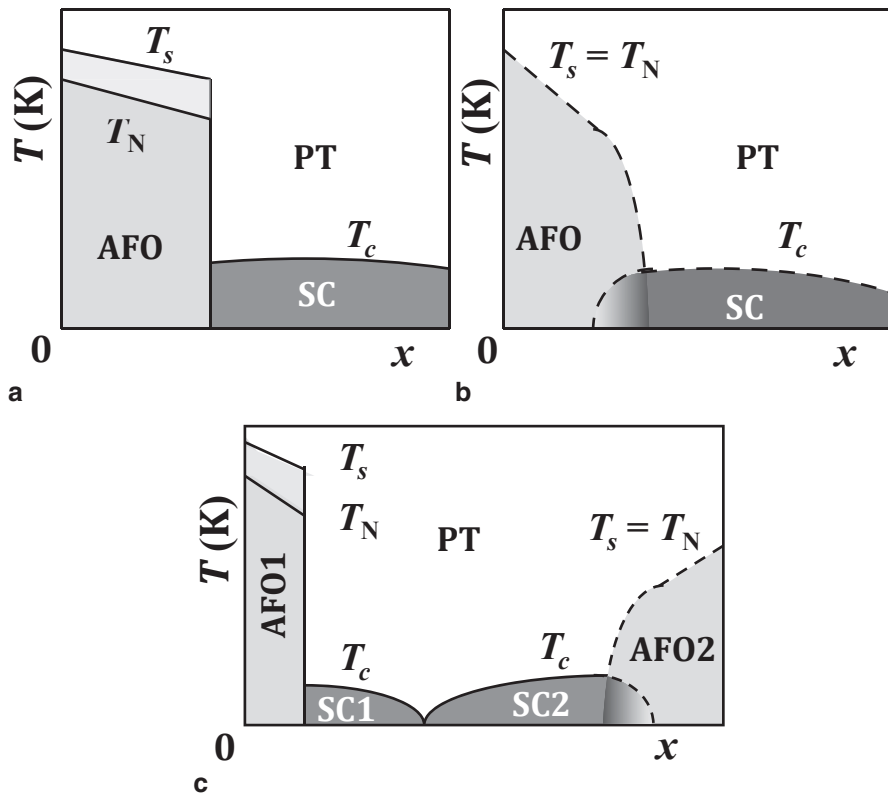


Fig. 4.7 a, b Two types of the temperature (T)—doping (x) phase diagram, schematically drawn. c A new type of phase diagram has been reported with double T_c domes and bipartite antiferromagnetic phases [19, 21]

T_N in 1111 compounds. The material parameters that make such difference are not known yet.

A hotly debated issue concerning the T - x phase diagram is on the presence or otherwise of a quantum critical point (QCP) near the AFO-SC phase boundary and ‘nematic’ fluctuations in the PT phase. The latter is conceivably associated with this putative QCP and with the electronic anisotropy seen in the AFO phase. The experimental results supportive for nematicity are the resistivity anisotropy persisting to well above T_s in the AFO phase of the Co underdoped $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ [17] and the weak magnetic anisotropy in the PT phase detected by magnetic torque measurements on $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ [18]. It is not clear yet if the nematic state/phase and/or QCP are generic to Fe-SCs, considering that such anisotropy has ever been observed for the doped SrFe_2As_2 (CaFe_2As_2) system which not only shows a sharp first-order phase transition at T_s from AFO to PT but also a sharp (first-order transition like) change from AFO to SC (PT) as a function of doping concentration.

T_c is always maximal near the boundary of AFO and SC phases including the coexisting region. As T_c tends to decrease at higher doping levels or as one moves away from the AFO phase, the T_c vs doping or pressure characteristics forms a flat-top half-dome shape. For one of the electron-doped systems, $\text{LaFeAsO}_{1-x}\text{H}_x$, two-dome structure is observed [19] (two domes are also observed for $\text{K}_x\text{Fe}_{2-y}\text{Se}_2$ and related compounds as a function of pressure [20]). In the former case, the second dome ends up when the second antiferromagnetic phase shows up at $x \sim 0.5$ [21]. Interestingly, in both cases T_c^{max} is higher for the second dome, 36 K in comparison with 26 K for the first dome (32 K for the first and 48 K for the second dome in the case of pressure-tuned $\text{K}_x\text{Fe}_{2-y}\text{Se}_2$). It remains to be seen if the two-dome structure in the phase diagram is a generic feature of Fe-SCs.

4.4.2 Nature of the Competing Order

4.4.2.1 Origin of Magnetism

It was hotly debated whether the magnetic order in the AFO phase is due to spins localized on Fe atoms or whether it originates from itinerant magnetism more properly described by a spin-density-wave (SDW) order due to (nesting) instability of the FS. Nominal Fe valence is Fe^{2+} with $3d^6$ electron filling which takes either high-spin state with spin quantum number $S=2$, shown in Fig. 4.6a or non-magnetic low-spin state with $S=0$, depending on the strength of the Hund’s rule coupling. Finite Fe magnetic moments are observed, though the magnitude is smaller ($0.5\text{--}2.1 \mu_B$), than that expected from the $S=2$ local spins which indicates that a localized spin picture appears more appropriate. Real-space spin arrangement consists of spins aligned antiferromagnetically along the tetragonal a -axis and ferromagnetically along the b axis, so-called “collinear” AF spin order (shown in Fig. 4.6b). A lot of efforts have been devoted to elucidate that a localized spin model has any validity for an obviously metallic system [22]. Regardless of the exact description of spins,

it is clear that magneto structural coupling between electrons, both spin and orbital degrees of freedom, and lattice is important in Fe-SC in the AFO phase and perhaps in the SC phase. In fact, the magnetic transition (at T_N) is always accompanied by a structural phase transition (at T_s)—from tetragonal to orthorhombic, and T_s is equal to or higher than T_N .

An antiferromagnetically ordered phase in proximity to the SC phase is universally observed in superconductors with strongly correlated electrons. The AF long-range order in the undoped and dilutely doped cuprates, which are insulating, is realized by an arrangement of Cu spins on a square lattice. On the other hand, the collinear (bi-collinear in FeTe) AF order in Fe-SCs, a stripy spin arrangement in the Fe layer, preserves a metallic state. Despite the high spin quantum number $S=2$ of Fe^{2+} , the AFO order is easily suppressed by chemical substitution (doping) and pressure, giving a way to SC. No doubt, the partner anion, As or Se, with high polarizability conspires to form this unique AFO order. It is the only known order that competes with SC in Fe-SCs in contrast to the cuprates with a variety of competing phases, SDW, CDW, stripe order, and in particular the pseudogap (PG) phase. As will be discussed below, its peculiar electronic state and close connection to SC are reminiscent of PG in the underdoped cuprates.

4.4.2.2 Electronic Anisotropy

BaFe_2As_2 is a representative parent compound and undergoes a tetragonal-orthorhombic structural phase transition at temperature T_s ($= 143$ K) with a shorter b axis and a longer a axis in the orthorhombic phase [23]. At the same temperature (or slightly lower temperature T_N in some other parent compounds) the collinear AF order takes place. Reflecting the tetragonal (4-fold rotation) symmetry breaking, the AFO phase shows various anisotropic electronic properties such as anisotropic spin and charge excitations detected by the neutron scattering [24] and by optical measurement [25], respectively. Among them probably the most unusual is the in-plane resistivity. The resistivity anisotropy measured on a BaFe_2As_2 single crystal detwinned by uniaxial pressure is vanishingly small at low temperatures (see Fig. 4.8a), but the anisotropy emerges upon doping Co.

