The relation between structure and superconductive properties of high-temperature superconductors

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Dedicated to Professor L. Valko, DrSc., in honour of his 60th birthday

In this paper a new model of high-temperature superconductivity comprising all hitherto known aspects of a new type of oxygen superconductors has been described. This model presumes the existence of extremely strong electron—phonon coupling of "small bond polarons" which are generated by the motion of excess charge on the Cu(III) ions present in small amounts in the Cu(II)—O layers. In this case, the combination of the bound charges of the Jahn—Teller distortion gives rise to a very strong electron—phonon coupling which leads to the creation of the bipolaronic hole Cooper pairs.

В работе описана новая модель высокотемпературной сверхпроводимости охватывающая все, до сих пор, известные аспекты нового типа окисных сверхпроводников. Эта модель предполагает существование чрезвычайно сильного электрон-фононового взаимодействия между "небольшими связочными поларонами". Эти образуются движением дополнительных зарядов на Cu(III) ионах, присутствующих в небольших количествах в Cu(II)—O слоях. В этом случае, сочетанием связанных зарядов смещения по Джан—Теллеру образуется очень сильное электрон—фонон взаимодействие, которое ведет к появлению биполяронных дыр пар Купера.

Until 1986, it was assumed on the basis of microscopic theory of superconductivity (BCS theory) [1, 2] that the limiting temperature of transition into superconductive state could not exceed 30 K [3—5]. For this reason, the paper by *Bednorz* and *Müller* [6] created a great sensation. In April 1986, these authors published a new type of superconductors on the basis of nonstoichiometric oxides La_2CuO_{4-x} of the perovskite structure the transition temperature of which varied in the range 12—30 K according to composition. This paper stimulated revival of the ambition to synthesize superconductors with higher critical temperature. As early as in January 1987 the superconductivity was observed in compounds of the $(La_{1-x}M_x)_2CuO_{4-y}$ type where La was partially replaced by M = Ba, Sr, and Ca [7—10]. In February 1987 the team of Professor *Chu* [11, 12] (a little later but not simultaneously other teams as well [13, 14])

synthesized a superconductor of the composition $YBa_2Cu_3O_{7-x}$ with critical temperature of 93 K. In the beginning of 1988, some superconductors on the base of nonstoichiometric oxides of Bi—Sr—Ca—Cu [15—18] with critical temperature up to 115 K and on the base of oxides of Tl—Ba—Ca—Cu [19—21] with critical temperature up to 125 K were synthesized. All these superconductors with critical temperature above 30 K were called high-temperature superconductors.

At present, there are many different theories aimed at explaining the mechanism of high-temperature superconductivity [22—29], *e.g.* theory of electron—phonon coupling, theory of sudden polarization, theory of valence bond resonance, polaron theory, bipolaron theory, *etc.* These theories put forward by physicists are fairly elaborated in mathematical and physical respect, but in most cases they are based on simplified models which disregard the most important structural aspects of high-temperature superconductors. But it is just the structural properties that control the possibility of a synthesis aimed at new types of superconductive materials.

Structural properties of high-temperature superconductors

The high-temperature superconductors exhibit a great number of specific structural aspects which determine their superconductive properties. The decisive structural aspects of high-temperature superconductors may be summarized as follows:

1. The presence of copper ions is necessary for all high-temperature superconductors. Up to now, no reproducibly synthesized high-temperature superconductor without copper ions has been prepared [30].

2. There are hitherto only polemics about the oxidation state of copper ions in high-temperature superconductors. The presence of the Cu(II) ions and small amounts of the Cu(I) ions was unambiguously proved by using the X-ray absorption spectroscopy [31]. The original interpretation of ESCA spectra referring to the presence of the Cu(III) ions in spectroscopically measurable quantity [32] is now considered to be unjustified [33]. According to present view, the Cu(III)—O^{2-} bond is rather polarized in the Cu(II)—O^- direction, which produces considerable problems in interpretation of these spectra.

However, it is remarkable that the best investigated superconductors $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$ exhibit unambiguous dependence of critical temperature on presence of the copper in formal oxidation state Cu(III). It results from Fig. 1 that the critical temperature of these superconductors increases approximately linearly with the ratio of amount of Cu(III) to total amount of Cu. The considerable scattering of data in this figure is a consequence of a great variability of conditions of the synthesis of these superconductors.

3. Another interesting structural aspect is the necessity of layered structure. For illustration we present some simplified schemes of structure of the typical high-temperature superconductors where the particular layers of copper polyhedrons can be distinctly seen.

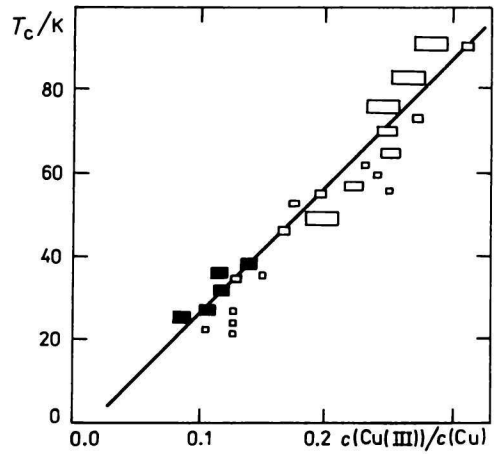


Fig. 1. Variation of critical temperature T_c with Cu(III) concentration in superconductors $La_{2-x}Sr_xCuO_4$ (■) and $YBa_2Cu_3O_{7-\delta}$ (□).

