

Introduction

Ever since 1911 when Heike Kamerlingh Onnes first discovered superconductivity, physicists have been interested to find out why the temperature of the transition to the superconducting state T_c is so low compared to the temperatures of other phase transitions. The temperatures of the transitions to ferromagnetic or antiferromagnetic (AF) states in metals are hundreds of kelvin, while for conventional superconductors T_c does not exceed 10–20 K. This fact seems surprising, since in the both cases the phase transitions take place in the electron subsystem of the crystals and are ultimately due to electron–electron interaction. To answer this question, we shall discuss in this chapter the history of the copper-oxide superconductor discovery by Bednorz and Müller [118, 120]. We also consider the generic properties of these compounds that distinguish them from the conventional superconductors. It is assumed that the reader is familiar with the conventional superconductivity theory, which is presented in a number of textbooks, for example, Parks [963], Ketterson and Song [598], and Buckel and Kleiner [185].

1.1 Problem of High-Temperature Superconductivity

It is natural, with respect to applications, to refer a superconductor as a high-temperature superconductor (after Ginzburg [393]) if its transition temperature T_c exceeds the boiling temperature of liquid nitrogen, $T_{b,N_2} = 77.4$ K, that is, if the superconducting state can be obtained by cooling in liquid nitrogen. A large number of papers (see, e.g., [392]) are devoted to the general problem of designing high-temperature superconductors. To discuss the factors that influence the temperature of the superconducting transition, we shall consider the pairing theory of Bardeen, Cooper, and Schrieffer (BCS) [104]. There are three specific parameters that characterize the interaction of electrons: the density of the electron states at the Fermi level $N(0)$ (per spin direction), an effective attraction coupling constant V , and an energy shell $\hbar\omega$ around the Fermi surface, over which this coupling is nonzero. In the weak

coupling limit $\lambda = N(0)V \ll 1$, the transition temperature according to the BCS theory is

$$kT_c \simeq \hbar\omega \exp(-1/\lambda). \quad (1.1)$$

This expression determines the temperature below which the normal state of electrons becomes unstable with respect to the formation of a condensate of electron (Cooper) pairs with opposite spins and zero orbital momentum (singlet s -wave pairing). The nature of the forces responsible for the effective attraction bears no relevance to the derivation of (1.1). The BCS theory and the relation (1.1) can therefore be used to treat superconductivity in the case of other, that is, nonphononic mechanisms of pairing. In these cases, one speaks of a *generalized BCS pairing theory*.

It is interesting to note that, besides the superconducting electron pairing, an instability with respect to the formation of electron–hole pairs below a certain temperature T_0 is possible, which results in the charge density waves (CDW) and the metal–insulator transition or in the spin density waves (SDW) and ferromagnetic or antiferromagnetic order. In certain cases (e.g., when the electron (hole) Fermi surface has perfect nesting), this temperature is determined by the same relation (1.1). In this case, the attraction V between an electron and a hole in the energy shell $\hbar\omega$ may be of purely Coulomb nature. For typical Coulomb energies $\hbar\omega \simeq 1$ eV, according to (1.1) we obtain $T_0 \simeq 400$ K even for a weak coupling $\lambda \simeq 0.3$. These phase transitions can occur at higher temperatures and often hinder the system from entering the superconducting state, especially for low dimensions: quasi-one- or two-dimensional metals (see, e.g., [392]).

