CHAPTER 6. HIGH-TEMPERATURE SUPERCONDUCTORS

In chapter 1 it was already told about the history of discovery of high-temperature superconductivity (HTSC). We remind that till 1986 the maximum critical temperature equal 23,2 K, was observed at an alloy of Nb_3Ge(1973). Despite considerable efforts of theorists and experimenters, scientists didn't manage to raise T_C above this value up to that moment when Bednorts and Müller found that the ceramics of $La-Ba-Cu-O$ showed signs of transition to a superconducting state when cooling lower than 35 K. The studied samples were a mix of different phases. In January, 1987 it was established that the phase $La_{2-x}Ba_xCuO_4$ is responsible for superconductivity. Critical temperature depends on structure and is maximum (35 K) at x=0.2.

The new direction of researches was so open. Physics of the whole world began search of superconductors close in structure. Replacement of La by other close elements from the 1st and 2nd groups of the table of Mendeleyev, and also the variation of structure created a large number superconducting ceramics. In 2 months on ceramics $YBa_2Cu_3O_{7-x}$ the critical temperature 92 K was reached. Thus the "nitric" barrier was broken, i.e. there was an opportunity to obtain superconductors not by means of expensive and inconvenient liquid helium with a temperature of boiling of 4,2 K, but with use of the cheap and simple in using liquid nitrogen boiling at 77 K. From that moment a large number of matters with critical temperature above a boiling point of liquid nitrogen is created. The record belongs to the ceramic $HgBa_2Ca_2Cu_3O_{8+x}$ opened in 2003, the critical temperature of which is equal 135 K.

The properties of HTSC are in many respects similar to usual superconductors, but at the same time there are both essential quantitative and qualitative differences.

1) As well as in case of usual superconductors, their resistance becomes zero when cooling below critical temperature. Thus values of the T_C are essentially higher and reach 100 K and above (nowadays to 135 K).

2) There is no allocation or absorption of heat, but a jump of a thermal capacity is observed, i.e. a phase transition of the 2nd type takes place.

3) Meissner effect takes place, but the penetration depth λ, equal 10^2-10^3 angstrom, is much more than in usual superconductors.

4) Experiments show existence of an energy gap, the order of value of which is coordinated with the theory of BCS ($2\Delta \approx 3{,}5kT_C$). However some experiments allow to find two various values of a gap. There are reasons to believe that a higher value is connected with the planes in a crystal, and a smaller - with linear chains.

5) A dependence of T_C on the mass of atoms (isotopic effect) is found out that testifies to a role of lattice fluctuations.

6) In a magnetic field HTSC behave as type II superconductors. It is connected both with a high penetration depth λ, and with very small length of coherence ξ - from 0.5 to the 30 angstrom (in usual - thousands angstrom). Thus, the condition $\lambda > \xi$ characterizing type II superconductors is carried out for certain.

7) The stationary effect of Josephson takes place, and from experiments on dependence of oscillation of the maximum Josephson current on a magnetic field (see §5.2.1) it follows that the

magnetic flux quantum Φ_0 is equal to $h/2e$ what points to transfer of current by Cooper pairs with a charge $2e$.

8) In the case of applying to Josephson contact direct and alternating voltages simultaneously the Shapiro steps (see §5.3) testifying to non-stationary effect of Josephson can be observed. Thus the period between steps is equal to $h\nu/2e$ what also speaks about the Cooper pairs with a charge $2e$.

9) The quantization of a magnetic flux takes place, i.e. a magnetic flux through an opening in a superconductor is equal to an integer of quanta of magnetic flux $\Phi_0 = h/2e$.

10) The lattice of vortex threads was observed, and it was established that each thread contains the same quantum of a magnetic flux $\Phi_0 = h/2e$.

The above-stated facts (points 7-10) give strong reasons to believe that current is transferred by Cooper pairs. However it appeared that in the majority of HTSC Cooper pairs are formed not by electrons, but by holes.

Apparently from all aforesaid, the majority of the phenomena, considered in previous paragraphs for usual superconductors, take place as well in HTSC. But there are also essential features, general for all HTSC, distinguishing them from usual superconductors.