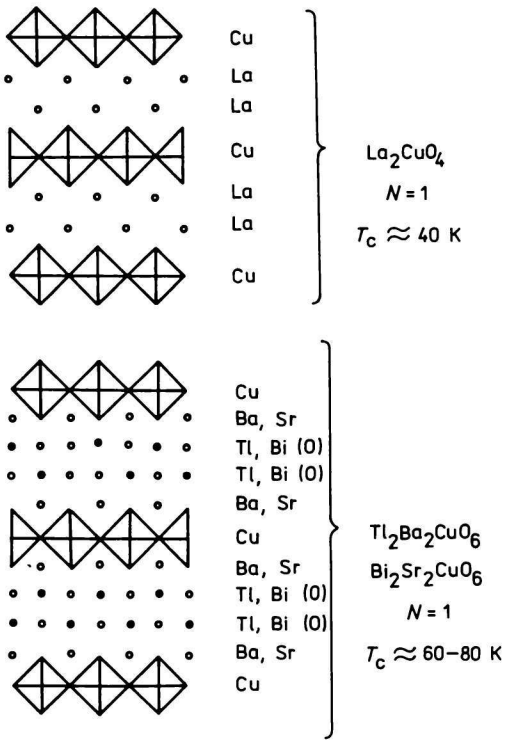


Fig. 2. Scheme of layered structure of one-layer oxygen superconductors La_2CuO_4, $Tl_2Ba_2CuO_6$, and $Bi_2Sr_2CuO_6$.

As to La_2CuO_4, it is a one-layer superconductor in which the individual layers of distorted CuO_6 octahedrons are separated by the layers of La [7, 34, 35]. Other two superconductors of this category $Tl_2Ba_2CuO_6$ and $Bi_2Sr_2CuO_6$ contain the layers of CuO_6 octahedrons separated by two layers of Tl or Bi oxides [36—41] (Fig. 2). The increase in critical temperature of the mentioned two superconductors (in comparison with La_2CuO_4) the structure of which differs from that of La_2CuO_4 only by differences in the layers separating copper polyhedrons is, however, remarkable.

The two-layer structures (Fig. 3) contain two layers of distorted square-pyramidal CuO_5 polyhedrons separated by Tl—O or Bi—O layers [36—41]. It is interesting that the increase in number of the Tl—O or Bi—O layers from one to two brings about a considerable increase in critical temperature.

The three-layer superconductors on the base of oxides of Tl—Ba—Ca—Cu and Bi—Sr—Ca—Cu (Fig. 4) contain a Cu—O layer consisting of distorted

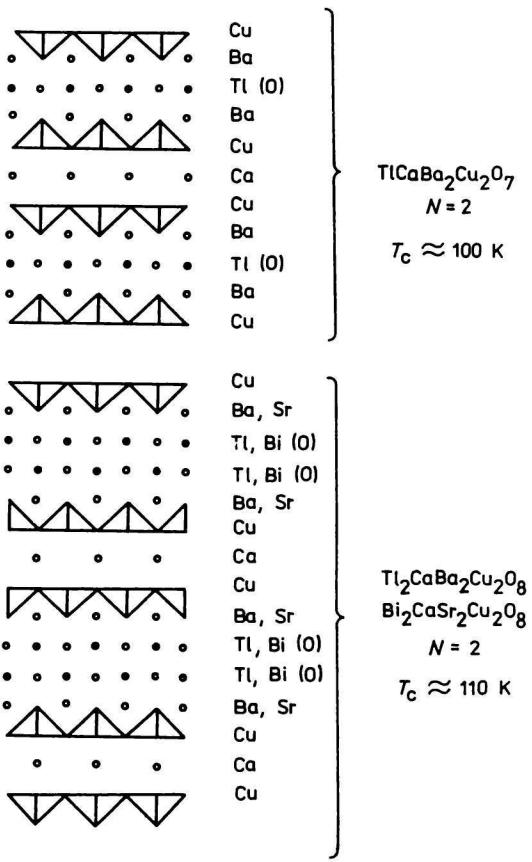


Fig. 3. Scheme of layered structure of two-layer oxygen superconductors $TlCaBa_2Cu_2O_7$, $Tl_2CaBa_2Cu_2O_8$, and $Bi_2CaSr_2Cu_2O_8$.

squares joined to each other between two layers of distorted tetragonal pyramids [36—41]. Like for two-layer types of superconductors, an increase in number of the Tl—O and Bi—O layers separating the layers of copper polyhedrons produces an increase in critical temperature in this case, too.

A special case is represented by the presently classical high-temperature superconductor $YBa_2Cu_3O_{7-\delta}$ (Fig. 5) which is formally a one-layer superconductor because the Cu—O layer joining two layers of distorted tetragonal pyramidal CuO_5 polyhedrons is not conductive [42—45]. As we are going to point out later, this layer of distorted square-planar CuO_4 polyhedrons plays the role of the Tl—O or Bi—O layers in the above-mentioned superconductors, which accounts for the rather high value of its critical temperature.