The almost isotropic resistivity for the undoped compound contrasts the robust and pronounced anisotropy seen in the optical conductivity spectrum [25] shown in Fig. 4.8b. In the AFO phase below T_s , the optical conductivity measured on a detwinned crystal of BaFe_2As_2 is higher for light polarization along the a axis ($\sigma_a(\omega)$) than that for b -axis polarization ($\sigma_b(\omega)$) in the energy region below 1350 cm^{-1} (~ 0.15 eV). The anisotropy is reversed above this energy, and the anisotropy persists up to energy ~ 2 eV. Upon lowering T below T_s , the spectra for both polarizations exhibit a gap feature—the low-energy conductivity is suppressed and transferred to the higher energy region as the AFO order develops. The anisotropy arises from a difference in the gap energy scales for different polarization. As displayed in Fig. 4.8c, the b -axis gaps are larger in energy than the a -axis ones which make σ_b lower than σ_a in the low energy region. One of the origins of the gap anisotropy is

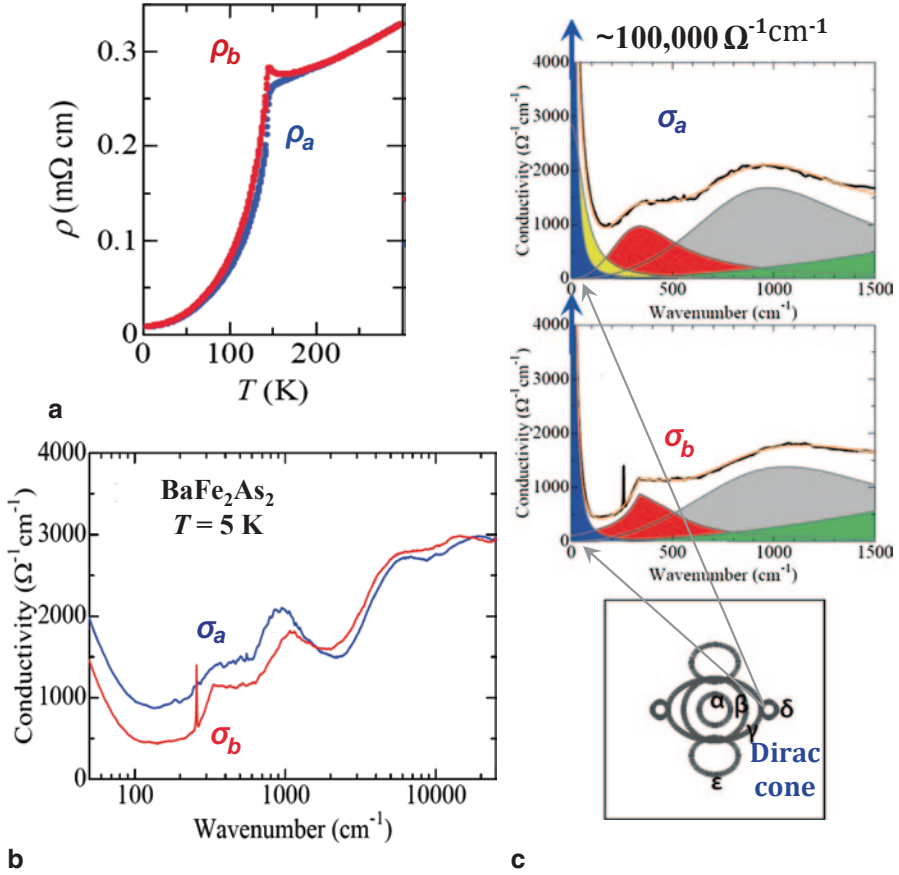


Fig. 4.8 **a** In-plane resistivity along two orthorhombic axes (a and b , defined in Fig. 4.6b) measured for a detwinned single crystal of BaFe₂As₂ with improved quality [25]. **b** Optical conductivity spectra of BaFe₂As₂ for light polarization along the a - and b -axis direction, measured at $T = 5$ K deep inside the AFO phase [25]. **c** Decomposition of the low-energy optical conductivity spectra for a -axis and b -axis polarization shown on a logarithmic frequency (wavenumber) scale. The pronounced sharp Drude peak observed in both spectra originates from the small Fermi surface pockets of Dirac electrons inherent to the AFO phase [27] as shown in the attached sketch below

the energy splitting between d_{xz} -orbital derived and d_{yz} -orbital derived bands [26], which are degenerate in energy in the PT phase, due to the (tetragonal) symmetry breaking in the AFO phase.

In the lowest energy region both spectra are dominated by a sharp Drude conductivity peak. The width of this peak becomes extremely narrow and its peak height becomes extremely large (exceeding 30,000 Ω⁻¹ cm⁻¹ at $T = 5$ K). The almost isotropic resistivity at low temperature stems from this gigantic Drude peak present in both spectra. This peak originates from small electron-FS pockets associated with the energy bands showing Dirac-cone-shaped dispersions (see the sketch in Fig. 4.8c). The presence of the “Dirac” bands is not accidental but is created by the

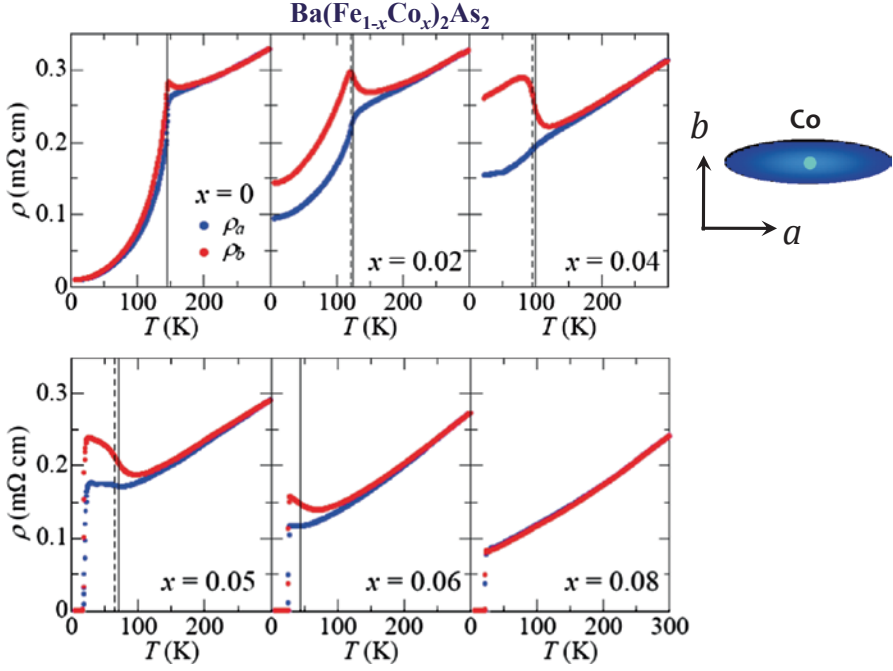


Fig. 4.9 Evolution of anisotropic resistivity with Co doping into BaFe_2As_2 [28]. An impurity state formed around a Co impurity is schematically sketched

special electronic situation in the AFO phase [27]. Unique topological nature of the band structure inhibits the backscattering of electrons from impurities, making the electron mobility very high. The Dirac electrons are robustly present in the Co doped compounds as long as the AFO order is established, as they are protected the unique topology (parity) of the relevant bands in the AFO phase.

