CRYSTAL STRUCTURE OF HIGH-TEMPERATURE SUPERCONDUCTORS

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1. Superconductivity

In 1911 a Dutch physicist G. Kamerling-Onnes in the course of a study of the behaviour of electric resistance of mercury upon temperature lowering discovered that for $T < T_c = 4.15$ K the resistance dropped down to zero. It was shown later that at the critical temperature T_c a second-order phase transition occurs. The new state was called superconducting. Then the discoverer found that application of a strong magnetic field eliminated superconductivity. A fundamental property of superconductors –the Meissner effect– was discovered only 22 years later. The experiments conducted by W. Meissner and R. Oxenfeld proved that the external field does not penetrate the bulk of the superconducting material, the appropriate sample being pushed from the magnetic field. The physical reason for the Meissner effect is as follows. Nonattenuating currents arise in the surface layer of a superconductor hundreds of angstroms thick under the effect of an external magnetic field. These currents compensate for the external field inside the sample. Theoretical grounds of superconductivity were being developed rather slowly. It was only in 1934 that brothers F. and G. Londons suggested the first version of the phenomenological theory of electrodynamic properties of superconductors. In 1937 L. D. Landau predicted the structure of an intermediate state of superconductors which was later determined experimentally by A. I. Shalnikov and co-workers. The generalized phenomenological theory of superconductivity was founded by V. L. Ginzburg and L. D. Landau in 1950. According to the behaviour of superconductors in a magnetic field they can be divided into two groups: first- and second-order superconductors. In the former one superconductivity is destroyed by a magnetic field in the entire bulk. The latter superconductors were predicted in 1952 by A. A. Abrikosov. These superconductors are characterized by two values of the critical magnetic field. At intermediate values of the external magnetic field a second-order superconductor is pierced by the Abrikosov swirls whose density increases with the field, the superconductivity being retained only beyond these swirls. The superconducting state is a quantum state of a macroscopic object. According to the theory, the magnetic flux piercing a superconducting ring with nonattenuating current is quantized. This effect was observed experimentally only in 1961 and enabled determination of the charge of the particles that are current carriers in superconductors. This charge was twice as large as the electron charge, which is in conformity with the effect of formation of stable pairs by electrons with opposite spins in a crystal lattice, predicted by L. Cooper in 1956. It is the Cooper pairs that are carriers of nonattenuating current in superconductors.

A rigorous microscopic theory of superconductivity was founded in 1957-1958 in works by J. Bardin, L. Cooper, G. Schiffer and N. N. Bogolyubov. It is based on the following. Electrons of a Cooper pair, exchanging phonons with the lattice, are attracted and form a particle with a zero spin. These particles obey the Bose-Einstein statistics. Both condensation of such particles and their superfluidity take place in such superconductors. Since each particle carries a 2e charge, superfluidity of a quantum electronic liquid leads to supeconductivity.

In the period 1911-1985 superconductivity was found experimentally in dozens of pure metals and in hundreds of various alloys and intermetallic compouds. An unrivalled superconductor was Nb_3Ge with $T_c = 23.2$ K. The structure of these crystals is shown in figure 1. Superconductivity was discovered in some strongly doped semiconductors and even in polymers. Organic superconductors hold a special place among other superconductors. A typical member of this family is the β-phase $(BEDT\text{-}TTF)_2I_3$ (bis ethylenedithio-tetrathiafulvalene two iodine three). The compound is a two-dimensional organic metal with $T_c \sim 1.5$ K. By varying preparation methods for these compounds, as well as their thermal treatment and the effect of high pressures on them one can raise T_c in organic superconductors up to 6-7 K.

2. HIGH-TEMPERATURE SUPERCONDUCTORS

A new era in superconductivity was opened in 1986 when Bednortz and Muller discovered superconductivity in ceramic $(La, Ba)_2CuO_4$ with $T_c = 36$ K [1]. They were awarded the Nobel prize, and that work was an impetus for a wide scale investigation in a new branch of solid state physics – high temperature superconductivity. Shortly afterwards this dis-