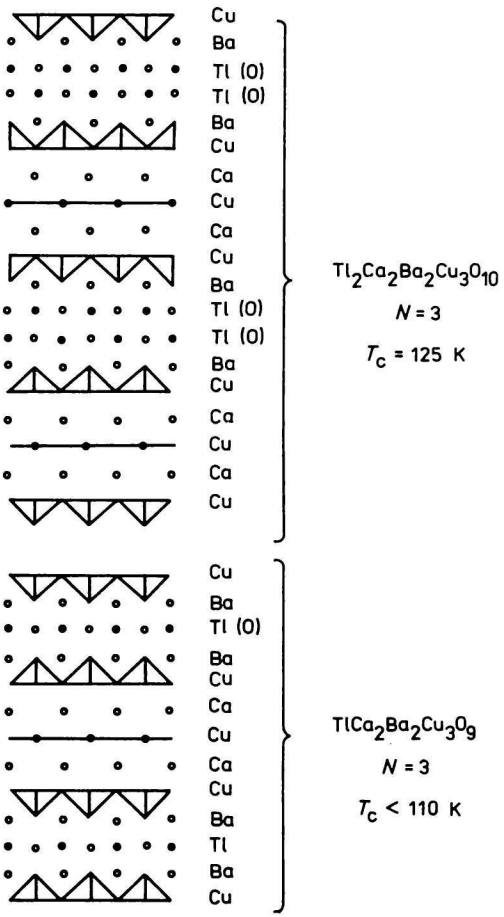


Fig. 4. Scheme of layered structure of three-layer oxygen superconductors $Tl_2Ca_2Ba_2Cu_3O_{10}$ and $TlCa_2Ba_2Cu_3O_9$.

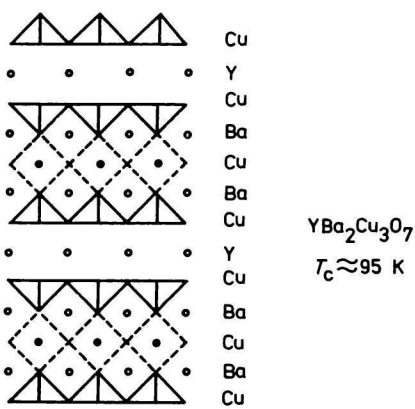


Fig. 5. Scheme of layered structure of superconductor $YBa_2Cu_3O_7$.

4. A dependence of critical temperature on number of the vicinal layers of copper polyhedrons unambiguously results from these structures. For homologous series this dependence exhibits an approximately linear course.

5. Another structural aspect which results from the comparison of the above structures with each other is the dependence of critical temperature on number of the layers of Tl or Bi oxides separating the pertinent sets of the layers of copper polyhedrons.

6. An important feature of the structure of high-temperature superconductors is the presence of oxygen vacancies or other structural defects which, in contrast to classical superconductors, have not to bring about any decrease in superconductive properties.

7. It is interesting that the dependence of the properties of high-temperature superconductors on replacement of all elements except copper by other elements with similar properties is very small. For instance, if Y in the superconductor $YBa_2Cu_3O_{7-\delta}$ was replaced by various rare-earth elements (Gd, Dy, Ho, Er, Tm, Lu, La, Yb, Nb, Sm, Eu, Ce, Tb, Pr), Ba was replaced by Sr or Ca and F or S was, to a certain extent substituted for oxygen, the critical temperature changed only insignificantly [22].

Model of high-temperature superconductivity

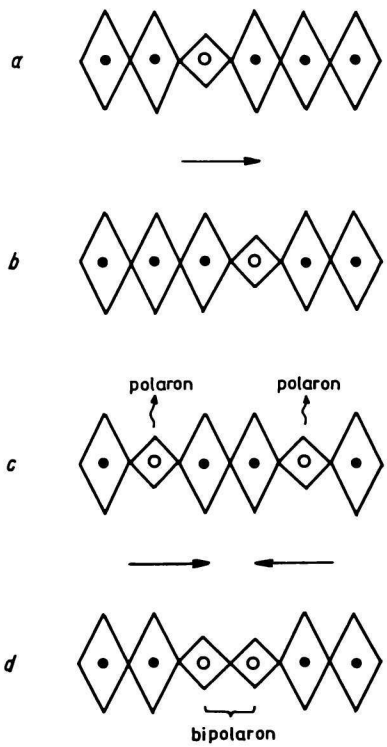
The known theory of superconductivity leads to the relationship for critical temperature which may be written in the simplest form

$$T_c \approx \omega_D \exp\left(-\frac{1}{N(E_F)\, E_{int}}\right)$$

where ω_D is the Debye frequency of crystal lattice, $N(E_F)$ is density of states near the Fermi level, and E_{int} stands for energy of a certain interaction giving rise to creation of the Cooper pairs which form the conductive medium of superconductors.

Let us consider a Cu(II)—O layer in which an excess charge is placed on a Cu(III) ion (Fig. 6). It is known from the physics of solid state that such charge has a great mobility due to the tunnel effect [27]. The overlapping of metal orbitals in different oxidation states through bridge ligands — in our case through the oxygen atoms (Fig. 7) — is sufficient for such mobility. The probability of such tunnelling may be enhanced by the Jahn—Teller effect.

The Jahn—Teller effect [46, 47] manifests itself in degenerate and pseudo-degenerate orbital states where a strong interaction between electronic and vibrational motions comes into existence. This kind of interaction is called vibronic interaction. It accounts for the fact that the less symmetrically distorted



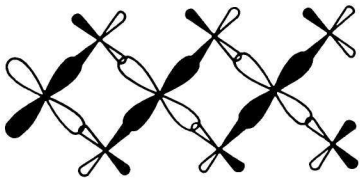


Fig. 7. Scheme of the overlapping of copper orbitals by orbitals of oxygen atoms in the $—CuO_2—CuO_2—CuO_2—$ chain.