The electron attraction that is responsible for superconductivity in conventional metals is caused by the retarded electron–phonon interaction. It is related to the phonon energy and comes into play only in a narrow energy shell of the order of $\hbar\omega/k_B \leq 400$ K near the Fermi surface. The coupling constant itself depends on the phonon spectrum (see, e.g., [48]):

$$\lambda = N(0)\langle g^2 \rangle \left\langle \frac{1}{M\omega^2} \right\rangle - \mu^*. \quad (1.2)$$

The first term is determined by the square of the matrix element g for the electron–ion interaction averaged over the Fermi surface and by the averaged static lattice susceptibility $\langle 1/M\omega^2 \rangle$, that is, the inverse lattice rigidity $\langle 1/\Phi \rangle$, which does not depend on the mass of lattice ions M . The second term μ^* describes the renormalized Coulomb repulsion of electrons [150, 857]:

$$\mu^* = \frac{V_C}{1 + V_C \ln(E_F/\hbar\omega)}, \quad (1.3)$$

where V_C is the bare Coulomb repulsion, which may be comparable or even larger than the electron–phonon interaction – the first term in (1.2). In conventional superconductors, the parameter μ^* is usually small, $\mu^* \simeq 0.1 - 0.2$, due to the large Fermi energy E_F in comparison with the phonon energy $\hbar\omega$.

A direct confirmation of the electron–phonon mechanism of pairing is the isotope effect, that is, the dependence of T_c on the mass M of the lattice ions, $T_c \propto M^{-\alpha}$. The exponent α in this dependence is given by the expression

$$\alpha = -d \log T_c / d \log M. \quad (1.4)$$

According to (1.1) and (1.2), for conventional superconductors $\alpha \simeq 1/2$ since the phonon frequency in (1.1) $\omega \propto M^{-1/2}$ and the coupling constant λ (1.2) does not depend on the mass (if we neglect μ^*). Only for superconductors with low T_c , the value of α can be considerably lower due to large μ^* , which depends on the cut-off frequency ω in (1.3).

Before the discovery of cuprate superconductors by Bednorz and Müller, much effort in boosting T_c was devoted to synthesizing materials with a high density of states, which can increase significantly the coupling constant (1.2). There is, however, a limit to the increase of the coupling constant λ , since a large value in metals leads to a strong renormalization of the phonon spectrum, that is, to its softening and to structural instability (see, e.g., [392]). The greatest success in this direction has been attained for intermetallic compounds of transition metals with the A15 structure of the A_3B type, where $A = \text{Nb, V}$ and $B = \text{Sn, Si, Ge, etc.}$ (see, e.g., [1323]). Despite immense research efforts, the maximum temperature $T_c \simeq 23.2 \text{ K}$ obtained for the compound Nb_3Ge in 1973 was not pushed up till the discovery of Bednorz and Müller [118].

Soon after Bednorz and Müller’s discovery, another idea of a strong enhancement of T_c proved to be fruitful. In the early 1960s, a high T_c was predicted for superconductors with light atomic mass such as metallic hydrogen. A high phonon frequency ω in the relation (1.1), of the order of several thousand kelvin, even for a weak coupling can provide high T_c . In the absence of metallic hydrogen, attention was focused on compounds with light elements like carbides and nitrides. On this road, quite high values of $T_c \simeq 40 \text{ K}$ have been attained in recent years in fulleride compounds R_xC_{60} [420, 447] and recently in magnesium diboride MgB_2 by Akimitsu and co-workers [878]. In fullerenes, the high density of electronic states in narrow bands and the strong coupling to high-frequency C_{60} molecular vibration modes result in strong enhancement of T_c . In the magnesium diboride, the record T_c for conventional electron–phonon superconductors was reached due to strong electron–phonon coupling $\langle g^2 \rangle$ at a modest density of electronic states and high-frequency phonons of light boron atoms. The quasi-two-dimensional character of electronic spectra and the two-band nature of superconductivity in MgB_2 further enhance T_c (for a review see [197]). Possibly, in these compounds it has been achieved the highest $T_c \simeq 40 \text{ K}$ mediated by the electron–phonon coupling mechanism, as it has been generally believed for long time.

An electronic mechanism of pairing like AF exchange in cuprates (see Sect. 7.3.2) could produce a really high superconducting temperature if instead of a phonon frequency $\omega \leq 0.1 \text{ eV}$ in the prefactor in the BCS formula (1.1) there would be an electronic energy, such as the Fermi energy, $E_F \simeq 0.5 \text{ eV}$, that results in $T_c \geq 200 \text{ K}$ even for weak coupling, $\lambda \simeq 0.3$. Therefore, it

is tempting to speculate that only an electronic pairing mechanism can compete with other instabilities (SDWs or CDWs) and promote high-temperature superconductivity.