Upon Co doping into BaFe_2As_2 , the resistivity becomes highly anisotropic, and to the contrary, the anisotropy in optical conductivity is diminished [28]. Co impurities induce a resistivity anisotropy on one hand, but suppress the anisotropic AFO order parameter on the other. As a consequence of this competition, the magnitude of the resistivity anisotropy, as a function of Co content, initially increases, eventually levels off, and then decreases as doping proceeds in the AFO phase, as shown in Fig. 4.9. The resistivity along the b axis (ρ_b , in the direction of shorter lattice constant and ferromagnetic spin alignment) is found always higher than that along the a axis (ρ_a , in the direction of longer axis and AF spin alignment). This is counter-intuitive to conventional wisdom, e.g., the double-exchange mechanism. The analysis of the optical conductivity spectrum indicates that anisotropy in resistivity arises from the anisotropic scattering cross-section of a Co impurity for the isotropic Dirac electrons. With Co doping, the peak in $\sigma_b(\omega)$ is more rapidly broadened and hence the peak height is more rapidly lowered with Co doping, resulting in the dc resistivity anisotropy $\rho_b > \rho_a$.

In the high-temperature PT phase, the Co atom substituted for Fe is not a strong impurity and only supplies one extra electron carrier. It dramatically changes its nature in the AFO phase. A Co atom introduced into the FeAs blocks is supposed to polarize its electronic and lattice surroundings anisotropically and thereby forms an anomalous impurity state with an anisotropic scattering cross section for charge carriers. The speculation is supported by the direct STM observation [29] of an anisotropic impurity state around a doped Co atom with electron cloud more extended along the a axis. It may be that an extra electron around a Co atom modulates the collinear AF spin arrangement locally and/or that it induces a local orbital order by distorting the underlying orthorhombic lattice. The same but weaker dopant induced anisotropy is observed in the AFO phase of P-Ba122, but almost no anisotropy is observed for K-Ba122 [30]. The dopant-site dependence indicates that the magnitude of resistivity anisotropy depends on the strength of dopant impurity potential.

The striking anisotropy in the phonon intensity is also seen in the optical conductivity spectrum [25, 28]. An optical phonon seen at 257 cm^{-1} in the spectrum in the PT phase (presumably the phonon mode corresponding to the relative displacements of Fe and As atoms) enhances its intensity in $\sigma_b(\omega)$ and entirely loses the intensity in $\sigma_a(\omega)$ (see Figs. 4.8b and c). It is not a new phonon mode appearing in the AFO ordered state, but its polarization-selective intensity appears to require the presence of an anisotropic polarization field induced by the dynamical lattice distortion. The induced polarization cancels the dipole field associated with the optical phonon mode in the a direction, whereas it reinforces the dipole field along the b direction. Both charge and orbital degrees of freedom would be involved to form this dynamical polarization field.

The AFO phase is thus an unusual metal showing strongly anisotropic response to static impurities and to a dynamical lattice distortion. This phase is unique to the compounds of Fe with $3d^6$ electronic configuration in combination with heavy As (Se) anions with high polarizability, and may be regarded as an ordered state of spin-charge-orbital-lattice complex. The fact that T_c attains maximum values near the AFO-SC phase boundary suggests that the fluctuations of this complex order might play a relevant role in the formation of Cooper pairs in Fe-SCs.

4.4.3 Unconventional Superconductivity

Superconductivity in Fe-SCs is almost certainly unconventional with sign-changing order parameter (Δ) [31]. In Fig. 4.10 are shown possible gap symmetries in Fe-SCs proposed so far. It turns out that, unlike the d -wave gap in the cuprates, the positions of the gap nodes are both material and doping dependent. In some cases no gap nodes are observed on FS and in others the nodes are located on FS [32]. In the former case, typically for $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ in the x region lower than 0.8 and Fe(Se, Te), gap on the electron-FS pockets around the BZ corner has an opposite sign to that on the hole-FS pockets around the zone center which are well separated in the BZ, so that, each FS is fully gapped like s -wave gap. The gap nodes should lie at

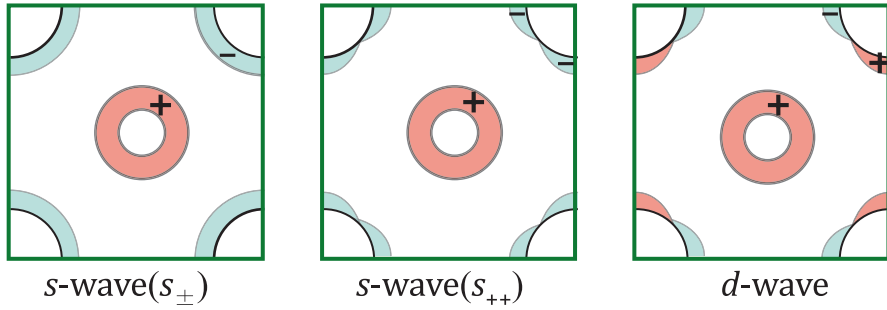


Fig. 4.10 Superconducting gap and its sign for three types of pairing symmetry, s_{+-} , s_{++} , and d , mapped on the Fermi surface of a typical iron-based superconductor. For simplicity, only one hole and one electron Fermi surface pockets are shown

some positions in between both types of FS which are not necessarily high symmetry points. This gap symmetry corresponds to that so-called s_{+-} wave. The interband electron-hole interaction presumably linked to the spin (orbital) fluctuations was thought to give rise to electron pairing. When the K-content further increases close to $x=1$ and the electron-FS pockets completely disappear, nodes appear on the hole-FS around the BZ center. This was interpreted as a change of the gap symmetry from s_{+-} to d . But the recent thermal conductivity and magnetic penetration depth measurements have suggested that the gap nodes shift to the positions between hole-FS pockets around the zone center with basically s -wave symmetry gap (s_{++} gap with accidental nodes). The shift of the nodes with change of doping and/or disorder indicates that the gap nodes are not symmetry protected due to multiband FS structure of Fe-SCs in stark contrast to the robust (symmetry protected) d -wave gap nodes in the cuprates.

Considering that the high- T_c superconductivity ($T_c^{\max}=32$ K) emerges in highly electron doped $\text{K}_x\text{Fe}_{2-y}\text{Se}_2$ with no hole-FS pocket and possibly with unconventional pairing, electron-electron interaction, not specific to the electron-hole interaction or nesting between electron- and hole-FS, is generically important for superconductivity of Fe-SCs with multiband FS structure. Basically s -wave symmetry of the gap explains the robustness of SC against disorder/impurity even if their location is in the FeAs (FeSe) block. Also, similar to the cuprates, the superfluid density is small in most of Fe-SCs [33].