Fig. 6. Scheme of creation of polarons in oxygen superconductors in which the admixture of the Cu(III) ions leads to fulfillment of the condition of the presence of ions of a given element in different oxidation states: *a*, *b* represents the relaxation of lattice in the course of motion of "extra" charge; *c*, *d* represents the formation of bipolaron structure in encounter of two polarons. The Cu(II) ions are denoted ●, the Cu(III) ions ○ and the oxygen atoms are in corners of the represented polyhedrons.

system is energetically preferable. This distortion brings about a corrugation of the adiabatic potential surface (Fig. 8). Owing to the existence of flat minima on the adiabatic potential surface very soft vibration modes are associated with the Jahn—Teller effect when compared with vibration modes of the systems where the Jahn—Teller effect does not take place.

In our case, this distortion takes place in the Cu(II) polyhedrons which have double degenerate electronic term. Therefore the vicinity of Cu(II) will be subjected to local anisotropic distortion which may be significantly enhanced by effects of the solid phase [47]. Moreover, the Cu(II)—O distances will be larger when compared with the Cu(III)—O distances. The considerable importance of the Jahn—Teller effect in high-temperature superconductors is also corroborated by the Cu—O distances which are rather different in a given polyhedron (Table 1).

We shall consider the case of the so-called antiadiabatic approximation in which the movement of charge through the lattice is much slower in comparison with the phonon vibration frequencies. It can be proved numerically that the condition of such antiadiabatic approximation is well fulfilled for high-temperature superconductors [27]. Then we can assume that the lattice has time

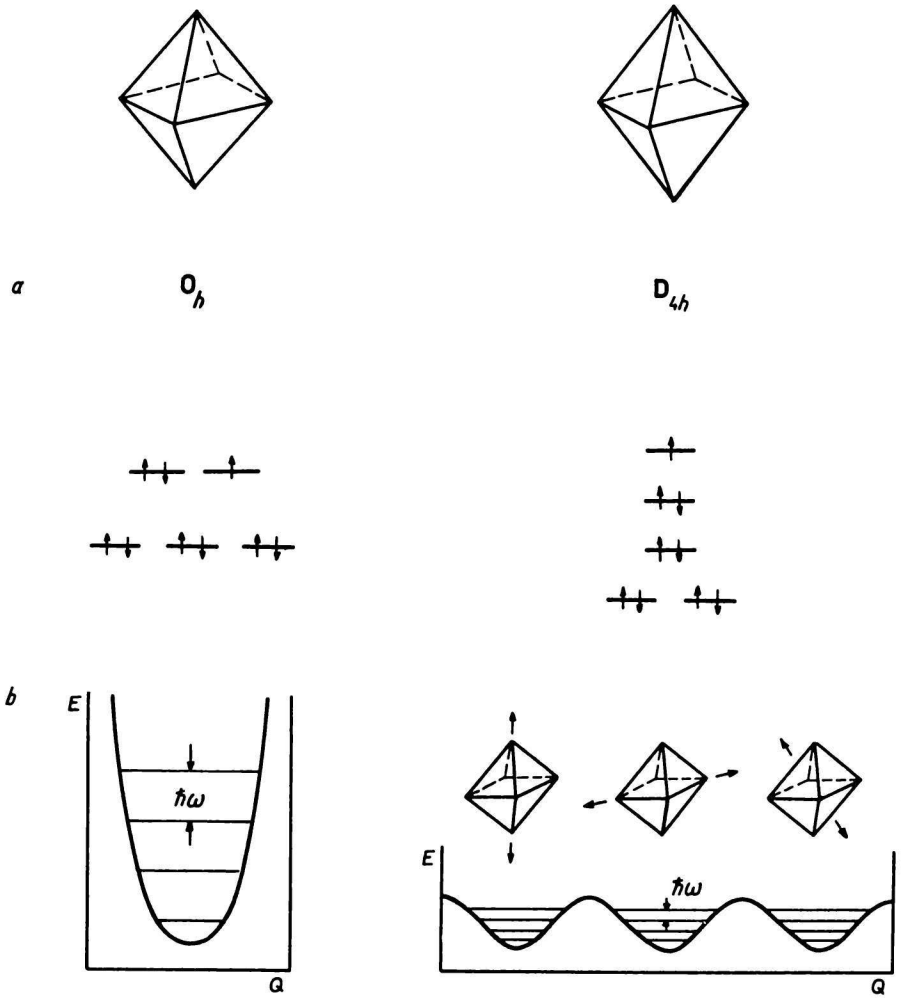


Fig. 8. Scheme of the Jahn—Teller distortion in the octahedral Cu(II) complex. *a*) Degenerate levels and removement of degeneration in the configuration of expanded tetragonal bipyramid; *b*) shape of adiabatic potential with the scheme of distortion of the octahedron in individual minima and the scheme of vibrational levels.

enough to relax in every new configuration during the migration of charge in a given Cu—O layer.

In this medium containing ions in different oxidation states, the combination of charge motion and distorted oxygen subsystem may be regarded as a small polaron. It is known that the encounter of such polarons can involve a strong electron—phonon coupling owing to which the bound pairs of polarons, the

Table 1

The Cu—O distances in CuO_n chromophores of some high-temperature superconductors

System	Chromophore	d_{Cu-O}/ppm		
		d_{eq1}	d_{eq2}	d_{ax}
$La_{2-x}Sr_xCuO_4$	CuO_6	266.2	268.2	241.1
$YBa_2Cu_3O_{7-\delta}$	CuO_5	238.2	194.6	195.1
$Tl_2Ba_2CuO_6$	CuO_6	193.3	193.3	271.4
$Bi_2Sr_2CuO_6$	CuO_6	190.0	190.0	258.0
$Tl_2Ba_2CaCu_2O_8$	CuO_5	192.0	206.0	250.0
$Tl_2Ba_2Ca_2Cu_3O_{10}$	CuO_5	192.7	192.7	248.0
	CuO_4	192.5	192.5	—

so-called bipolarons arise (Fig. 6*c*, *d*). Then these bipolarons play the part of the Cooper pairs in high-temperature superconductors. In oxygen superconductors containing the Cu(II) and Cu(III) ions the change in bond lengths is still more expressive due to the Jahn—Teller distortion, owing to which not only the electron polarization of the oxygen atoms but also the strong ionic polarization which involves especially the nearest oxygen atoms takes place during movement of the excess charge on the Cu(III) ion.