Concerning the general problem of high-temperature superconductivity, we should also mention another scenario of attaining high T_c based on the Bose–Einstein condensation (BEC) of local electron pairs proposed by Schafroth [1108, 1109]. In this approach, contrary to the BCS pairing theory, the formation of singlet electron pairs – bipolarons – is assumed at some higher temperature, while the superconducting transition occurs at the temperature of BEC, $T_c = T_{\text{BEC}}$. Since the correlation length in cuprates is much smaller in comparison with conventional superconductors, this scenario is considered to be relevant to high-temperature superconductivity (for reviews, see Micnas et al. [827], Alexandrov and Mott [29], Alexandrov [43, 44]). A simple estimate for the BEC temperature of the three-dimensional ideal Bose gas,

$$T_{\text{BEC}} \simeq \frac{3.3 \hbar^2 n^{2/3}}{m^* k_B} \simeq 2.9 \times 10^{-11} \frac{m}{m^*} n^{2/3} \text{ K}, \quad (1.5)$$

for the effective mass of bipolaron $m^* \simeq 10m$, where m is the electron mass, and the density of bipolarons $n \simeq 10^{21} \text{ cm}^{-3}$ gives quite a high $T_c \simeq 300 \text{ K}$. While in the underdoped region a pseudogap is observed in cuprate materials at $T^* \gg T_c$, which can be considered as caused by the preformed bipolaron pairs, in the optimal doped or overdoped regions no preformed pairs were detected. Bipolarons, the Bose quasiparticles, have no Fermi surface, which has been unambiguously detected in cuprates (see Sect. 5.2.2). Therefore, a crossover from the BEC at low doping to the Cooper pairing of fermions in the overdoped region should occur if we adopt the bipolaron scenario of the high-temperature superconductivity in cuprates (see Sect. 7.4.3).

1.2 Discovery of High-Temperature Superconductors

One might try to achieve high T_c in compounds with large value of the electron–ion interaction $\langle g^2 \rangle$. However, in conventional metals with high electron density, the matrix element of the electron–ion interaction g is considerably weakened due to strong screening and cannot attain high values. Taking into account this circumstance and the absence of progress in studying compounds of transition metals, in 1983 Bednorz and Müller addressed their attention to another class of compounds, namely, the oxide superconductors. The high polarizability of oxygen ions and the poor screening of the electron–ion Coulomb interaction due to a low density of carriers could result in a strong electron–phonon coupling in these compounds. By that time, conducting oxides with relatively high transition temperatures $T_c \simeq 13 \text{ K}$ at very low densities of electron states were already known. The most interesting was a perovskite $\text{Ba}(\text{PbBi})\text{O}_3$ discovered by Sleight et al. [1176]. At a sufficiently

low concentration of carriers ($n = 4 \times 10^{21} \text{ cm}^{-3}$, i.e., two orders of magnitude smaller than in transition metals) and therefore a small value of $N(0)$, the high value of T_c could be accounted for in the frame of the electron–phonon model (1.2) only, if one assumes a large value of the electron–ion interaction. However, attempts to raise T_c in this compound by increasing the density of states $N(0)$ by varying the ratio Pb to Bi failed. With increasing density of states, the compound underwent a metal–insulator transition with the formation of a CDW (see, e.g., [1281]).

The search for new oxide superconductors undertaken by Bednorz and Müller was based on the idea of creating conducting oxides containing so-called Jahn–Teller ions. Such ions, for example, Ni^{3+} or Cu^{2+} , are characterized by a strong interaction of electrons with local distortions of a crystal lattice. The distortion considerably decreases the electronic energy of the ion because of a lifting of the degeneracy of electron levels. (The Jahn–Teller effect for Cu^{2+} ions is considered in Sect. 5.1.1.) The strong interaction of electrons with displacements of surrounding ions can result in the formation of polarons whose BCS type pairing or BEC of bipolarons can also lead to high-temperature superconductivity as discussed above (1.5).

