

Reason for the formation of two superconducting phases in yttrium–barium cuprates

A. P. Saiko and V. E. Gusakov

Institute of Solid-State Physics and Semiconductors, Belarus Academy of Sciences, 220072 Minsk, Belarus
(Submitted 31 March 1995)

Zh. Éksp. Teor. Fiz. **108**, 757–764 (August 1995)

It is shown that the existence of two superconducting phases in the compound $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is a consequence of alternating (as δ varies) dominant contributions to the BCS pairing from two branches of the effective vibrational frequencies of the apical O(4) atoms, which form a bistable sublattice. The concentration ranges for the existence of these phases are evaluated using percolation theory. The disparity between the critical superconducting transition temperature during cooling and the critical temperature for destruction of the superconducting state during heating of the compound from absolute zero is noted. © 1995 American Institute of Physics.

1. INTRODUCTION

The critical superconducting transition temperature T_c in the high- T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is a complicated step function of the oxygen content (stoichiometric coefficient $7-\delta$).¹ The plot of $T_c(\delta)$ exhibits two plateaus, i.e., two superconducting phases: $T_c \approx 91$ K for $\delta \approx 0.08-0.15$ and $T_c \approx 60$ K for $\delta \approx 0.35-0.55$. For $\delta > 0.55$ a structural transition to a tetragonal phase takes place, and the superconductivity vanishes. Structural investigations² have shown that when $\delta=0.5$ and the crystal is grown under a slow-cooling regime, a superstructure (orthorhombic phase II) forms. The orthorhombic phase II is characterized by the alternation of Cu–O–Cu and Cu–Cu chains in the basal plane and has a domain character with correlation lengths equal to $18a$, $135b$, and $6c$. The appearance of the 60 K plateau on plots of $T_c(\delta)$ is usually associated specifically with the formation of orthorhombic phase II. However, the plateau at $\delta \approx 0.35-0.55$ is also observed when the sample is cooled rapidly and it is difficult to expect the formation of a superstructure in a large volume.³ There are other approaches which consider the nonmonotonic character of the variation of $T_c(\delta)$ qualitatively (see, for example, Ref. 4); however, not only the reasons for the formation of two superconducting phases and the width of the range for their existence on the δ axis, but also the origin of the abrupt change in the critical temperature ($|\Delta T_c| \approx 30$ K) in the $0.1 < \delta < 0.2$ concentration range must be regarded as unexplained.

2. BASIC ASSUMPTIONS AND FORMULATION OF THE MODEL

In the present work we wish to show that the step-like dependence of $T_c(\delta)$ can be obtained in an explicit form using a previously formulated model.⁵ Before proceeding to an analysis of the problem, we mention some important experimental data,^{1,6} which point out the intimate relationship between the behavior of the apical O(4) oxygen atom and the critical temperature T_c as a function of the oxygen content: the distance between the Cu(2) and O(4) atoms, as well as the frequency of the A_g mode of vibration of the apical oxygen atom, vary with δ in practically the same manner as $T_c(\delta)$. Taking into account the exceptionally important role of the

apical O(4) atoms in the electron-pairing mechanism,^{5,7,8} we will base our further analysis on the following assumptions, which have been confirmed experimentally: a) the potential energy of the apical O(4) atoms in yttrium–barium cuprates has two inequivalent minima along the crystallographic c axis^{9,10} (which suggest bistability of the oxygen sublattice); b) the position of the universal minimum of the potential relative to the CuO_2 plane depends on the stoichiometric coefficient $7-\delta$ (see Fig. 1); c) the BCS pairing mechanism “operates.” We note that these model conceptions made it possible for us^{5,11–14} to explain not only the high values of T_c , but also the experimentally observed hysteretic behavior of the specific heat, thermal conductivity, and rate of propagation of ultrasonic waves in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ in the 60–270 K temperature range.