4.5 Role of Doping and Electronic Correlations

As was stated in the previous section, doping in Fe-SC is not simply changing charge (electron/hole) density or electron filling. Both electron and hole doping and even doping by substitution of isovalent atoms are possible to transform non-SC parent compound to superconductors. Also, modulation of local structure, FePn_4

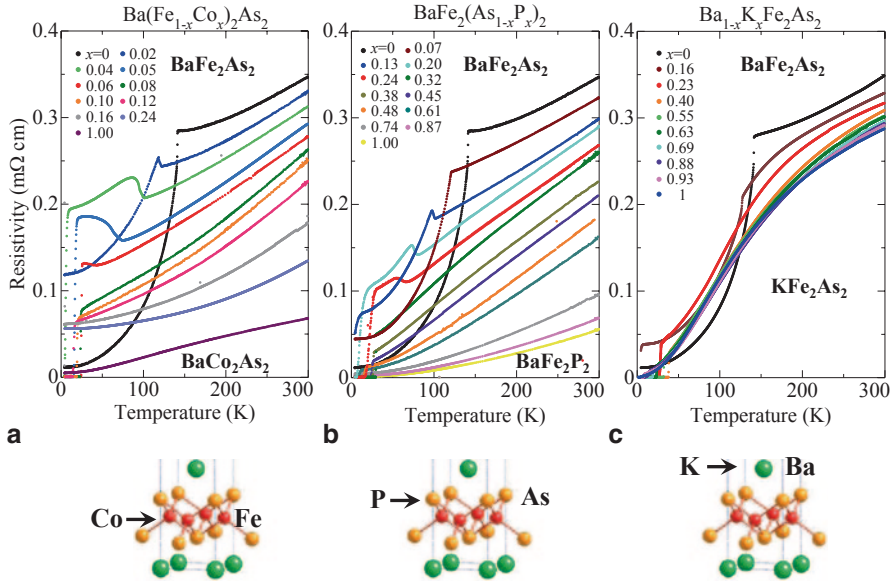


Fig. 4.11 Doping evolution of the temperature dependent in-plane resistivity for three types of doping into BaFe₂As₂; **a** electron (Co) doping, **b** isovalent P doping, and **c** hole (K) doping [40]

tetrahedron, significantly affects the electronic state and hence superconductivity, SC gap symmetry and/or T_c . The systematic and comparative study of various doping processes in the parent compound BaFe₂As₂ has given an important insight into the physical implication of the doping in Fe-SC. Doping, atomic substitution, is possible into all the three different lattice sites: Ba_{1-x}K_xFe₂As₂ (K-Ba122), BaFe₂(As_{1-x}P_x)₂ (P-Ba122), and Ba(Fe_{1-x}Co_x)₂As₂ (Co-Ba122) corresponding to hole, isovalent, and electron doping, respectively. Doping evolutions of the temperature-dependent resistivity are shown in Figs. 4.11a–c measured for the three types of doping into BaFe₂As₂.

4.5.1 Role of Doping

The resistivity of the parent BaFe₂As₂ rapidly decreases below $T_s = 143$ K, following T^2 dependence, to very low values at lowest temperature [25]. It is, on the other hand, high above T_s , $\rho_{ab} \sim 300 \mu\Omega$ cm, comparable with that for optimally doped cuprates and shows only a weak T dependence. The optical conductivity spectrum of BaFe₂As₂ in the PT phase shows a small peak at $\omega = 0$ and a long tail merging into a peak of interband transitions at higher energies, similar to that of the high- T_c cuprates in the normal state. The spectrum in the low energy region is better described by two Drude components with distinct character; one is narrow in width and having much smaller spectral weight (SW) and the other is broad with much bigger SW.

Hereafter, focus is on the PT phase. Upon Co substitution, *electron doping*, the resistivity gradually decreases toward $x=1$ (BaCo_2As_2). This is in contrast to that in the AFO phase, where major role of Co dopant is to produce an anisotropic impurity potential which electrons move more strongly in one direction. Certainly, Co with one extra electron with respect to Fe supply electron carriers in the PT phase, as is also confirmed by a decrease in the Hall coefficient with negative sign [34] as well as by the ARPES study of FS with electron-FS pockets expanding and hole-FS shrinking with doping [35].

The *isovalent P doping* makes resistivity to gradually decrease as in the case of the Co doping which is rather surprising, since the isovalent P substitution for As does not supply either electron or hole. The ARPES-FS does not show an appreciable change with doping to explain a similar evolution of resistivity to that with Co doping [36]. What is actually going on is that the P doping increases the spectral weight (SW, $\sim n/m^*$) of the narrow (coherent) Drude component [37] which is most likely associated with the electron-FS. The effect of P doping on the lattice is also appreciable. The substitution of P with smaller ionic radius results in a shrink of the unit-cell volume which leads to an increase of the bond angle α_{bond} (or decrease in the pnictogen height). So, a possible mechanism of P doping is to apply chemical pressure, making the electron mobility larger (more coherent) by widening the bandwidth or decreasing m^* which explain the increase of the coherent spectral weight.

Similarity of electron and isovalent doping effect is suggestive of striking electron-hole asymmetry in the PT phase of Fe-SCs. This corroborates the contrasting doping dependence of resistivity for *hole-doped K-Ba122*. The K substitution for Ba, hole doping, increases the hole density, as evidenced by ARPES-FS measurement—the hole FSs expand while the electron FSs shrink and eventually disappear [38, 39]. Nevertheless, the change of resistivity is modest, and the T dependence in the high T region remains weak. To reconcile the doping evolution of resistivity with that of ARPES-FS it is necessary to suppose that quasiparticles (QPs) on the hole-FS are incoherent, comprising a broad Drude component in the optical spectrum. In fact, the mean-free-path $l_h = v_F \tau$, estimated from the Drude width ($1/\tau$) and the Fermi velocity (v_F) determined by the ARPES measurement, is shorter than the lattice spacing a [40].

It is thus inferable that the doping evolution of resistivity, the $\omega=0$ conductivity, is predominated by the electron-FS, forming the coherent Drude component, while the hole-FS contributes to conductivity as a nearly constant, incoherent, term. The contribution of the holes becomes apparent at high temperatures as a tendency for resistivity saturation, in particular, for K-Ba122, when the peak of the narrow, coherent, Drude is suppressed by its T -broadening. This indicates that the hole carriers are always subject to strong scattering. As plotted in Fig. 4.12, the coherent Drude spectral weight (SW) N_D , or the fraction of N_D in the low-energy SW, increases with Co (P) doping by increasing the density of electrons (or by decreasing the effective mass), whereas it does not, even decreases with K-doping. The decrease of N_D in the case of K doping might be due to an increase of the effective mass, as the

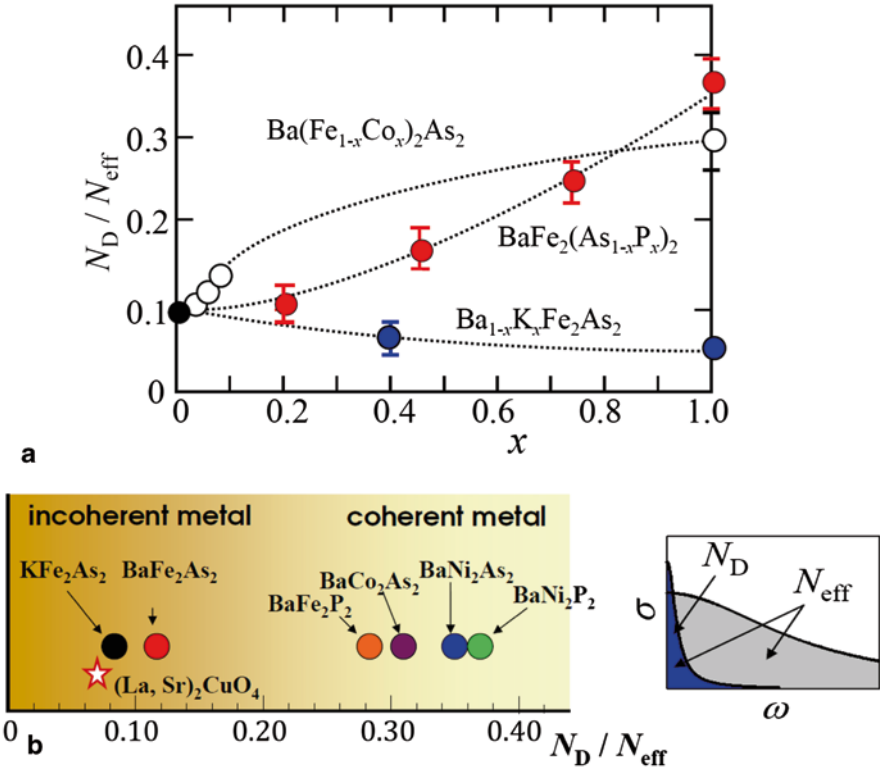


Fig. 4.12 **a** Doping dependence of the fraction of the coherent Drude spectral weight N_D/N_{eff} in the low-energy optical conductivity spectrum for Co-, P-, and K-doped BaFe₂As₂. **b** Diagram showing the values of N_D/N_{eff} for various transition-metal pnictides with the same “122” crystal structure and one typical cuprate

measurement of quantum oscillations for KFe₂As₂ reported an enhancement of the hole-carrier effective mass by a factor of 4–5 with respect to that for BaFe₂As₂ [41].