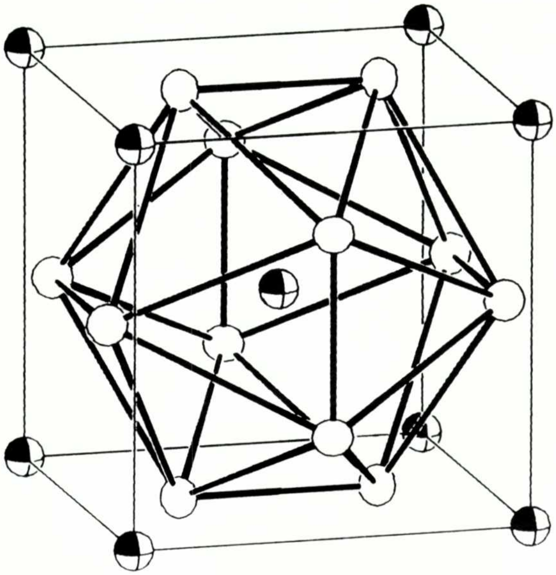

Fig. 1. Atomic structure of a classic superconductor ($Ge_{0.8}$ $Nb_{0.2}$) Nb_3, $T_c = 23.2$ K.

covery, in 1987, Wu with co-workers published a communication reporting synthesis and study of $YBa_2Cu_3O_{7-\delta}$ with $T_c = 93$ K [2]. In the following five years about twenty various crystalline superconductors were obtained at different laboratories all over the world (Table 1). The total amount of superconducting compounds, including isostructural ones which differ greatly in their chemical composition, now exceeds 500-600 and their number is rapidly increasing [3-6]. The superconducting transition temperature range now reaches $T_c = 125$ K. This record, reliably reproduced in various laboratories, belongs to the Tl-phase of $Tl_2Ca_2Ba_2Cu_3O_{10}$.

In the first two years starting from the discovery of superconductivity the list of superconductors was supplemented only by copper-containing compounds. It was in 1988 that a compound with the perovskite structure (Ba, K)BiO_3 and $T_c = 30$ K was synthesized. This compound did not contain copper atoms. In 1975 a study reporting $T_c = 12$ K of Ba(Rb, Bi)O_3 was published, but at that time it did not seem interesting. Later, those results were recalled. Of principal importance was the discovery of superconductivity in (Nd, Ce)$_2CuO_4$ crystals in 1989. This compound was the first one among other high-T_c superconducting materials that exhibited electronic conductivity. All the previously obtained high-T_c materials had hole conductivity. A comparison of the hole (La, Sr)$_2CuO_4$

Table 1. High-temperature superconductors, differing in their crystal structure and their maximum superconducting transition temperature.

Chemical formula	Symmetry	a, A	b, A	c, A	Tc, K
$(La, Ba)_2CuO_4$	I4/mmm	3.782	–	13.249	36
$(Nd, Ce)_2CuO_4$	I4/mmm	3.948	–	12.088	24
$(Nd, Ce)(Nd, Sr)CuO_4$	P4/mmm	3.856	–	12.490	20
$IBa_2Cu_3O_7$	Pmmm	3.820	3.886	11.688	94
$IBa_2Cu_4O_8$	Ammm	3.842	3.871	27.240	80
$Y_2Ba_4Cu_7O_{15}$	Pmmm	3.842	3.881	50.500	40
$(Ba, Nd)_2(Nd, Ce)_2Cu_3O_8$	I4/mmm	3.875	–	28.600	40
$Bi_2(Sr, Ca)_2CuO_6$	A2/a	5.362	5.362	24.300	40
$Bi_2(Sr, Ca)_3Cu_2O_8$	Amaa	5.408	5.413	30.871	80
$Bi_2(Sr, Ca)_4Cu_3O_{10}$	I4/mmm	3.811	–	37.080	100
$TlBa_2CuO_5$	P4/mmm	3.847	–	9.600	17
$TlBa_2CaCu_2O_7$	P4/mmm	3.847	–	12.730	91
$TlBa_2Ca_2Cu_3O_9$	P4/mmm	3.853	–	15.913	116
$TlBa_2Ca_3Cu_4O_{11}$	P4/mmm	3.847	–	18.730	122
$Tl_2Ba_2CuO_6$	I4/mmm	3.866	–	23.225	85
$Tl_2Ba_2CaCu_2O_8$	I4/mmm	3.856	–	29.186	110
$Tl_2Ba_2Ca_2Cu_3O_{10}$	I4/mmm	3.850	–	35.638	125
$Tl_2Ba_2Ca_3Cu_4O_{12}$	I4/mmm	3.850	–	41.940	108
$Pb_2Sr_2YCu_3O_8$	Cmmm	5.394	5.430	15.731	70
$(Ba, K)BiO_3$	–	–	–	–	30