The electron—phonon coupling in classical superconductors is effected by relatively "hard" phonons of the symmetrical vibrations of crystal lattice [1—5]. This coupling in oxygen superconductors is made by extremely "soft" phonons of the Jahn—Teller type. This principal difference between classical and high--temperature superconductors becomes more evident if we realize that the energy of the electron—phonon coupling is inversely proportional to the squared phonon frequency [48].

On the basis of this model, the Cooper pairs are created from the holes on the Cu(III) ions in high-temperature superconductors, which is confirmed by the fact that the superconductors of this type exhibit the hole conductivity as it has been evidenced by studying the Hall effect [49, 50].

This mechanism accounts for the high values of the electron—phonon coupling in high-temperature superconductors, *i.e.* for the high value of E_{int} in the expression for critical temperature. At the same time it points out the necessity of the presence of copper ions in different oxidation states as well as the necessity of layered structure. The experimentally ascertained defects in structure of the oxygen superconductors can enhance the Jahn—Teller distortion and thus in contrast to classical superconductors they have not to produce an impairment of superconductive properties.

For elucidating some fine structural effects the quantum-chemical INDO method was used [51]. As the known oxygen superconductors contain atoms of

heavy elements, owing to which the relativistic effects may play a dominant role, the quasi-relativistic INDO method respecting the dominant relativistic effects [52] was applied. The calculations were performed with cluster models containing from one to four basic cells [53, 54].

The results of calculations cleared up the role of the mentioned Tl—O and Bi—O layers. By comparing the superconductors La_2CuO_4 and $Tl_2Ba_2CuO_6$ which exhibit equal structure of the CuO_6 polyhedrons in superconductive layer (Fig. 2) with each other it appeared that thallium was able to withdraw electrons from the conductive layer, which made precondition for the formation of necessary electron holes in the copper ions of this layer. This ability is due to the possible reduction of the Tl(III) ions to the Tl(I) ions.

An analogous effect can be observed by comparing the two-layer superconductors with each other because the structures of $TlCaBa_2Cu_2O_7$ and $Tl_2CaBa_2Cu_2O_8$ differ only in containing one or two Tl—O layers separating the tetragonal-pyramidal polyhedrons of copper. Their critical temperatures are, however, quite different (Fig. 3).

A similar effect was also found by comparing the compounds $Tl_2Ca_2Ba_2Cu_3O_{10}$ and $TlCa_2Ba_2Cu_3O_9$ with each other (Fig. 4). As to the first compound, both layers of tetragonal-pyramidal CuO_5 polyhedrons have in their vicinity a Tl—O layer of their own while the Tl—O layer is common for two layers of CuO_5 polyhedrons in the second compound.

The results of calculations [53] have shown that the relatively high value of critical temperature of the superconductors $YBa_2Cu_3O_{7-\delta}$ which is formally a one-layer superconductor is a consequence of the ability of the nonconductive layer of square-planar CuO_4 units to withdraw electrons from the conductive layer of tetragonal-pyramidal CuO_5 polyhedrons.

The correctness of these conclusions has also been confirmed by the results obtained by partial replacement of oxygen atoms by fluorine atoms in the compound $YBa_2Cu_3O_{7-\delta}$ because the critical temperature of this superconductor increases or decreases according to the position or the degree of substitution [55, 56].

The calculations concerning the band structure of high-temperature superconductors [57—59] have shown that the bands corresponding to the $3d$ orbitals of copper atoms and to the $2p$ orbitals of oxygen atoms occur near the Fermi level (Fig. 9). That is why the density of these states is one of the critical quantities influencing the temperature of transition in superconductive state (the value of $N(E_F)$ in the expression for critical temperature). That indicates the aptitude of the Cu(II) ions which possess the d^9 electron configuration. Other elements of the first transition series liable to the Jahn—Teller distortion [60] have a lower number of electrons in the d level and thus a lower density of states near the Fermi level. The atoms of higher transition periods with the d^9 con-

figuration are less convenient because of the proportionality of critical temperature to the Debye frequency ω_D, which means that the critical temperature is inversely proportional to the squared root of the effective mass of these elements which significantly increases in higher periods.

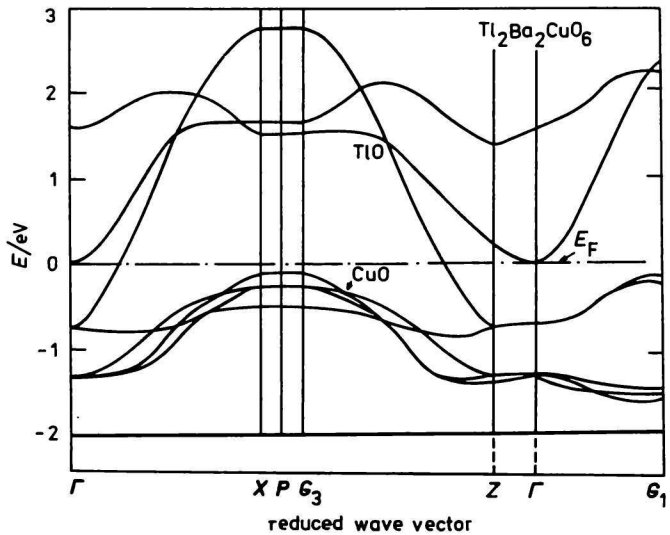


Fig. 9. Energy spectrum of band structure of the system $Tl_2Ba_2CuO_6$ as a function of the reduced wave vector.