The study of nickel oxide compounds, however, did not yield encouraging results. In 1985, Bednorz and Müller turned to compounds of copper oxides. Among them, lanthanum and barium copper oxides with metallic conductivity were known (see [1139]). On varying the ratio La^{3+} to Ba^{2+} in these compounds, it was easy to control the valence of copper and the concentration of carriers. In January 1986 when performing measurements of conductivity in compounds with various concentrations of barium, Bednorz and Müller discovered a dramatic fall of the resistivity in some samples at temperatures below 35 K. The results of the measurements were published in the September issue of *Zeitschrift für Physik* [118]. The final confirmation of the superconducting nature of the phase transition in these samples was obtained after a verification of the Meissner effect [119].

The publication of this discovery attracted the attention of many scientists who, in a short period of time, confirmed the occurrence of superconductivity in the ceramics La–M–Cu–O , where $\text{M} = \text{Ba}, \text{Sr}, \text{Ca}$ [120]. Later on, it became clear that the oxide superconductors of this type have a layered perovskite structure $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ (LMCO) (see Sect. 2.2.1). Still higher superconducting transition temperatures were reached in January 1987 by the group of C.W. Chu at the University of Houston in collaboration with the group of M.-K. Wu at the University of Alabama. Having replaced La by Y, they obtained $T_c = 90 \text{ K}$ in a multiphase ceramic sample [1371]. The superconducting phase in this compound has the layered perovskite structure $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ (YBCO) with a deficit in oxygen (see Sect. 2.4.1). Thus, within one year, the temperature of the superconducting transition increased several times as compared to the value $T_c = 23 \text{ K}$, the record known in 1973. It is very important that T_c in the new copper-oxide superconductors exceeds the boiling

point of liquid nitrogen which is a criterion defining a true high-temperature superconductor.

Further active search for new compounds with higher values of T_c led to the discovery of superconductivity in the systems Bi–Sr–Ca–Cu–O [767] and Tl–Ba–Ca–Cu–O [450, 1147] in which T_c reached 110–120 K. A new class of mercury compounds was discovered by Putilin et al. [1034]. A maximal value of $T_c \simeq 135$ K was found in the three-layer mercury compound $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ at ambient pressure [1035, 1112] and 164 K at 30 GPa [375].

The synthesis of the compound (K–Ba)BiO₃ [212, 813] with $T_c = 30$ K considerably exceeding the $T_c = 13$ K in Ba(Pb–Bi)O₃ was important for understanding the mechanisms of superconductivity in oxide compounds. The absence of copper ions with spin 1/2 and the large isotope effect exclude, for these compounds, magnetic mechanism of superconductivity proposed for copper-oxide superconductors.

The above oxide superconductors have hole-type conductivity. Therefore, the discovery of superconductivity in the electronically doped compounds $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ [1211, 1248] with $T_c = 20$ K points to the existence of a presumably general mechanism of high-temperature superconductivity in copper-oxide compounds.

1.3 Generic Properties of Cuprate Superconductors

At present, there are more than 150 superconducting compounds with T_c higher than the record of 23 K for conventional intermetallic superconductors [232]. However, only cuprates can be called the true high-temperature superconductors since only they have T_c above the liquid-nitrogen boiling point and many of them even have $T_c > 100$ K.¹ The composition of these compounds and their transition temperatures T_c are given in Table 1.1. It is convenient to subdivide them into several classes: the $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ (LMCO) type, the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ (YBCO) type, and Bi-, Tl-, and Hg-type compounds described by a general formula $\text{A}_m\text{M}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x$, where A = Bi, Tl, Hg and M = Ba, Sr. These are the hole-doped materials. The Nd-based compounds $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ have an electronic conductivity. It should be mentioned that the value of T_c strongly depends on the concentration of oxygen or other doping ions and on various types of disorder as impurities, cation nonstoichiometry, etc. (see Sect. 5.1.2). In Table 1.1, the maximum values of T_c^{max} are shown at the optimal doping and at ambient pressure. A comprehensive list of T_c^{max} was presented by Eisaki et al. [304].