and electronic $(Nd, Ce)_2CuO_4$ superconductors indicates remarkable differences in their atomic structure (figure 2). However, of major significance here is the fact that in the first case some trivalent lanthanum cations are replaced by divalent strontium ions, while in the second one trivalent neodymium is partially replaced by tetravalent cerium. Among the works investigating into specific features of the structure and composition of new materials that are responsible for superconductivity of major importance are experimental studies of La-phases. The La_2CuO_4 compound of the stoichiometric composition does not possess superconducting properties. These properties are not only a result of replacement of some La atoms by Ba or Sr atoms, as it was found by the pioneers. It suffices to obtain samples with some lanthanum deficiency, $La_{2-\delta}CuO_4$ or with oxygen redundancy $La_2CuO_{4+\delta}$. In other words, there should be some deviation from the stoichiometric composition responsible for the presence of current carriers in the material with certain atomic and electronic structure.

The atomic structures of high-temperature superconductors (La, Ba)$_2$CuO$_4$, (Nd, Ce)$_2$CuO$_4$ and their derivatives (Nd, Ce)(Nd, Sr)CuO$_4$ are shown in figure 2. In the structure of the first compound with the hole conductivity the (La, Ba)-cations are located in nine-cornered polyhedra, while Cu atoms are located in greatly elongated octahedra (the Jan-Teller effect). In the second electronic conductor the geometry of cationic arrangement is the same as in the first structure. As far as oxygen atoms, half of them occupy totally different sites as compared to the first structure, that leads to the arrangement of (Nd, Ce) cations in cubes, while copper atoms are confined to plane square coordination. The third structure is a combination of the first two ones. Copper atoms in this structure are located in semioctahedra, (Nd, Ce) cations are in cubes, while (Nd, Sr) cations are in nine-cornered polyhedra.

Superconductivity was discovered in a ceramic material of the composition (La, Ba)$_2$CuO$_4$ and for a long time the attempts to obtain superconducting single crystals with T$_c$ = 36 K did not yield good results. First (La, Sr)$_2$CuO$_4$ crystals with T$_c$ = 5 K were obtained. It took over a year to synthesize single crystals with T$_c$ = 17 K, then with T$_c$ = 24 K and only in recent times single crystals with T$_c$ comparable with the superconducting transition temperature of the best ceramics have been obtained. This is in view of the fact that record values of T$_c$ in YBa$_2$Cu$_3$O$_7$ superconductors were characteristic of single crystals.

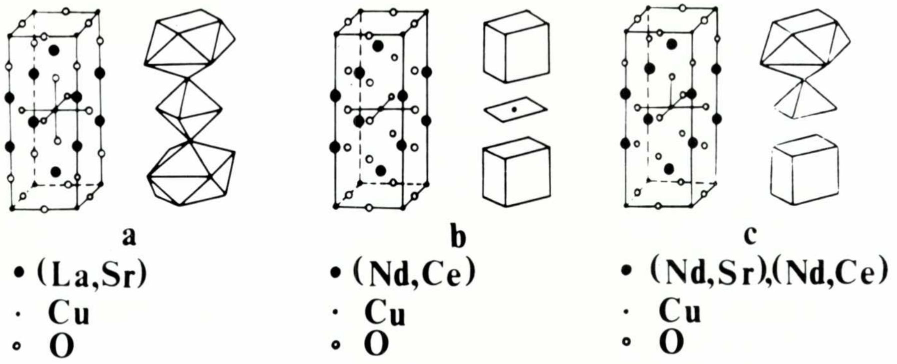

Fig. 2. Atomic structure models of high – T$_c$ superconductors in spheres and polyhedra:
a) (La, Sr)$_2$CuO$_4$ – hole conductivity.
b) (Nd, Ce)$_2$CuO$_4$ – electrone conductivity.
c) (Nd, Sr) (Nd, Ce) CuO$_4$ – derivative structure.