3. DYNAMICS OF A BISTABLE SUBLATTICE AND EVALUATION OF T_c

To describe the dynamics of the sublattice of apical oxygen atoms along the c axis, we use the scalar one-component ϕ^4 model¹⁵ (see also Ref. 16):

$$H = \sum_i \left(\frac{p_i^2}{2m} + V(q_i) \right) + \frac{1}{4} \sum_{i,j} f_{ij} (q_i - q_j)^2, \quad (1)$$

where $q_i(p_i)$ and m are the generalized coordinate (the canonically conjugate momentum) and the mass of the i th atom in the two-minimum asymmetric potential $V(q_i) = (\alpha/2) q_i^2 - (\beta/3) q_i^3 + (\gamma/4) q_i^4$ created by the matrix atoms at the sites of the O(4) atoms, f_{ij} are harmonic coupling constants, and $\alpha, \beta, \gamma > 0$. In the case of weak long-range forces, i.e., $f_{ij} \approx f/N$ (N is the number of unit cells), it is natural to use the molecular-field approximation. Then the problem becomes a one-particle problem, and to describe the behavior of the bistable sublattice it is sufficient to consider the 0-dimensional version of the ϕ^4 model:

$$H = \frac{p^2}{2m} + V(q),$$
$$V(q) = \frac{\alpha + f}{2} q^2 + \frac{\beta}{3} q^3 + \frac{\gamma}{4} q^4 - f \langle q \rangle q, \quad (2)$$

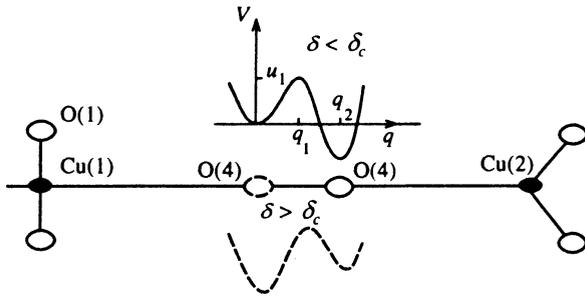


FIG. 1. Fragment of the compound $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, including a superconducting CuO_2 plane, an apical O(4) oxygen atom in a bistable potential (for $\delta=0$ and $\delta > \delta_c$), and a Cu(1)–O(1) chain.

where $\langle \dots \rangle$ denotes the operation of quantum-statistical averaging. Performing the substitution $q = \langle q \rangle + \delta q$ [δq is a small correction to some averaged position $\langle q \rangle$ of the O(4) atom], we rewrite (2) in the form

$$H = E(\langle q \rangle) + H_0 + H_1, \quad (3)$$

$$H_0 = \frac{p^2}{2m} + \frac{1}{2} \Omega^2 (\delta q)^2,$$

$$H_1 = (\alpha \langle q \rangle - \beta \langle q \rangle^2 + \gamma \langle q \rangle^3) \delta q - \frac{3}{2} \gamma \sigma (\delta q)^2 - \frac{1}{3} (\beta - 3\gamma \langle q \rangle) (\delta q)^3 + \frac{\gamma}{4} (\delta q)^4,$$

where E is a c -number function, $\sigma = \langle (q - \langle q \rangle)^2 \rangle$, and

$$\Omega^2 \equiv [\alpha + f - 2\beta \langle q \rangle + 3\gamma(\sigma + \langle q \rangle^2)]/m \quad (4)$$

is the effective frequency characterizing the sublattice. We find the standard deviation σ in the zeroth approximation with respect to H_1 using the fluctuation–dissipation theorem:

$$\sigma = \frac{1}{2m\Omega} \coth \frac{\Omega}{2k_B T}, \quad (5)$$

where we set $\hbar=1$. To establish the relationship between σ and $\langle q \rangle$ we use the explicit form of the condition for stability of the sublattice, i.e., $\langle \partial H / \partial (\delta q) \rangle = 0$:

$$\alpha \langle q \rangle - \beta \langle q \rangle^2 + \gamma \langle q \rangle^3 + (\Omega^2 - 3\gamma\sigma) \langle \delta q \rangle - (\beta - 3\gamma \langle q \rangle) \times \langle (\delta q)^2 \rangle + \gamma \langle (\delta q)^3 \rangle = 0. \quad (6)$$

Since the averaging in (6) is performed over the states of the Hamiltonian H_0 , the correlation averages are $\langle \delta q \rangle = \langle (\delta q)^3 \rangle = 0$ and $\langle (\delta q)^2 \rangle = \sigma$, and as a result we have the following matching equation:

$$(\beta - 3\gamma \langle q \rangle) \sigma = \alpha \langle q \rangle - \beta \langle q \rangle^2 + \gamma \langle q \rangle^3. \quad (7)$$

The self-consistent approach to the calculation of averages makes it possible to obtain a qualitatively correct picture of the dynamics of the sublattice of apical oxygen atoms in an asymmetric two-minimum potential characterized by abrupt variation of their mean position $\langle q \rangle$ and effective frequency Ω as a function of the temperature and by the presence of a certain region of bistability, i.e., hysteresis, even in the lowest approximation. Figure 2 presents plots for $\langle q \rangle$ and Ω , which were constructed on the basis of Eqs. (4), (5), and (7).