All cuprate superconductors have layered structure with a stacking sequence of CuO_2 planes and charge-reservoir blocks. In stable, one-phase compounds, the number n of CuO_2 planes is usually less than four. Under high

¹A claimed hole superconductivity with $T_c = 117$ K in $\text{C}_{60}/\text{CHBr}_3$ by Schön et al. [1160] was later retracted.

Table 1.1. Representative classes of cuprate superconductors

Superconducting compounds	T_c^{\max} (K)
<i>LMCO-type compounds</i>	
$\text{La}_{2-x}\text{M}_x\text{CuO}_4$ (LMCO) M = Ba, Sr, Ca	39
$\text{La}_2\text{CuO}_{4+y}$	45
$\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$	26
$\text{R}_{2-x}\text{M}_x\text{CuO}_4$ (RMCO) (electronically doped cuprates)	24
R = Pr, Nd, Sm, Eu, M = Ce, Th, Ce+Sr	
$\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ (ladder compound)	12
– superconducting under high pressure at $x = 13.6$)	
<i>YBCO-type compounds</i>	
$\text{RBa}_2\text{Cu}_3\text{O}_{6+x}$ ($x > 0.4$) (R-123) R = Y, La, Ca, RE;	93
RE = Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu	
$\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y-124)	80
$\text{YBa}_2\text{Cu}_{3.5}\text{O}_{8-y}$ (Y-247)	87
$\text{Pb}_2\text{Sr}_2\text{ACu}_3\text{O}_{8+y}$, A = R + Sr, R + Ca	80
$\text{La}_{2-x}\text{Sr}_x\text{CaCu}_2\text{O}_8$	60
$\text{RuSr}_2\text{GdCu}_2\text{O}_{8-\delta}$ (Ru-1212) (superconducting ferromagnet)	46
<i>Bi-, Tl-, Hg-type compounds</i>	
$\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}$ Bi-22($n-1$) n^a ($n = 1-3$)	
$\text{Bi}_2\text{Sr}_2\text{CuO}_{6+\delta}$	10
$\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$	110
$\text{Tl}_m\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+m+2+\delta}$ Tl- $m2(n-1)n^a$ ($m = 1, 2; n = 1-4$)	
$\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$	93
$\text{Tl}_1\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{9+\delta}$	133
$\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$	125
$\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ Hg-12($n-1$) n^a ($n = 1-5$)	
$\text{HgBa}_2\text{CuO}_{4+\delta}$	98
$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$	135
$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ (under pressure of 30 GPa)	164

^aThe sequential numbers represent the composition ratio of the cations

pressure, it is possible to synthesize compounds with larger n . With increasing number of CuO_2 planes, a certain increase in T_c is observed, with maximum T_c usually attained for $n = 3$. The values range from $T_c = 38$ K in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with a single CuO_2 plane to $T_c = 134$ K in compounds of Hg-1223 with three CuO_2 planes. The highest $T_c = 164$ K was obtained in Hg-1223 by applying external pressure $P = 30$ GPa [375]. It was suggested that the mercury-based compounds have the highest T_c (even the one-layer compound Hg-1201 has $T_c = 97$ K) because their copper–oxygen layers have the most ideal tetragonal structure without pronounced buckling as compared with other cuprate materials. They have also the largest apical Cu–O distance and therefore the apex oxygen produces only a small perturbation on the electronic structure of a CuO_2 plane (see Sect. 2.5).