3. ATOMIC STRUCTURE AND THE SUPERCONDUCTIVITY TRANSITION TEMPERATURE OF $(La, Sr)_2CuO_4$

A dependence of T_c on Sr content in $(La, Sr)_2CuO_4$ was established for ceramic materials. As for single crystals, such an unambiguous dependence was not found. There were samples with identical Sr contents and essentially different superconducting transition temperatures. The structural studies of single crystals with Sr content ranging from $(La_{0.97} Sr_{0.03})_2CuO_{4-\delta}$ to $(La_{0.88} Sr_{0.12})_2 CuO_{4-\delta}$ permitted one to find reasons why there is no regular T_c dependence on Sr content in single crystals.

Precisional structural studies of crystals of La-phases are hindered due to twinning. The analysis of only ϑ-profiles of reflections often does not provide an unambiguous solution of the question whether there is twinning in particular samples. Twinning and its character can be reliably established by means of two-dimensional $\omega/2\vartheta$ scanning of reflections. All the samples studied exhibited twinning over (1 1 0) and/or $(1\ \bar{1}\ 0)$ planes. Volume ratios of twin components in different samples varied from 1:1 practically to a monodomain state. The analysis of the symmetry with an account of twinning showed that all the samples belong to two centrosymmetric orthorhombic space groups Abma and Pbma. A centered Bravais lattice characterizes crystals with a low Sr content. For samples with a higher Sr content reflections that disturb the A centering were established reliably. The space group in this case is Pbma.

A principal difference between crystals belonging to different space groups as far as their structure is concerned, consists in the fact that there is only one crystallographically independent La atom in the independent part of a centred unit cell. If we take space group Pbma with a primitive Bravais lattice there are two independent La atoms in the structure. A physical difference between these two structural types consists in the fact that Sr atoms are distributed statistically uniformly over all La sites in crystals with space group Abma. In the case of crystals with a primitive Bravais lattice we have found partial or full order in Sr distribution over La sites. In crystals of $(La_{0.97} Sr_{0.03})_2CuO_{4-\delta}$ La is replaced by Sr at any La site with an equal probability. In crystals of $(La_{0.94} Sr_{0.06}) CuO_{4-\delta}$ $(La_{0.86} Sr_{0.14}) CuO_{4-\delta}$ there is partial order in Sr distribution over La sites. The probability of Sr atom occupation of the first La site is 6%, while the probability of the occupation of the second La site is 14%. And, finally, we have established full order in Sr atoms distribution in La $(La_{0.76} Sr_{0.24}) CuO_{3.92}$. In this case one crystallographic site is 100% La occupied, all Sr atoms are concentrated at the second La site. At the latter site La is replaced by Sr with a probability of 24%. In the case of a fully ordered Sr distribution strontium is concentrated in double layers between layers of Cu-octahedra. A direct result of replacement of trivalent La atoms by divalent Sr atoms when the latter are concentrated in double layers is a deficiency in positive valence forces in these layers. As a result, some O atoms from parts of the structure enriched with Sr, leave the crystal. Accurate structural studies allowed one to establish reliably the oxygen deficiency in such layers where all Sr atoms are concentrated. Neutron diffraction studies have shown that in $La_2CuO_{4.032}$ crystals the compound neutrality is ensured by the formation of $[O_2]^{2-}$ groups with the O–O distance of 1.64 Å [7, 8]. Supposedly, in our case the formation of such groups compensates for La replacement by Sr only if Sr atoms are evenly distributed over all La sites. When Sr atoms are ordered and contained at certain layers of the structure there occur some oxygen atom losses in the structure. This, in its turn, affects the physical properties of crystals and leads to a lowering of T_c.

The results concerning the ordered Sr atom distribution when Sr atoms replace La atoms suggest two conclusions. 1. The T_c of $(La, Sr)_2CuO_{4-\delta}$ crystals depends not only on Sr content in the sample but also on Sr atom distribution over La sites. 2. The differences in the properties of single crystals and ceramic materials when Sr content in them is the same are due to differences in Sr atom distribution. The techniques of growing single crystals are closer to equilibrium ones as compared to ceramics. That is why the probability of Sr order is higher in single crystals. In ceramics an even Sr atom distribution and the formation of $[O_2]^{2-}$ groups without O losses is more probable. This result yields a higher T_c in ceramics as compared to single crystals with a fixed total Sr content [9].