The results of calculation of band structure have shown [58, 59] that the density of states near the Fermi level increases with number of the vicinal Cu—O layers. Table 2 illustrates the values calculated for the superconductors on the base of oxides of Tl—Sr—Ca—Cu which enable us to make up a homologous series containing one, two or three parallel Cu—O layers. It follows from this table that the density of states near the Fermi level and consequently the value of critical temperature significantly increases with number of the layers as well.

Table 2

Density of electronic states near the Fermi level in the series of superconductive oxides of the composition $Tl_2Sr_2Ca_{L-1}Cu_LO_{4+2L}$ ($L = 1, 2, 3$)

System	$Tl_2Sr_2CuO_6$	$Tl_2Sr_2CaCu_2O_8$	$Tl_2Sr_2Ca_2Cu_3O_{10}$
Number of layers	1	2	3
Density of states	4.31	6.54	8.12
Critical temperature	60 K	100 K	120 K

As already stated, the bands of the 3*d* orbitals of copper and of the 2*p* orbitals of oxygen are localized near the Fermi level. The bands corresponding to antibonding orbitals of the oxides of heavy elements (Tl—O, Bi—O) occur above the orbitals of copper oxides. Because of symmetry restrictions no interaction of these two kinds of bands can take place. However, if the pertinent oxides contain oxygen vacancies or other structural inhomogeneities, the symmetry of the system decreases and the symmetry restrictions are removed. Then an effective interaction of these bands may occur in such structures. This

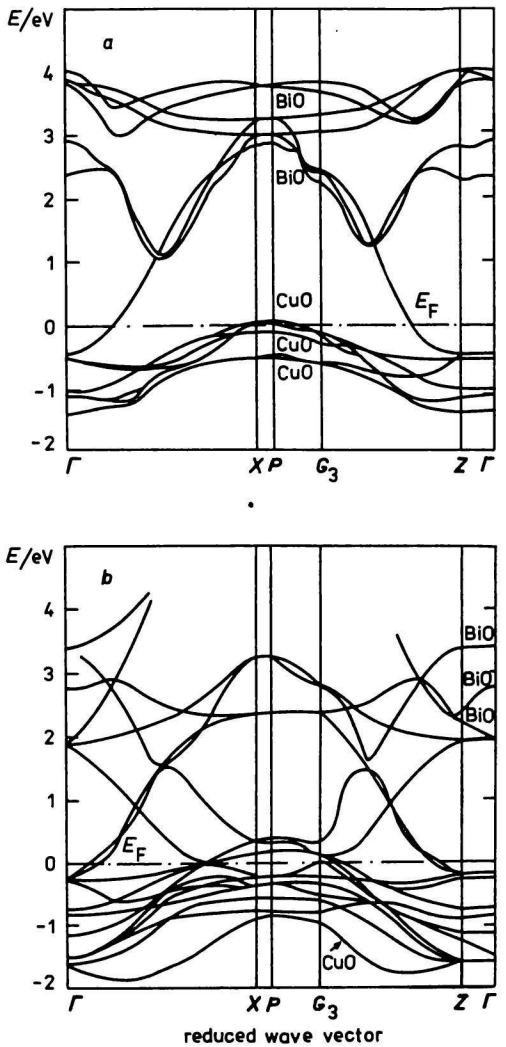


Fig. 10. Energy spectrum of band structure of the system $Bi_2Sr_2CaCu_2O_8$. *a*) Ideal crystal structure; *b*) structure with model introduction of oxygen vacancies.

interaction can produce a decrease in energy of a part of the bands of heavy element oxides to the values of the Fermi level and thus an increase in density of the states in this region. The model calculations of band structure of a superconductor on the base of $Bi_2CaSr_2Cu_2O_8$ [57] have shown that such interaction appears and brings about an increase in density of the states near the Fermi level (Fig. 10).

Conclusion

From the chemical point of view there is an interesting possibility of the synthesis aimed at new types of high-temperature superconductors. Therefore we tried to elaborate a qualitative model of high-temperature superconductivity which should respect all present knowledge concerning the relationships between structure and properties of the hitherto known high-temperature superconductors and could make possible a synthesis aimed at new types of superconductors. The model is based on the presence of transition elements in different oxidation states allowing the creation of the bipolaronic Cooper pairs owing to coupling with soft phonons of the Jahn—Teller type which are optimum for such interaction. In this respect, the dominant role is played by the copper ions which are able to occur in different oxidation states (Cu(II)—Cu(III) or Cu(II)—Cu(I)) and possess the highest number of electrons in the critical *d*-orbitals among all transition elements of the first transition series liable to the Jahn—Teller distortion. A precondition of high-temperature superconductivity is also the layered structure containing the conductive layers of copper polyhedrons. The critical temperature of superconductive oxides significantly increases with number of the parallel vicinal layers of conductive CuO_n polyhedrons. On the other hand, it is opportune if the electron-acceptor layers promoting the formation of electron holes in copper ions occur in vicinity of these conductive layers.