1) Unlike the usual superconductors which are in a normal state metals or metal alloys, HTSC represent oxides of metals and in a normal state have considerably big resistance. Though it should be noted that the linear growth of specific resistance with a temperature testifies nevertheless to metal nature of their conductivity.

2) It is difficult to receive these metal-oxide compounds in the form of monocrystal. The existing technology (agglomeration of previously mixed mixture of ingredients) allows to obtain ceramics being set of crystals ("granules") of the sizes from units to hundreds of microns, the space between which is filled by dielectric.

3) In places of contacts of granules with each other Josephson contacts on which there can be processes connected with Josephson effects are formed. As the sizes of granules are small, the number of such contacts is very great. Therefore superconducting ceramics sometimes are called Josephson mediums. Josephson effects are described by nonlinear equations. Therefore when such samples are placed into external constant and alternating electromagnetic fields there can occur different complicated processes in them which weren't observed in other substances earlier.

4) The transition to a state with zero resistance in HTSC happens in a wider temperature range, than in usual superconductors. So, for example, in Bednorts and Müller's first article it was reported that a sharp falling of resistance of oxide $La_{2-x}Ba_xCuO_4$ with $x = 0.2$ began at 35 K and the resistance reached zero at $T \approx 25$ K. Big blurring of the transition is explained by the existence in ceramics of various phases with different values of the T_C.

5) Monocrystals of HTSC are prepared on special technologies. They have small sizes (to several millimeters), have layered structure and associated with it strong anisotropy of the majority of properties.

In fig. 6.1 the elementary cell of a crystal $YBa_2Cu_3O_{7-x}$ is represented. Its distinctive feature is the existence of two nonequivalent positions of atoms of copper: Cu(1) and Cu(2). Atoms of Cu(2) are put into a pyramid with the square basis formed by four atoms of oxygen - O(2) and O(3)

- and are almost in the basis plane. These layers located perpendicularly to the axis c are called planes of CuO_2. Unlike atoms of Cu(2) atoms of Cu(1) in the plane, perpendicular to the axis c, adjoin only to two atoms of oxygen O(1), forming so-called chains of CuO. Thus, in the structure of the $YBa_2Cu_3O_{7-x}$ there are two various elements - planes of CuO_2 and chains of CuO - which are weakly interact with each other through bridge oxygen O(4). The positions of O(5) remain vacant.

The planes of CuO_2 are available in all ceramics, in some of them there are CuO chains. There are bases to believe that both planes and chains play very important roles in high-temperature superconductivity.