The dependence of the critical temperature on the effective frequency Ω and the effective interaction constant of the sublattice with the electronic system $\lambda = \eta/m\Omega^2$ (η is the Hopfield parameter) is described by the Kresin equation:¹⁷

$$k_B T_c = \frac{0.25\Omega}{\sqrt{e^{2/\lambda} - 1}}. \quad (8)$$

Since $\Omega = \Omega(\langle q \rangle, \sigma)$ and $\lambda = \lambda(\langle q \rangle, \sigma)$, we can use (4), (5), (7), and (8) to construct a plot of $T_c(T)$ (Fig. 3). The real values of the critical temperature in Fig. 3 are determined as the points of intersection of the plot of $T_c(T)$ and the straight line of T . For bistable potentials with parameters corresponding to cases of nonstoichiometry with $\delta < \delta_c$ (see the caption to Fig. 3 and the ensuing text in the article), the plots of $T_c(T)$ have two points of intersection, viz., T_c^0 and T_c^1 , while only one critical temperature, T_c^1 , is realized for $\delta > \delta_c$. This means that as the oxygen nonstoichiometry varies in the upward direction, the system should exhibit a sharp drop in the critical superconducting transition temperature, which is equal in the particular case shown in Fig. 3 to $\Delta T_c = T_c^0 - T_c^1 \sim 30$ K.

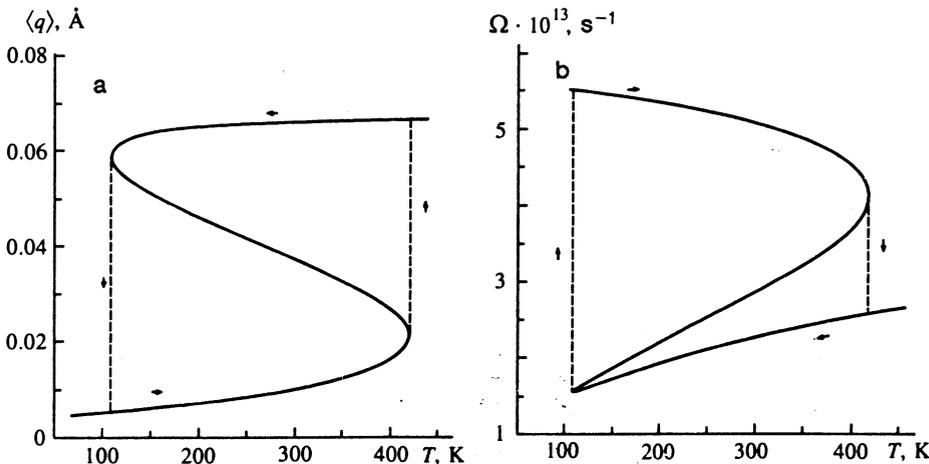


FIG. 2. Bistable behavior of the statistical-mean displacement $\langle q \rangle$ (a) and of the vibrational frequency Ω of the O(4) atom (b) as a function of the temperature.