As regards the SC phase induced by doping, it is surprising that either of three different types of doping leads to the emergence of SC. The critical doping level above which SC appears more or less depends on the suppression rate of the AFO ordering temperature T_s . The same factors that influence T_c value, disorder, electron filling, and local structure, would also affect T_s , but it is still open why AFO and SC phases are sharply separated in some classes of materials, while they coexist in others.

Two important features emerge from these systematic studies. One is that, on looking at the change of the T -dependence of resistivity with doping, it is found that in the SC doping region the normal-state resistivity shows a sizable T -linear term and its coefficient is particularly large at dopings near the AFO-SC boundary or coexisting region where T_c is highest. This tendency is often seen for SC in strongly correlated electron systems [42], such as the cuprates, heavy fermions, and

organic compounds. SC in these systems is argued in the context of quantum critical fluctuations near a QCP. The presence of a QCP at $x \sim 0.3$ near the end point of the AFO-SC coexisting region is suggested for P-Ba122 [18]. At present, the quantum critical behavior does not seem a generic to Fe-SCs. No signatures suggestive of QCP are observed for Co-Ba122 and K-Ba122. For $\text{LnFeAsO}_{1-x}\text{F}_x$ (Ln: La and Nd), the AFO and SC phases are sharply separated by a first-order like phase transition, and T_c is high over a wide range of doping, even two T_c domes are observed for $\text{LaFeAsO}_{1-x}\text{H}_x$. Apparently, a simple QCP scenario does not apply to Fe-SC as in the case of high- T_c cuprates. Nevertheless, considering the fact that T_c attains large values near the AFO phase, it is likely that the fluctuations associated with the AFO phase play a crucial role in superconductivity.

4.5.2 Electronic Correlations

Now there is wide consensus on the unconventional nature of the Cooper pairs with sign-changing SC gap (order parameter) in the momentum space. The phase diagram, T vs doping x and/or pressure P , is also quite similar to the cuprate phase diagram. The “parent” compound is an antiferromagnet with localized magnetic moment, and the AFO and SC phases are always next to each other. These facts are strongly suggestive of electronic correlations playing a dominant role in Fe-SCs as in the cuprates.

The origin of striking electron-hole asymmetry or incoherence/strong scattering of hole carriers deserves to explore to understand a role of electronic correlations in the emergence of superconductivity and unconventional pairing in Fe-SC. The parent compounds are metals, albeit not good metals, and are not close to a Mott insulating state, so the Fe arsenides and selenides are usually thought to be in the intermediate correlation regime. Nevertheless, they show features of strong correlations such as frozen spin magnetic moments and T -linear resistivity characteristic of a non-Fermi liquid. There exist theoretical attempts to solve this controversy by incorporating the effect of the Hund’s rule coupling (J_H) in addition to the on-site Coulomb interaction (U) [43]. It is suggested that, even when J_H and U are not large enough, both may cooperate to strengthen the correlation effect on particular $3d$ orbitals in multi-orbital metals.

Optical spectroscopy is used to probe the dynamical response of electrons to an external electromagnetic field and can provide information on the electronic correlations which impede the electronic motion. Figure 4.5 displays the in-plane resistivity for BaFe_2As_2 and related isostructural compounds with various TM and Pn atoms. In the high T region, these are clearly separated into two groups. The iron arsenides, BaFe_2As_2 and KFe_2As_2 , have distinctly high resistivity from others. High resistivity in iron arsenides arises from the small SW, N_D ($\sim n/m^*$), of the narrow (coherent) Drude component in the optical conductivity spectrum. The low-energy spectrum is also dominated by another Drude component with extremely broad width (incoherent Drude). This is more the case with FeTe and $\text{K}_x\text{Fe}_{2-y}\text{Se}_2$

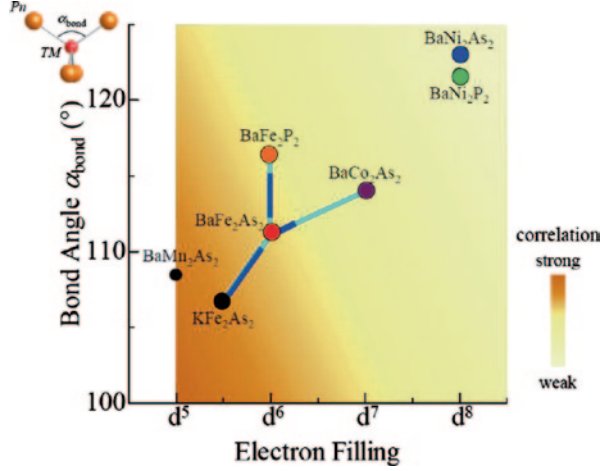
which have even higher resistivity and a tiny N_D in the optical conductivity. The low-energy spectra of other TM pnictides are also roughly decomposed into two, but the distinction between the two is much less clear and N_D occupies a substantial fraction of the low-energy SW. A fraction of N_D , N_D/N_{eff} , in the low-energy SW, N_{eff} which is approximated by the sum of dominant two Drude components, is a measure of the degree of coherence of carriers. If the incoherence arises from the electronic correlations, as, for instance in the cuprates, then, N_D/N_{eff} is a good indicator of the strength of correlations. The values of N_D for iron arsenides are indeed small as compared with those for other TM pnictides, as displayed in Fig. 4.12b. They are comparable with the similarly estimated vales for the hole underdoped cuprates, e.g., $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with $x=0.10$ [44]. The incoherent charge dynamics in the cuprates certainly originates from strong U (or superexchange J) that frustrates coherent hole motion. Although U is not so large in FeAs, it is conceivable that the electronic correlations stem also from the Hund's coupling J_H reflecting the multi-orbital nature of the Fe-based compounds.

The two iron arsenides are found to have smaller Pn-TM-Pn bond angles than others. α_{bond} is nearly equal or somewhat smaller than 109.5° ($\alpha_{\text{bond}}=111.1$ and 106.7° for BaFe_2As_2 and KFe_2As_2 , respectively), the bond angle for an ideal tetrahedron, whereas α_{bond} 's for other pnictides are significantly larger than 109.5° ($\alpha_{\text{bond}}=116.4^\circ$ for BaFe_2P_2 and 114.0° for BaCo_2As_2). In view of the trend that the width (W) of the relevant electronic bands (TM- $3d$ and Pn- p orbitals derived bands) becomes larger for larger bond angles, an increase of α_{bond} works to weaken the electronic correlations by decreasing U/W and J_H/W . In this regard, the major effect of P substitution for As in BaFe_2As_2 is an application of chemical pressure, leading Ba122 toward weaker correlations. The Co doping works similarly, but the K doping goes the other direction, applying negative chemical pressure.