4. ATOMIC STRUCTURE AND T_c OF Y-PHASES OF HIGH-TEMPERATURE SUPERCONDUCTORS WITH VARIOUS OXYGEN CONTENT

The second superconducting compound discovered was $YBa_2Cu_3O_7$ with T_c = 93 K, that exceeds the nitrogen boiling temperature and puts all the technical applications of superconductivity to a qualitatively new level. Depending on the conditions of synthesis and treatment of samples, Y-phases with various oxygen contents and related to it T_c were obtained. In such cases the maximum transition temperature T_c = 93 K was observed in orthorhombic samples with oxygen content close to 7 atoms per chemical formula. Tetragonal $YBa_2Cu_3O_6$ crystals do not undergo a superconducting phase transition. A phase with the composition $YBa_2Cu_3O_{6.5}$ with T_c of the order of 60 K was found using electron microdiffraction technique. Figure 3 shows atomic structures of two orthorhombic and a tetragonal phase of the compositions, respectively, $YBa_2Cu_3O_7$, $YBa_2Cu_3O_{6.5}$

and $YBa_2Cu_3O_6$. Of special interest are Y-phases with intermediate oxygen content. In this case the question of oxygen atom arrangement in the appropriate crystal is the main one.

Accurate structural studies of $YBa_2Cu_3O_{7-\delta}$ single crystals with O content ranging from 6.24 to 6.97 per unit cell have been carried out. The oxygen content was varied by dosage annealing in an argon atmosphere. All the studied samples were, in fact, twins with (1 1 0) and $(1\ \bar{1}\ 0)$ twinning planes. Two-dimensional $\omega/2\vartheta$ scanning of reflections enabled separate estimation of intensities of reflections from different domains of twins. According to these data volume ratios of twin domains and unit cell parameters of single-domained regions were found.

In the crystal with 6.95 oxygen atoms per unit cell the reflections from different twin domains are practically fully resolved. Integrated intensities of these reflections are readily measured because they do not overlap. However, this problem becomes more difficult to solve in the case of crystals with a smaller oxygen content. Reflection profiles for crystals with 6.46 and especially 6.24 oxygen atoms cannot be interpreted so easily by superimposing on one another the reflections from orthorhom-

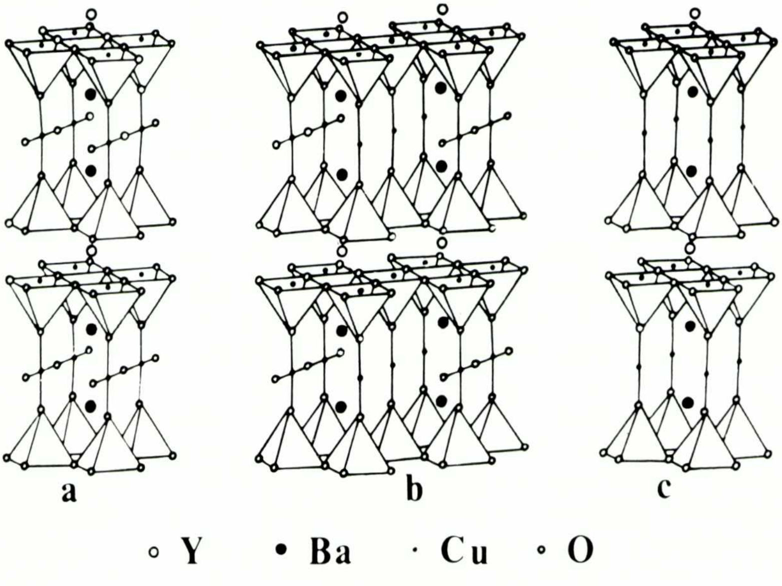

Fig. 3. Atomic structures of compounds $YBa_2Cu_3O_{7-\delta}$ with various oxygen content:
a) Orthorhombic phase I $YBa_2Cu_3O_7$ with $T_c = 93$ K.
b) Orthorhombic phase II $YBa_2Cu_3O_{6.5}$ with $T_c = 60$ K.
c) Tetragonal phase $YBa_2Cu_3O_6$ which does not undergo a superconducting phase transition.