Our recent study of the halogen—Cu(II) complexes has shown that the complexes of this type exhibit a considerable Jahn—Teller effect [61, 62]. Moreover, it is known that the halogen—copper complexes are able to create layered structures, which is another precondition for high critical temperatures. In this connection it is worth mentioning that the first paper dealing with possible superconductivity in the system $[CuBr]_xCuBr_2$ [63] at the record temperature of 346 K has been already published. At present, the quantum-chemical study has started [64] in order to verify the model proposed by us.

Owing to our backward equipment in comparison with advanced world laboratories we are not able at the present development of research to compete with the contemporary advancement in the region of the classical high-

-temperature oxygen ceramics (150—200 publications in a week). Just for this reason, the field of the synthesis aimed at new types of superconductors on the basis of convenient theoretical models could be the most attractive for our institutes.

References

1. Bardeen, J., Cooper, L. N., and Schrieffer, J. R., *Phys. Rev. 106,* 162 (1957).
2. Bardeen, J., Cooper, L. N., and Schrieffer, J. R., *Phys. Rev. 108,* 1175 (1957).
3. Schrieffer, J. R., *Theory of Superconductivity*. Benjamin, New York, 1964.
4. Bardeen, J. and Schrieffer, J. R., *Recent Development in Superconductivity*. North Holland, Amsterdam, 1961.
5. Blatt, J. M., *Theory of Superconductivity*. Academic Press, New York, 1964.
6. Bednorz, J. G. and Müller, K. A., *Z. Phys. B64,* 18 (1986).
7. Ushida, S., Takagi, H., Hitazawa, K., and Tanako, S., *Jpn. J. Appl. Phys. 26,* L1 (1987).
8. Chu, C. W., Hor, P. H., Heug, R. L., Gao, L., Huang, Z. J., and Wang, Y. Q., *Phys. Rev. Lett. 58,* 405 (1987).
9. Cava, R. J., van Daver, R. B., Batlogg, B., and Rietman, E. A., *Phys. Rev. Lett. 58,* 408 (1987).
10. Zhao, Z. X., Chen, L. Q., Cui, C. G., Huang, Y. Z., Lin, J. X., Chen, G. H., Li, S. L., Gao, S. Q., and He, Y. V., *Sci. Rev. China 32,* 522 (1987).
11. Wu, M. K., Ashburn, J. R., Torng, C. J., Hor, P. H., Meng, R. L., Gao, L., Huang, Z. J., Wang, Y. Q., and Chu, C. W., *Phys. Rev. Lett. 58,* 908 (1987).
12. Hor, P. H., Gao, L., Meng, R. L., Huang, Z. J., Wang, Y. Q., Foster, K., Vassilions, J., Chu, C. W., Wu, M. K., Ashburn, J. R., and Tong, C. J., *Phys. Rev. Lett. 58,* 911 (1987).
13. Tarascon, J. M., Greene, L. H., McKinnon, W. R., and Hull, G. W., *Phys. Rev. B35,* 7115 (1987).
14. Zhao, Z. X., Chen, L. Q., Yang, Q. S., Huang, Y. Z., Chen, G. H., Tang, R. M., Liu, G. R., Cui, C. G., Chen, L. Q., Wang, L. Z., Guo, S. S. Q., Li, S. L., and Bi, J. Q., *Kexue Tongbao 32,* 661 (1987).
15. Hazen, R. M., Prewitt, C. T., Angel, R. J., Ross, N. L., Finger, L. W., Hadidiacos, C. G., Gao Veblen, L., Bechtold, J., and Chu, C. W., *Phys. Rev. Lett. 60,* 1174 (1988).
16. Veblen, D. R., Heaney, P. J., Angel, R. J., Finger, L. W., Hazen, R. M., Prewitt, C. T., Ross, N. L., Chu, C. W., Hor, P. H., and Meng, R. L., *Nature 332,* 335 (1988).
17. Shaw, T. M., Shivanshankar, S. A., La Placa, S. J., Cuomo, J. J., McGuire, T. R., Roy, R. A., Kelleher, K. H., and Yee, D. S., *Phys. Rev. B37,* 9856 (1988).
18. Torrance, J. B., Tokura, Y., La Placa, S. J., Huang, T. C., Savoy, R. J., and Nazzal, A. I., *Solid State Commun. 66,* 703 (1988).
19. Sheng, Z. Z. and Hermann, A. M., *Nature 332,* 55, 138 (1988).
20. Sheng, Z. Z., Hermann, A. M., El Ali, A., Almason, C., Estrada, J., Datta, T., and Matson, R. J., *Phys. Rev. B60,* 937 (1988).
21. Hazen, R. M., Finger, L. W., Angel, R. J., Prewitt, C. T., Ross, N. L., Hadidiacos, C. G., Heaney, P. J., Veblen, D. R., Sheng, Z. Z., El Ali, A., Hermann, A. M., *Phys. Rev. Lett. 60,* 1657 (1988).
22. *Novel Superconductivity*. (Wolf, S. A. and Kresin, V. Z., Editors.) Plenum Press, New York, 1987.
23. Matsen, F. A., *J. Chem. Educ. 64,* 842 (1987).
24. Mott, N., *Nature 327,* 185 (1987).