By applying the high-pressure technique, new types of cuprate superconductors have been synthesized. The ladder type compound $\text{Sr}_{0.4}\text{Ca}_{13.6}\text{Cu}_{24}\text{O}_{41}$, which consists of two-leg Cu_2O_3 ladders and edge-sharing CuO_2 chains, undergoes a superconducting transition below $T_c \simeq 12\text{ K}$ under high pressure $P = 3\text{--}4\text{ GPa}$ [1287]. Under pressure, a crossover from one-dimensional to two-dimensional electronic structure occurs that enforces superconductivity in copper–oxygen planes (see Sect. 2.2.3).

A novel superconducting state has been observed in rutheno-cuprates $\text{RuSr}_2\text{GdCu}_2\text{O}_{8-\delta}$ [130] and $\text{Ru}_2\text{Sr}_2(\text{Gd}_{0.7}\text{Ce}_{0.3})_2\text{Cu}_2\text{O}_{10-\delta}$ [328], where superconductivity occurs below the transition to a ferromagnetic state at $T_m > T_c$. The Ru-sublattice is responsible for the unusual magnetic properties though the real magnetic structure is not precisely known (see Sect. 2.4.3).

Despite the great diversity of the cuprate superconductor compounds, they have a common structural element – the CuO_2 planes. It is generally believed that the high values of superconducting T_c and the anomalous normal state physical properties of cuprate materials are determined by the unique electronic and magnetic structure of the CuO_2 plane. It allows us to single out these materials into a class of cuprate superconductors.

Even the first studies of cuprate superconductors have shown that they exhibit many properties in common with the conventional superconductors. In particular, measurements of the Shapiro steps in the Josephson effect, observation of a flux lattice in a magnetic field, and a direct measurement of the flux quantum $\phi_0 = hc/2e$ have shown that Cooper pairs with charge $2e$ occur in the superconducting state. Tunneling experiments unambiguously indicate the formation of a superconducting gap in the spectrum of the charge carriers below T_c , which also confirms the picture of Cooper pairs. The decrease in the Knight shift in the superconducting state and the temperature dependence of the penetration depth of a magnetic field point to the singlet nature of pairing as in the usual BCS scenario.

However, the cuprate compounds have revealed a number of anomalous physical properties by which they essentially differ from the conventional metals [175]. Here, we discuss these properties only briefly, since they will be considered in more detail in the subsequent chapters.

As structural studies show, the cuprate superconductors with a general chemical formula $A_m\text{M}_2\text{R}_{n-1}\text{Cu}_n\text{O}_{2n+m+2}$ have a layered structure: n (CuO_2)-layers interleaving with $n - 1$ R-layers define the active conducting block, while $[(\text{MO})(\text{AO})_m(\text{MO})]$ -layers form the charge-reservoir block. As a result, a high anisotropy of the electronic and, in particular, the superconducting properties are specific for the quasi-two-dimensional copper-oxide superconductors. The physical properties and the superconducting T_c are strongly influenced by the concentration of charge carriers, which is regulated by variation of the charge-reservoir block composition. Generally, the superconducting transition temperature T_c for copper-oxide superconductors has a parabolic dependence on the concentration of charge carriers p with a maximum at an *optimal doping* p_{opt} . As suggested by Presland et al. [1028], a universal formula for $T_c(p)$

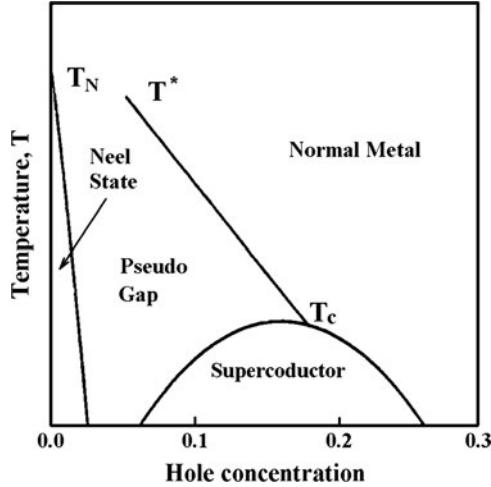


Fig. 1.1. Generic phase diagram of the cuprate superconductors

can be proposed:

$$T_c(p) = T_{c,\max} [1 - \beta (p - p_{\text{opt}})^2], \quad (1.6)$$

where the parameters β and p_{opt} have the constant values, $\beta = 82.6$, $p_{\text{opt}} = 0.16$ for a large number of compounds [1221]. In the *underdoped* region, $p < p_{\text{opt}}$, the cuprate superconductors exhibit anomalous physical properties below a characteristic temperature T^* when the so-called *pseudogap* in the electronic spectrum is opened. Therefore, the underdoped region is called a “strange” metal. In the *overdoped* region, $p > p_{\text{opt}}$, “normal” metal properties are regained. The generic phase diagram in the temperature T and hole concentration p (per CuO_2 layer) coordinates is shown in Fig. 1.1. The crystal structure and the phase diagram for cuprate compounds are discussed in Chap. 2

A unique feature of the parent copper-oxide materials is an AF long-range ordering of spins, which are almost localized at the copper sites, in the CuO_2 planes in the insulating Mott–Hubbard phase. The exchange energy for the copper 1/2 spins is extremely large, $J \simeq 1,500\text{K}$, which would result in the record Néel temperature for AF ordering, $T_N \simeq 1,500\text{K}$, if the spin lattice had a three-dimensional structure. Due to the layered structure of copper oxide materials, it is much lower, $T_N \simeq 300\text{--}500\text{K}$, and is rapidly suppressed if holes are doped in the CuO_2 plane (see Fig. 1.1). However, strong dynamical short-range AF fluctuations survive in the metallic phase. A resonant peak around 40 meV in the dynamical spin susceptibility at the AF wave vector was observed below T_c in YBCO, Bi-2212 and Ta-2212 compounds even at optimal doping [170, 1168]. The AF correlations strongly affect the properties of the cuprate compounds in the normal phase and they are believed to be the source of nonphononic mechanisms of superconductivity. Chapter 3 is devoted

to the description of the AF phase transitions in LSCO and YBCO compounds and neutron inelastic scattering and nuclear magnetic resonance experiments, which confirm the existence of strong dynamical AF fluctuations.

Studies of the thermodynamic properties of copper-oxide superconductors evidenced a number of peculiarities of the temperature dependence of the critical magnetic fields, the penetration depth, and the specific heat. Due to a low density of charge carriers, the cuprate superconductors have a large magnetic penetration depth λ and a small correlation length ξ . This results in a very large value of the Ginzburg–Landau parameter $\kappa = \lambda/\xi \gg 1$, which means that the cuprates are strong type II superconductors with an extremely large upper critical magnetic field H_{c2} . The quasi-two-dimensional character of the electronic structure leads to a large anisotropy of the penetration depth and the critical magnetic fields in-plane and perpendicular to the copper–oxygen plane. The small pinning energy and high transition temperature T_c with large anisotropy result in a very complicated magnetic phase diagram (Fig. 1.2). We notice the occurrence of a phase transitions from the normal state to the vortex liquid at the upper critical magnetic field H_{c2} , then a transition to the vortex solid with pinned vortices, and at the lower first critical magnetic field H_{c1} the transition occurs to the Meissner phase (see Sect. 4.3.1).

The large anisotropy of the electronic structure leads also to anisotropic correlation lengths for the order parameter. The estimation of the correlation length shows that its in-plane value equals several lattice constants, while in the direction perpendicular to the plane it is approximately equal to or even smaller than the lattice constant in this direction. Such small values of the correlation length show that the number of electrons (holes) n_s in the