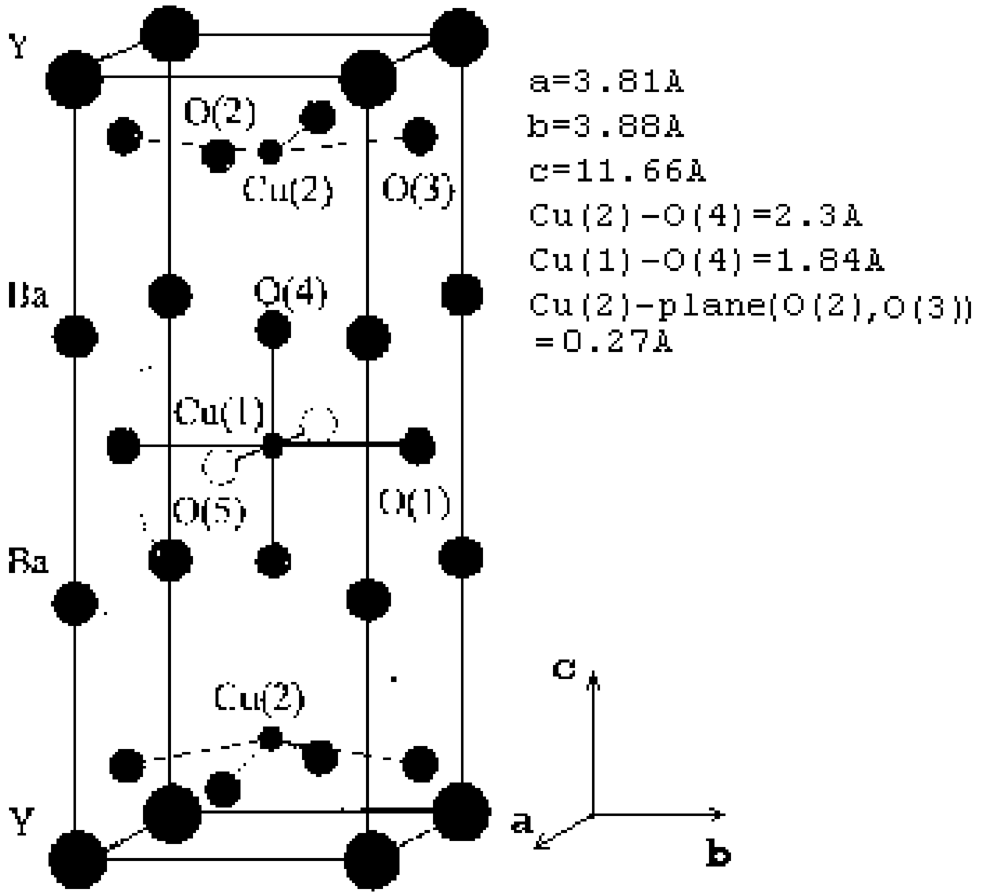

Fig. 6.1. An elementary cell of a crystal $YBa_2Cu_3O_{7-x}$.

The theory of HTSC is not created yet. There are essential bases to believe that for its construction it is enough to modify the theory of BCS, having found new, other than phonon, mechanism of an attraction of electrons (or holes) leading to their association in Cooper pairs. The phonon mechanism doesn't allow to receive so high values of critical temperature. It is necessary to find some other, stronger type of interaction. The exchange of some particles can be the cause of such attraction. As the elementary cell of a crystal of HTSC is very complicated (fig. 6.1), in a sample there can be a large number of different types of particles - phonons, excitons, polarons, bipolarons, magnons, etc. It is possible also that in different substances various particles are responsible for pairing.

The answer to a question of the nature of this interaction isn't found so far as there is no explanation for some other facts, such as existence of two gaps in one sample, anomaly in dependence of a thermal capacity on temperature, etc.

In 2008 the new class of superconducting substances with high values of critical temperature - layered compounds on the basis of iron and elements of the 5th group (pniktid) or Se - was discovered. These substances are called ferropniktids (or selenids of iron). The superconducting state at substances containing magnetic atoms (Fe) was revealed for the first time, because usually magnetic field suppresses superconductivity. The crystal structure of all ferriferous superconductors (6 families are already known) has a form of alternating layers in which atoms of iron are surrounded with a tetrahedron from atoms of As or Se what suppresses magnetic properties of atoms of Fe. At the moment the champion on critical temperature is a compound of $GdOFeAs$ (Gd-1111), doped by F which replaces oxygen. Its T_C reaches 55 K.

In 2001 MgB_2 alloy (magnesium diborid) with $T_C = 40$ K - record for intermetallid (chemical compounds of two or more metals) – was discovered.

Use of very high pressure allows to increase critical temperatures. For example, the critical temperature of the ceramic $HgBa_2Ca_2Cu_3O_{8+x}$ mentioned above (with record-breaking high $T_C = 135$ K) at a pressure of 40 GPa increases to 165 K.

Mentioned before selenid of iron loses superconducting properties at 10 GPa, but at 11.5 GPa gets them again, and zero resistance remains to record for iron selenid critical temperature 48 K.

At high pressures superconducting properties can arise even in substances which couldn't be suspected of such abilities. For example, in 2014 it was revealed that sulfide of hydrogen (H_2S) at a pressure of 180 GPa and a temperature of 190 K suddenly sharply reduces the resistance that suggests an idea of superconductivity. However, this interpretation still needs to be tested.

The reasons for all these phenomena are still unclear.