bic twin domains. These complex profiles could be interpreted only by the superposition of the scattering from three regions of different local symmetry: two orthorhombic twin partners and one tetragonal. Thus, it was found that there is order in oxygen atom distribution in the sample which we regarded as a single crystal. This order results in the above mentioned three types of regions rather large in size, that have different local symmetries and yield three superimposed diffraction patterns. Two types are the orthorhombic twin domains, and the third one is a tetragonal symmetry region. These regions are characterized by different unit cell parameters. Such a difference is best manifested in a sample with 6.24 oxygen atoms. As is is well known, there is a correlation between oxygen content in a sample of Y-phase and the period c of this phase. Thus, we can assume that the regions differing in symmetry unit cell parameters have different composition (namely, oxygen content). We have determined mean oxygen content in the sample from statistical O atom site occupancies. According to the unit cell volume of tetragonal symmetry regions, the composition of these regions can be regarded as $YBa_2Cu_3O_6$, from crystal chemical considerations. The volume ratio of tetragonal and orthorhombic regions is calculated from reflection intensities. These data taken as a whole are sufficient to determine the local chemical composition of orthorhombic symmetry regions. In the considered case for a crystal with mean oxygen content 6.24 the estimation of the local chemical composition of orthorhombic regions yields 6.56 oxygen atoms per unit cell. Within the accuracy of X-ray data this value is in good agreement with the composition of the so-called orthorhombic phase II $YBa_2Cu_3O_{6.5}$, to which a superconducting phase transition at $T_c = 60$ K is related. In the crystals where oxygen content is lower than 6.5 atoms per unit cell there are regions of local tetragonal symmetry. The lower is O content the larger is the relative volume of tetragonal symmetry regions with respect to the volume of orthorhombic symmetry regions. The refinement of atomic models of these structures was complicated due to a strong correlation between structure parameters.

A strictly tetragonal phase does not undergo a superconducting phase transition and has the chemical composition $YBa_2Cu_3O_6$. If such a crystal is enriched with oxygen, the –Cu–O–Cu–O–chains appear in the plane of Cu atoms. Each such chain alternates with a –Cu–Cu– –chain. Thus, an orthorhombic phase II with $T_c = 60$ K is formed, with the local chemical composition $YBa_2Cu_3O_{6.5}$. With an increase in oxygen content the relative value of this region as compared to the initial tetragonal phase $YBa_2Cu_3O_6$ is also increased. The crystal with the mean total oxygen content 6.5 atoms per unit cell is fully composed of phase II and undergoes a superconducting phase transition at $T_c = 60$ K. A further increase in oxygen content results in the appearance of an orthorhombic $YBa_2Cu_3O_7$ phase with $T_c =$

93 K. Superconductivity (resistance fall) in the entire sample takes place when regions of orthorhombic phases of $YBa_2Cu_3O_7$ become connected. The patterns of equilibrium atomic structure of $YBa_2Cu_3O_{7-\delta}$ crystals with different oxygen content were later confirmed by electron microscopy studies of Y-phases.

In $YBa_2Cu_3O_{7-\delta}$ samples which are single crystals as far as their features are concerned, there are regions with ordered oxygen atom arrangement. These regions have different local chemical compositions and local symmetries. Such "single crystals", in fact, are not single-phase crystals. Their atomic structure and physical properties essentially depend not only on the method of sample preparation but also on the treatment: annealing, quenching, saturation with oxygen etc. [10].

5. ATOMIC STRUCTURE OF TL-PHASES OF HIGH-TEMPERATURE SUPERCONDUCTORS

As mentioned above, an unprecedented superconducting $T_c = 125$ K was found in 1991 in $Tl_2Ba_2Ca_2Cu_3O_{10}$. The family of Tl-phases is the largest one among high-temperature superconductors. It can be divided into two classes, with the general chemical formulae $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ and $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+3}$. The main structural difference between these two classes consists in the fact that in the first case there are single T1O layers, while in the second one there are double $(T1O)_2$ layers. The compounds of the first class contain crystals with n = 1 – 5, which were synthesized and studied, in the second class n is equal to 1-4. The chemical compostion of all these compounds can be expressed by a common formula $Tl_mBa_2Ca_{n-1}Cu_nO_{2n+m+2,}$ where m = 1, 2 and n = 1, 2, 3, 4. A conditional notation m2(n – 1)n was adopted for Tl-phases which indicates the number of appropriate cations in the chemical formula. Figure 4 presents schematically the atomic structures of various Tl-phases. The easiest to fix feature which identifies compouds of Tl-phases is the *c* period of the unit cell. It is defined by the (m, n) indices which fix the number of atomic layers in the unit cell. The *c* periods are 9.69, 12.73, 15.87,19.10, 23.15, 29.39, 36.26, 42.00 Å and correspond, respectively, to compounds 1201, 1212, 1223, 1234, 2201, 2212, 2223, 2234. In this case the *a* and *b* periods practically coincide in all the structures and are about 3.85 Å.