In the plot of N_D/N_{eff} as a function of x for three types of doping into BaFe_2As_2 (Fig. 4.12), a remarkable difference is seen even between Co-Ba122 and P-Ba122. For Co-Ba122 N_D/N_{eff} steeply increases upon Co doping, while the increase is gradual for P-Ba122 in contrast to the larger chemical pressure effect of P doping. This is suggestive of presence of additional effect of doping that probably originates from a change of the electron (hole) density with doping. The K substitution for Ba reduces the Fe $3d$ orbital filling from d^6 to $d^{5.5}$, whereas the Co substitution increases it toward d^7 . Note that d^5 is special, all the five $3d$ orbitals are singly occupied—just half filling, at which the electronic correlation is maximally strong [45]. In fact, BaMn_2As_2 with d^5 is probably a Mott insulator and has a robust magnetic order [46]. In this regard, the hole (electron) doping, the decrease (increase) in the electron filling from d^6 points toward stronger (weaker) correlation, explaining the striking electron-hole asymmetry in the doping effect. As was discussed in 4.5.1, even in a compound where both electron and hole carriers coexist, there is a remarkable asymmetry in the dynamics (scattering strength) between electrons and holes. So, it is likely that the asymmetry between quasiparticles on electron and hole FS is conceived to have an intimate connection to the above doping asymmetry.

Microscopically, the asymmetry would arise from the “orbital differentiation” or orbital-selective correlation effect [43]. Theoretically the electronic correlations

Fig. 4.13 Various transition-metal pnictides mapped on the diagram of Pn-TM-Pn bond angle vs $3d$ electron filling of TM in the TM^{2+} state. The dotted lines are trajectories of three types of doping into BaFe_2As_2 . Superconductivity is observed on the trajectories indicated by solid lines. Variation of the strength of electronic correlations on the map is roughly shown in a gray scale



are considerably stronger on the $3d_{xy}$ orbital as compared to those on $3d_{yz}$ and $3d_{xz}$ orbitals, so that electrons/holes on the $3d_{xy}$ orbital are almost Mott localized [47]. The ARPES study has indeed confirmed that the states on the hole-FS in FeAs are predominantly of $3d_{xy}$ character, while the states on the electron FS have relatively large $3d_{yz}/3d_{xz}$ character [48]. The strong correlation, in particular the strong Hund's correlation tends to inhibit mixing of the orbitals, which would highly frustrate the hole motion. As the hole and electron FS pockets are located at different places in the momentum space, the orbital differentiation is at the same time the momentum differentiation which also characterizes the normal state of the high- T_c cuprates, particularly in the underdoped region.

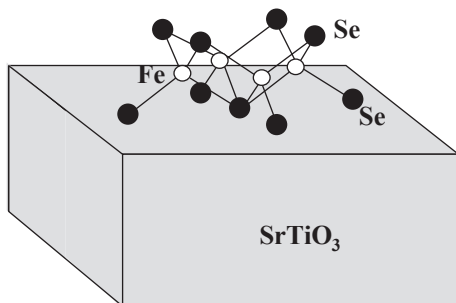
Putting the structural parameter (α_{bond}) together with the electron filling (n) of the $3d$ orbitals, the diagram of α_{bond} vs n , shown in Fig. 4.13, maps the strength of electronic correlations for various TM pnictides [49]. Both small α_{bond} and low electron filling locate KFe_2As_2 at the strongest correlations among various TM pnictides investigated here, and the Ni pnictides with larger α_{bond} and higher filling are the weakest counterparts. This map just corroborates the result of N_D/N_{eff} shown in Fig. 4.12a. The diagram clearly indicates that a major role of doping into BaFe_2As_2 is to tune the correlation strength, to weaker (stronger) correlations by Co and P doping (K doping). The diagram also suggests that superconductivity in the TM pnictides emerges in the doping region where fairly strong electronic correlations are sustained, and that either too strong or too weak correlations are not favorable for superconductivity with high T_c values. From the diagram high T_c turns out to be realized when the electron filling is near d^6 , in between d^5 (BaMn_2As_2) and d^7 (BaCo_2As_2) and when the bond angle is around 109.5° , the angle for an ideal tetrahedron. The “optimal” bond angle is consistent with the empirical relationship between T_c and α_{bond} shown in Fig. 4.3, and the 1111 members with 50 K-class T_c are also located in the vicinity of d^6 filling and $\alpha_{\text{bond}} = 109.5^\circ$. The parent BaFe_2As_2 itself is near this “optimal” point. Its ground state is the AFO ordered state, but it is readily converted to SC upon doping and by application of pressure.

4.6 Possibility of Enhancing T_c

$T_c^{\max}=55$ K recorded for 1111 in 2008 remains to be highest among so-far known Fe-SCs, although $T_c^{\max}$ of other classes has been gradually improved. For 122 $T_c^{\max}=45\text{--}49$ K was reported in $\text{Ca}_{1-x}\text{Ln}_x\text{Fe}_2\text{As}_2$ [50] albeit small SC volume fraction (a new structure, $\text{Ca}_{1-x}\text{Ln}_x\text{FeAs}_2$ (112), was proposed which might be a superconductor with $T_c^{\max}$ higher than 40 K [51]). The iron arsenide with big building block, $\text{Sr}_4\text{V}_2\text{O}_6\text{Fe}_2\text{As}_2$, has $T_c=37$ K at ambient pressure, but one of its relatives, $\text{Ca}_4(\text{Mg}, \text{Ti})_3\text{Fe}_2\text{As}_2\text{O}_{8-y}$, shows SC at $T_c=47$ K [52]. The potassium-doped iron-deficient selenides, $\text{K}_x\text{Fe}_{2-y}\text{Se}_2$ and $(\text{Tl}, \text{Rb})_x\text{Fe}_{2-y}\text{Se}_2$, also shows higher $T_c^{\max}=48\text{--}49$ K in its second T_c dome realized under high pressure. Even for the 11-FeSe, T_c goes up to 37 K upon application of pressure [53].

At the present stage, it seems that every family of Fe-SCs has a potential $T_c^{\max}$ of ~ 50 K when optimized in structure and/or doping or disorder. This, in turn, suggests that there might be a ceiling of $T_c^{\max}$ in Fe-SCs. Unlike the cuprates which apparently have a room for T_c to be enhanced over the maximum value of 135 K at ambient pressure, there is no indication of a rise of T_c for the 1111 system with $T_c=55$ K. However, a monolayer FeSe film grown on a SrTiO_3 (STO) substrate, schematically sketched in Fig. 4.14, was found to show a big magnitude of SC gap corresponding to a mean-field $T_c^{\text{MF}}=65$ K [54]. The ARPES measurement on the same system observed a gap opening at 60–65 K [55], although zero-resistivity is observed only below ~ 30 K (recently one group has reported the film resistance drops to zero at $T\sim 100$ K [56]). The recent ARPES measurement has suggested the coupling to the high-frequency ($\sim 1000\text{ cm}^{-1}$) phonon in the STO substrate might enhance T_c of FeSe with respect to the value that is sustainable for FeSe alone [57]. The T_c enhancement with a help from phonons in SCs is also one of the proposed scenario explaining the T_c enhancement in the cuprates with multilayer structure [58]. Fabrication of such a hetero-structure might a promising route toward higher T_c .