25. Anderson, P. W., *Science 235,* 1796 (1987).
26. Harrison, W. A., private communication.
27. de Jongh, L. J., *Physica* (Utrecht) *C152,* 171 (1988).
28. Svrček, M., *Advances in Chemical Physics,* in press.
29. Schneider, T., de Raedt, H., and Frick, M., *Z. Phys. b76,* 3 (1989).
30. Pelikán, P., *Chem. Listy,* in press.
31. Bianconi, A., Budnick, J., Chamberland, B., Clozza, A., Dartyge, E., Demazeau, G., De Santis, M., Flank, A. M., Fontaine, A., Jegonder, J., Lagarde, P., Lynds, L. L., Michel, C., Otter, F. A., Tolentino, H., Raveau, B., and Revcoleschi, A., *Physica* (Utrecht) *C153,* 113 (1988).
32. Jaeger, H., Hofmann, S., Kaiser, G., Dchulze, K., and Petzow, G., *Physica* (Utrecht) *C153,* 133 (1988).
33. Hoste, S., Vlaeminck, H., Vermeire, K., Persyn, F., and van der Kelen, G. P., private communication.
34. Cava, R. J., Santoro, A., Johnson, D. W., Jr., and Rhodes, W. W., *Phys. Rev. B35,* 6716 (1987).
35. Takagi, H., Uchida, S., Kitazawa, K., and Tanaka, S., *Jpn. J. Appl. Phys. 26,* L123 (1987).
36. Parkin, S. S. P., Lee, V. Y., Savoy, R., and Beyers, R., private communication; Beyers, R., Parkin, S. S. P., Lee, V. Y., Gorman, G., Savoy, R., La Placa, S. J., private communication.
37. Parkin, S. S. P., Lee, V. Y., Engler, E. M., Mazzal, A. I., Huang, T. C., Gorman, G., Savoy, R., and Beyers, R., private communication.
38. Torardi, C. C., Subramanian, M. A., Calabrese, J. C., Gopalakrishnan, J., McCarron, E. M., Morrissez, K. J., Askew, T. R., Flippen, R. B., Chowdry, U., and Sleight, A. W., *Phys. Rev. B38,* 225 (1988).
39. Hewat, E. A., Capponi, J. J., and Marezio, M., *Physica* (Utrecht) *C157,* 502 (1989).
40. Parise, J. B., Gopalakrishnan, J., Subramanian, M. A., and Sleight, A. W., *J. Solid State Chem. 76,* 432 (1988).
41. Liang, J. K., Huang, J. Q., Rao, G. H., Xie, S. S., Zhang, Y. L., Che, G. C., and Cheng, X. R., *J. Phys. D: Appl. Phys. 21,* 1031 (1988).
42. Hazen, R. M., Finger, L. W., Angel, R. J., Prewitt, C. T., Ross, N. L., Mao, H. K., Hadidiacos, C. G., Hor, P. H., Meng, R. L., and Chu, C. W., *Phys. Rev. B35,* 7238 (1987).
43. Jorgensen, J. D., Beno, M. A., Hinks, D. G., Soderholm, L., Volin, K. J., Hitterman, R. L., and Grace, J. D., *Phys. Rev. B36,* 3608 (1987).
44. Siegrist, T., Sunshine, S., Murphy, D. W., Cava, R. J., and Zahurak, S. M., *Phys. Rev. B35,* 7137 (1987).
45. Capponi, J. J., Chaillout, C., Hewat, A. W., Lejay, P., Matezio, M., Nguyen, N., Raveau, B., Soubeyroux, J. L., Tholence, J. L., and Tournier, R., *Europhys. Lett. 3,* 1301 (1987).
46. Jahn, H. A. and Teller, E., *Proc. R. Soc. London, A 161,* 220 (1937).
47. Boča, R., Breza, M., and Pelikán, P., *Structure and Bonding 51,* 57 (1989).
48. Takács, S. and Cesnek, L., *Supravodivosť.* (Superconductivity.) Alfa Publishers, Bratislava, 1979.
49. Fiory, A. T. and Grader, G. S., private communication.
50. Grader, G. S., Gallagher, P. K., and Fiory, A. T., *Phys. Rev. B38,* 84 (1988).
51. Pople, J. A. and Beveridge, D. L., *Approximate Molecular Orbital Theory.* McGraw-Hill, New York, 1970.
52. Boča, R., *Int. J. Quantum Chem. 34,* 385 (1988).
53. Breza, M. and Boča, R., *Solid State Commun.,* in press.
54. Boča, R. and Breza, M., *Czech. J. Phys.,* in press.
55. Hsu, W. Y., Kasowski, R. V., and Herman, F., *Phys. Rev. B37,* 5824 (1988).
56. Temmerman, W. M., Szotek, Z., Durham, P. J., Stocks, G. M., and Sterne, P. A., private communication.

57. Herman, F., Kasowski, R. V., and Hsu, W. Y., private communication.
58. Kasowski, R. V., Hsu, W. Y., and Herman, F., private communication.
59. Herman, F., Kasowski, R. V., and Hsu, W. Y., *Phys. Rev. B36,* 6904 (1987).
60. Pelikán, P. and Boča, R., *Kvantová chémia koordinačných zlúčenín.* (Quantum Chemistry of Coordination Compounds.) VEDA, Publishing House of the Slovak Academy of Sciences, Bratislava, 1988.
61. Pelikán, P., Breza, M., and Boča, R., *Polyhedron 5,* 753, 1607 (1986).
62. Breza, M. and Pelikán, P., *Collect. Czechoslov. Chem. Commun. 53,* 1134 (1988).
63. Tennakone, K., Lokuhetti, C. S., Wickramanayake, S., Kahanda, G. L. D. K. K. S., and Fernando, C. A. N., *J. Phys. C: Solid State Phys. 21,* L643 (1988).
64. Pancíř, J. and Haslingerová, I., private communication.

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