A specific feature of superconducting Tl-phases is the fact that they are nonstoichiometric in cations. This influences the number of current carriers in the compound and determines the T_c. For instance, in the 1212 compound some Ca cations are replaced by Tl cations. In 2212 crystals some Tl atoms are replaced by copper and, like in the case of 1212, Tl atoms partially replace Ca atoms. Similar replacements were found in 1223

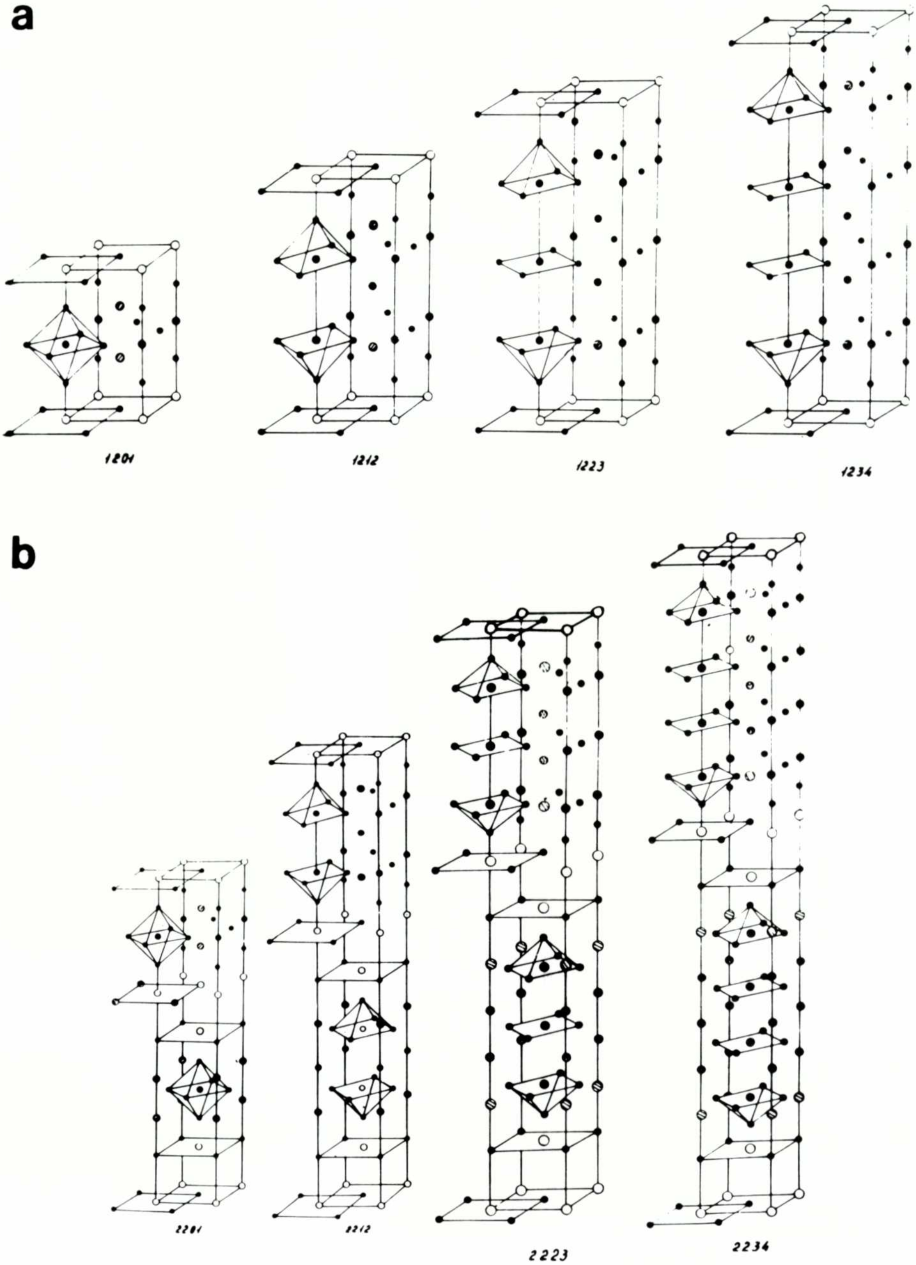

Fig. 4. Atomic structures of Tl-phases:
a) $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$: 1201, 1212, 1223, 1234.
b) $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$: 2201, 2212, 2223, 2234.

and 2223 compounds. Isomorphous cationic replacements in Tl-phases by cations of higher or lower valencies enable purposeful variations of the oxidaton degree of copper atoms practically from Cu^{2+} to Cu^{3+} that is responsible for superconductivity and the value of T_c. Crystal structure of high-temperature superconducting Tl-phases is considered in detail in a separate paper of this book [11].