Fig. 4.14 Schematic picture of monolayer FeSe deposited on a SrTiO_3 substrate



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Chapter 5

Summary and Perspectives

Abstract One of the lessons learned from the study of the diverse families of high- T_c superconductors is that there are common ingredients for high T_c . They are (i) layer structure, (ii) low carrier density in the normal state, (iii) low superfluid density in the superconducting state, (iv) light element and strong chemical bond giving rise to high phonon frequency. These lead to poor screening of electron-electron interaction which acts to enhance electron-phonon coupling in some families and to prepare a purely electronic channel for pairing in others. Instead of the old Matthias rules, these ingredients are a guiding principle for searching new high- T_c material families. In the two distinct highest T_c families, the cuprates and the iron arsenides/selenides, 3d transition-metal elements, Cu and Fe, play an indispensable role. What makes them unique is the electron filling of the 3d orbitals, one electron less than the complete filling in the former and one electron more than half-filling in the latter. Based on this a candidate high- T_c material is discussed that is expected to have T_c comparable with or hopefully higher than these two.

5.1 What Have We Learned from the Known High- T_c Materials?

One of the lessons that we have learned from the history of HTSCs is that every epoch-making jump in T_c does not result from a theoretical deduction nor from any empirical guide but simply from serendipity. The cuprates, fullerenes, borocarbides, β -HfNiCl, MgB_2 , and Fe-SCs were actually discovered by serendipity. There were no systems from which the amazing high T_c 's of these 6 materials were foreseen. $Ba_{1-x}K_xBiO_3$ (BKBO) had a precedent, $BaPb_{1-x}Bi_xO_3$ with $T_c = 12$ K, and the realization of $T_c \sim 30$ K in BKBO was a outcome of systematic research scheme. This is more or less the case with Ca at high pressures and possibly in a class of organic compounds, PAH.

The Matthias rules [1] which were a guiding principle for finding new superconducting materials with high T_c before the discovery of the cuprates are; #1: find high-symmetry cubic crystals, #2, 3: find d -electron metals with the average

number of valence electrons, preferably odd numbers 3, 5, and 7, #4, 5: stay away from metals showing or in close vicinity of magnetism and from metals near a metal-insulator transition. These rules were based on the notion that higher electron density, n_e , or higher electron density of state at the Fermi level, $N(E_F)$, is favorable for higher T_c in the framework of the (BCS) Migdal-Eliashberg theory. Generally, high (atomic) density solids take the cubic structure, face-centered cubic (fcc) or body-centered-cubic (bcc), and d -electron metals have narrow d -bands, both making n_e and/or $N(E_F)$ larger. It was empirically known that $N(E_F)$ tends to show maximum (minimum) for d -band metals with odd (even) number of valence electrons. A metal in the vicinity of insulating phase tends to have low carrier density, and magnetism is an enemy of s -wave BCS superconductors.

As described in the preceding chapters, the new high- T_c materials are completely outside the Matthias rules. Many of them have **layer** structures, the cuprates, borocarbides, β -HfNCl, MgB_2 , Fe-SCs, and polycyclic aromatic hydrocarbons (PAHs). They, except for borocarbides and MgB_2 , are in close vicinity of metal-insulator phase transition boundary or in close contact with the AF ordered phase, and become superconductors by **doping** into insulating or AF parent compounds. As a consequence, most of them are metals with **low carrier density** in the normal state, pointing toward poor screening of electron-electron. Related to this, superconductivity is characterized by **low superfluid density (phase stiffness)**. In addition, most of them contain **light elements** (B, C, N, or O) which take part in **strong chemical bond**.

Notably, **strong electronic correlations** [2] play a dominant role in the formation of Cooper pairs in the cuprates and the iron-based compounds with the highest T_c 's among all—correlations are actually strong enough to favor the *unconventional Cooper pairs* and to sustain the *spin magnetic moment* of substantial fraction of the moment in the AF ordered phase. **Electronic correlations** are perceived also to play a role in enhancing electron-phonon interaction and hence T_c in most of the families, $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ (BKBO), doped C_{60} , doped β -HfNCl, and possibly doped PAHs (Chap. 2). These features are in remarkable contrast to the Matthias rules for conventional superconductors. High $N(E_F)$ do not necessarily favor SC with high T_c , and instead poor screening of electron-electron interactions arising from e.g., low-carrier density and layered structure, appears to be a necessary ingredient for HTSCs. Enhanced Coulomb repulsive interaction is harmful for conventional pairing, but it provides a ground favorable for superconductivity with high T_c either by enhancing electron-phonon coupling or by creating a new channel, purely electronic, for pairing.

In addition to them, a possible new scheme for enhancing T_c is to fabricate some structure which enhances pairing interactions and/or provides an additional pairing channel like multilayer structure in the cuprates (Chap. 3) or FeSe monolayer on SrTiO_3 substrate (Chap. 4).

(*) Footnote: High- T_c superconductors suitable for application If a high- T_c superconductor with T_c near room-temperature could be realized, it would be an important issue to discuss about what is the constraint on the practical application.

Researchers agree that s -wave superconductors are more suitable for device application because enormous quasiparticles are excited in superconductors with gap nodes (unconventional pairing) and the inelastic scattering between quasiparticles is more at work with increasing temperature. From the viewpoint of critical current (J_c), anisotropy and low superfluid density will be troublesome factors. With increasing anisotropy, J_c in high- T_c superconductors is expected to sharply decrease [3]. From this, one of the future challenges in application will be to discover isotropic room-temperature superconductors with s -wave Cooper pairs. BKBO and doped C_{60} are *isotropic* and possibly s -wave superconductors, but isotropic HTSC with high superfluid density is difficult to foresee at present.

5.2 What is a Candidate for Next High- T_c Superconductors?

The cuprates and the iron-based superconductors are distinct in their outstandingly high T_c values, $T_c^{\max} = 135$ and 55 K, respectively. An obvious commonality is that Cu and Fe are the elements in the 3d-transition-metal TM series. Common with these two systems is superconductivity with unconventional pairing symmetry with sign-changing order parameter and emergent by doping into parent compounds showing an antiferromagnetic order. Both evidence an important role of strong electronic correlation in the formation of Cooper pairs.

As was discussed in Chap. 4, the origin of striking electron-hole asymmetry in Fe-SCs is most likely the electronic correlations which are also deeply involved in the emergence of superconductivity and unconventional pairing in Fe-SCs. Incorporation of the effect of the Hund's rule coupling (J_H) in addition to the on-site Coulomb interaction (U) is conceived to cooperatively strengthen the correlation effect on particular 3d orbitals in multi-orbital metals, even when J_H and U are not large enough. The hole doping into the parent compound reduces the Fe3d orbital filling from d^6 toward d^5 . The filling d^5 is special with all the five 3d orbitals are singly occupied—just half filling—due to the effect of the Hund's coupling and on-site Coulomb. At the d^5 filling realized in $BaMn_2As_2$ the electronic correlation is maximally strong, making $BaMn_2As_2$ a Mott insulator. On the other hand, the electron doping increases the filling toward d^7 moving away from d^5 . Thus, the hole (electron) doping points toward stronger (weaker) correlation (see the periodic table shown in Fig. 5.1).