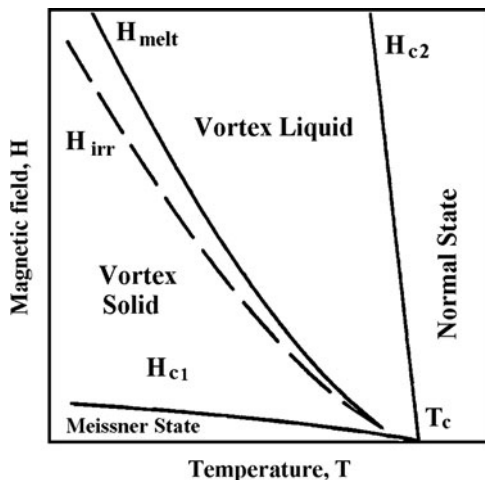


Fig. 1.2. Magnetic phase diagram of the cuprate superconductors

Cooper pair is several orders of magnitude smaller than those in conventional superconductors, in which $n_s = 10^4$ – 10^6 . A small number of electrons in Cooper pair results in considerable fluctuations effects. The anomalous thermodynamic properties of the cuprate superconductors, in particular, specific heats, penetration depths and critical magnetic fields, are discussed, within the anisotropic Ginzburg–Landau theory, in Chap. 4.

The large anisotropy of the electronic properties of the copper-oxide superconductors was predicted by the very first theoretical calculations of their electronic band structure (Sect. 7.1). It was shown that the main contribution to the states near the Fermi surface is made by the strongly bonded 3d electron states of copper Cu^{2+} and 2p states of oxygen O^{2-} in the CuO_2 planes. Rather accurate experimental investigations have confirmed this picture at a qualitative level only. They have found a considerable contribution of electron single-site correlations at copper ions, which were not taken into account in the first theoretical calculations. In particular, metal–insulator transition with a charge transfer gap and the formation of the AF state in the undoped compounds, the considerable localization of the spin density at copper sites, the appearance of excitations related to the p–d charge transfer, and a number of other phenomena observed in electron spectroscopy can be accounted for only by taking into consideration strong electronic correlations. Experimental studies of electronic properties in the normal and superconducting phases are discussed in Chap. 5. The unconventional pairing of the *d*-wave symmetry is specific for the cuprate superconductors.

In the conventional superconductors, the electron–phonon pairing mechanism is verified by large values of the isotope effect (1.4). In the copper-oxide compounds, the isotope effect is suppressed, $\alpha = 0.2$ – 0.05 , although in some cases it reveals an anomalous growth for small values of T_c . In this respect, studies of phonon spectra of oxide superconductors and the observation of manifestations of electron–phonon interaction are important for clarifying the mechanisms of high-temperature superconductivity. The results of these studies are considered in Chap. 6.

To explain such unusual properties of the cuprate high-temperature superconductors, various types of theoretical models, ranging from the standard models of the Fermi-liquid with strong electron–phonon coupling to rather exotic models of quantum spin liquids with unusual ground states, have been proposed. Chapter 7 is devoted to the discussion of basic models and mechanisms of high-temperature superconductivity.

After the discovery of high-temperature superconductivity in cuprates, many laboratories all around the world hoped to develop useful applications of these materials. However, mechanical (brittleness) and electric (high anisotropy, *d*-wave gap symmetry) properties of these materials, which are not conventional metals, considerably hindered the technological progress in the development of their applications. We consider several successful applications of the high-temperature superconductors in Chap. 8.

Now, there are more than 100,000 publications devoted to the problem of the high-temperature superconductivity in cuprates. The main results of studies of high-temperature superconductors, materials, and mechanisms of superconductivity are presented in the proceedings of various International Conferences, in particular, “Proceedings of the International Conference on High-Temperature Superconductors and Materials and Mechanisms of Superconductivity” [754–761]. Early results of studies of the high-temperature superconductors are reported in the monographs edited by Ginsberg [384–388] and also can be found in the books edited by Fukuyama et al. [367], by Bednorz and Müller [121], and by Maekawa and Sato [768]. There are many excellent and detailed reviews devoted to the theoretical and experimental studies of the high-temperature cuprate superconductors published in last years in review journals and as separate monographs, which will be cited in the subsequent chapters.



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