6. SPECIFIC FEATURES OF THE STRUCTURE OF HTSC.

High-temperature superconductivity was first found in a ceramic sample. Single crystals are, naturally, preferable for physical studies. Thin films are most promising objects for practical applications nowadays. High-temperature superconductivity in single crystals, ceramics and thin films evidences that the real structure of a sample does not account for this phenomenon. The real structure is responsible for the critical current destroying superconductivity but not the superconductivity effect as such.

A common property of all known HTSC is the presence of at least one element with alternating valency. Chronologically, high-temperature superconductivity was discovered in compounds containing copper, bismuth, thallium. Their common crystal chemical feature is as follows. They are characterized by distorted polyhedra of their first coordination sphere. For copper this is a semioctahedron or an octahedron with the Cu-O distances 4 + 1 or 4 + 2, respectively (the Jan-Teller effect). The shape of oxygen polyhedra of bismuth and thallium also differs significantly from the regular shape.

Accurate structural studies of HTSC single crystals, as a rule, reveal deviations from an exact stoichiometric composition. Cationic and anionic deficiency in the structures as well as alternating valency in cations and a possible formation of anionic O_2^{2-} groups ensure current carriers of the hole or electronic origin.

A major structural element in all superconducting cuprates is copper-oxygen planar nets. The main difference in the structures of a nonsuperconducting $YBa_2Cu_3O_6$ and superconducting crystals of $YBa_2Cu_3O_{6+\delta}$ up to the extreme member of this family $YBa_2Cu_3O_7$ with T_c = 94 K is oxygen occupation of the net formed by copper atoms. There is an intermediate phase with a full order in oxygen arrangement, $YBa_2Cu_3O_{6.5}$ with T_c = 60 K.

However, superconductivity found in (Ba, K)BiO_3 with T_c = 30 K characterized by a purely perovskite motif of atomic arrangement and a complete absence of copper prevents interpretation in terms of the above two-dimensional nets. Moreover, the recently discovered superconductivity with $T_c = 18$ K in K doped fullerane K_xC_{60} opens up a new page in an exciting history of superconductivity. Later, superconductivity of Rb_xC_{60} was reported with $T_c = 24$ K. Such crystals are closely packed spherical formations of C_{60}. K or Rb atoms are statistically distributed over voids typical of close packings.

A new branch of solid state physics –high-temperature superconductivity makes quite impressive progress. The large scale high-temperature investigations and search for new materials possessing this property do not only evidence a major importance of this effect in solid state physics but also open up wide prospects for its practical application in science and technology. Energy losses due to ohmic resistance are estimated as 30% of the total amount of energy to be transmitted. Application of superconductors will save this energy. Practically the entire electrical engineering can be raised to a new level. Solenoids with superconducting windings permit one to obtain unique magnetic fields. Wide prospects for a new generation of current generators, electric motors, magnetic ball-bearings and levitation means of transport are opened. Presumably, microelectronics with superconducting elements will be a leading branch in superconductivity applications. Logic elements with supershort resolving times will lead to a new generation of computers. Thin film elements, however, are pioneers in the practical applications of high-temperature superconducting materials. They are used in magnetometers operating at nitrogen temperatures, which are immensely sensitive and widely used everywhere, from geology to medical equipment. These achievements in the field of high-temperature superconductivity are used in practice already today.

Abstract

This paper is a review of developments in investigations of superconductivity starting from the discovery made by Kamerling-Onnes till the discovery of high-temperature superconductivity made by Bednortz and Muller. The structural aspects of the superconducting phase transition in phases of $(La, Sr)_2CuO_4$, $YBa_2Ca_3Cu_3O_{7-\delta}$, and in the family of Tl superconductors with the general formulae $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ and $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ are considered. Specific features of the chemical composition and crystal structure of all the reported phases exhibiting high-temperature superconductivy are discussed.

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