The cuprates also show asymmetry with respect to electron and hole doping. Although it is difficult to dope both electrons and holes into one parent compound, various properties, including charge and spin dynamics and pseudogap phenomena, are quite different between hole-doped and electron-doped cuprates. One reason for the asymmetry is that doped holes enter the O2p orbitals, while doped electrons enter the Cu3d orbital. It is also ascribable to the “effective” filling in the 3d orbitals. The filling of 3d orbitals is d^9 for the parent compound, e.g., La_2CuO_4 . Hole doping changes the formal filling from d^9 toward d^8 (as in, e.g., La_2NiO_4 for which

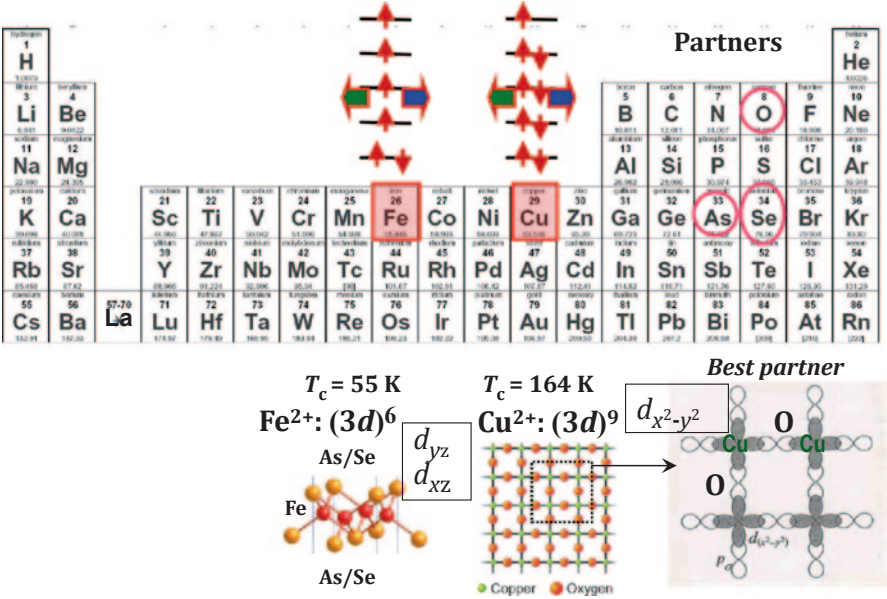


Fig. 5.1 Part of the periodic table emphasizing 3d-transition-metal elements and showing the effective electron filling of the 3d orbitals for Cu^{2+} and Fe^{2+} and the common structural units for the cuprate and iron-based high- T_c superconductors. The effect of electron and hole doping is indicated by the *arrows directing right and left*, respectively

the Mott/CT insulating state is robust), whereas electron doping changes the filling toward d^{10} (Zn) in which the electronic correlation is weakest. Similar to the doping in the case of Fe-SCs, different type of doping changes the correlation strength in a different way.

From this and also from the discussions in Chaps. 3 and 4, we realize a common circumstance that makes the cuprates and the Fe-SCs special and distinct from others. That is, the 3d orbital filling d^9 of Cu^{2+} is one electron less than the complete filling d^{10} and the filling d^6 of Fe^{2+} is one electron more than the half filling d^5 . If there were the third HTSC with high T_c values comparable with or hopefully higher than T_c of cuprates or Fe-SC, it might be discovered in 3d transition-metal (TM) compounds with 3d orbital filling one electron less or more than the special filling. There are three special fillings, complete filling d^{10} , half filling d^5 , and empty d^0 . Therefore, candidate HTSCs would have 3d TM element with fillings either d^9 , d^6 , d^4 , or d^1 . In addition to the search for 3d-TM element with these special fillings, one has to find a partner anion with which 3d-TM forms a layered structure and which make the AF order of 3d-TM spins fragile, as oxygen or arsenic/selenium does in the cuprates or Fe-SCs.

Typical d^4 is Mn^{3+} or Cr^{2+} ionic state. However, Mn and Cr compounds tend to have high-spin states due to strong Hund's rule coupling, and thereby have robust magnetic ground states in which the AF order is difficult to collapse by doping. Thus, a possibility for HTS exists in d^1 compounds with Ti^{3+} or V^{4+} valence (see the

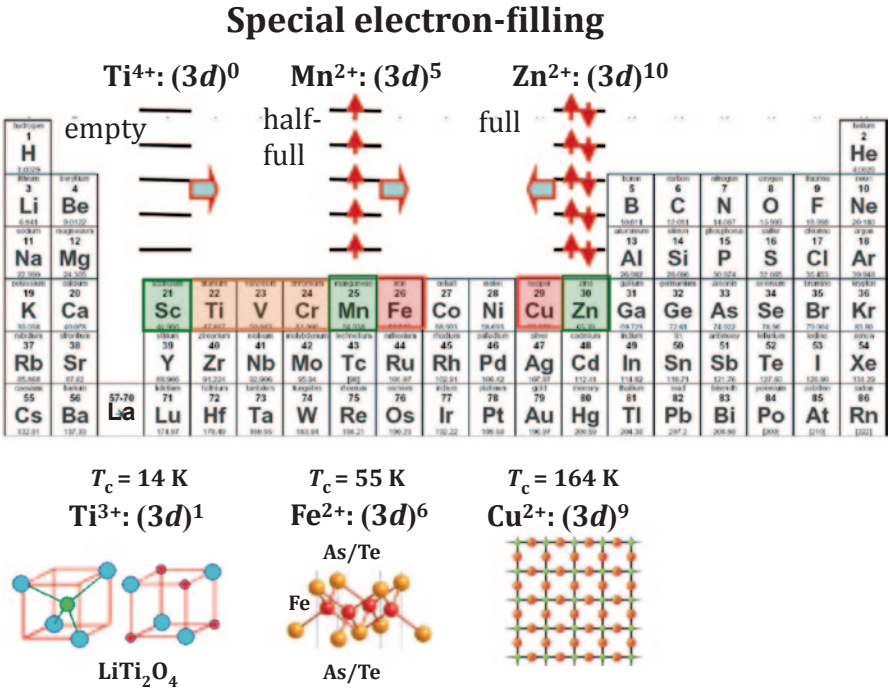


Fig 5.2 The same periodic table as that shown in Fig. 5.1 with a particular note to the $3d^1$ electron filling in the Ti^{3+} state. The structure of $LiTi_2O_4$ with $T_c = 14\text{ K}$ is shown as an example of superconducting Ti compounds

periodic table in Fig. 5.2) in which the minimal spin quantum number $S=1/2$ is a source of strong quantum fluctuations as in the case of the cuprates with d^1 “hole” filling. A vanadium oxide, electron-doped $Sr_{2-x}La_xVO_4$ [4], has many features in common with the high- T_c cuprates, but is never be a superconductor probably due to the large energy difference in $V3d$ and $O2p$ levels and degeneracy of the lowest d_{xz} and d_{yz} orbitals, as was mentioned in Chap. 3. On the other hand, Ti compounds are promising, since the electron-doped $SrTiO_3$ ($T_c^{\max} < 1\text{ K}$) [5] is an old known oxide superconductor and $LiTi_2O_4$ is a superconductor with fairly high $T_c = 14\text{ K}$ [6]. These two Ti compounds are oxides with three-dimensional crystal structures, perovskite and spinel, respectively. Oxygen is probably not a best partner of titanium, since the $Ti3d$ levels are well separated from the $O2p$ levels as in the case of the above-mentioned vanadium oxide. Sulphur or selenium might be a better partner to Ti, but in the well known hexagonal TiS_2 and $TiSe_2$ [7] with layer structure, the electronic correlations are too weak to favor unconventional pairing and to sustain localized magnetic moment. Therefore, a route to finding a next HTSC is to search for best partner of Ti that forms layer structure with Ti and preserve strong electronic correlations.

This book ends up by listing new rules for searching high- T_c superconductors:

1. #1: Search materials with layer structure.
2. #2: Search materials near the boundary of metal-insulator transition or in proximity to antiferromagnetically ordered phase, thereby having low carrier density.
3. #3: Search materials preferably composed of light elements and strong chemical bond.
4. #4: For extremely high T_c , search materials with strong electronic correlations in which magnetic order is fragile due to strong fluctuations and/or frustrations.

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