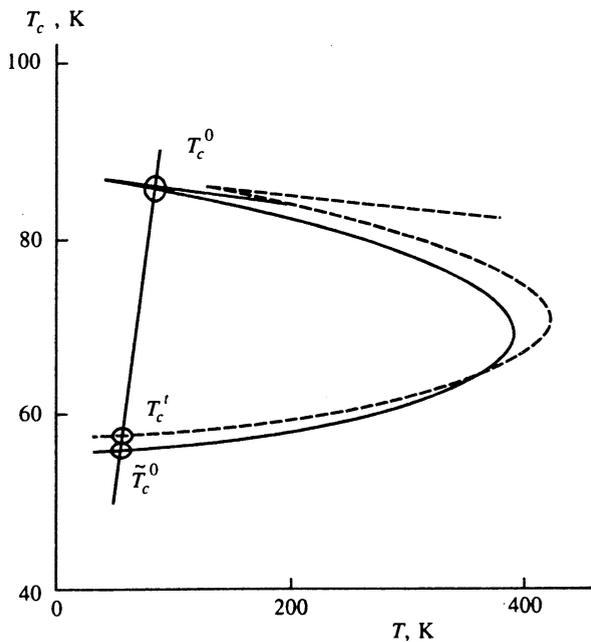


FIG. 3. Plots of $T_c(T)$ for two types of bistable potentials of the O(4) oxygen sublattice in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$: solid curve - $q_1^0=0.0649 \text{ \AA}$, $q_2^0=0.13 \text{ \AA}$, $u_1^0=0.051 \text{ eV}$ ($\delta=0$); dashed curve - $q_1^0=0.692 \text{ \AA}$, $q_2^0=0.136 \text{ \AA}$, $u_1^0=0.055 \text{ eV}$ ($\delta > \delta_c$).

On the other hand, the existence of the two critical temperatures T_c^0 and \tilde{T}_c^0 for samples with a nonstoichiometry index $\delta < \delta_c$ means that there is a possibility, in principle, to obtain a nontrivial effect, in which the superconducting transition temperature depends on the direction in which the sample temperature varies: as it is cooled, the main contribution to the BCS pairing is made by the low-frequency branch of Ω [with the resultant formation of the upper branch of $T_c(T)$], and superconductivity appears at $T=T_c^0$; as it is heated from absolute zero, the main contribution is made by the high-frequency branch Ω [which corresponds to the lower branch of $T_c(T)$], and the superconducting state in the system will vanish at a different, lower temperature \tilde{T}_c^0 . Thus, the existing hysteresis of the critical temperature ($\Delta T_c^0 = T_c^0 - \tilde{T}_c^0$) is caused by the hysteretic behavior of the sublattice of apical oxygen atoms, which makes the dominant contribution to the BCS pairing. It is seen from Fig. 3 that $\Delta T_c^0 \approx \Delta T_c \approx 30 \text{ K}$; however, this value of ΔT_c^0 is a severe overestimate, since it is impossible in practice to coherently transport all the nonlinear oscillators [O(4) atoms] from one minimum of the bistable potential to the other (and back) during the cooling and subsequent heating of a sample, so as to obtain the maximum effect contained in the foregoing theoretical calculations.

4. DETERMINATION OF $T_c(\delta)$ USING THE CONCEPTS OF PERCOLATION THEORY

Let us consider the preconditions for the critical temperature to depend on the oxygen content. The removal of oxygen atoms from the O(1) sites (an increase in δ) alters the coordination number of the Cu(1) copper atom ($N_{\text{Cu}(1)}=4$

for $\delta=0$) and, as a consequence, changes the character of the bonding of the Cu(1) and O(4) atoms¹⁸ and, accordingly, the profile of the double-minimum potential, in which the apical O(4) atoms move. A significant change in the potential profile throughout the entire crystal occurs when the relative concentration x of Cu(1) atoms with a coordination number $N_{\text{Cu}(1)} < 4$ becomes equal to or greater than a certain threshold concentration x_c , which is specified [when there is a random distribution of vacancies along the Cu(1)–O(1) chains] by percolation theory.¹⁹ The value of the percolation threshold x_c depends on the geometry of the problem and is defined as the lower limit of the relative concentration x of Cu(1) atoms with a coordination number $N_{\text{Cu}(1)} < 4$ for which the probability $P^{(b)}(x)$ of the formation of a continuous sublattice of O(4) atoms (bonded to these copper atoms) in the crystal differs from zero. Since the Cu(1) atom in yttrium–barium cuprates is located on a bond joining neighboring O(4) atoms, the geometry corresponds to the problem of bonds in a cubic lattice of O(4), and therefore, according to Ref. 19, $x_c=0.25$. Near the percolation threshold we have $P^{(b)}(x) \sim (x-x_c)^\beta$, where $\beta \approx 0.4$ is the critical index. Thus, in the case of $\delta=0$, the critical superconducting transition temperature is determined by the bistable lattice of apical O(4) atoms with the parameters of the potential (q_1^0, q_2^0, u_1^0), and the sublattice of apical atoms moving in the transformed potential (q_1^t, q_2^t, u_1^t) begins to dominate for $\delta > 0$ and $x \geq x_c$ (see Fig. 1). Therefore, the critical superconducting transition temperature can be calculated as the expected value of the critical temperature realized in a crystal with a sublattice of O(4) atoms having the potential (q_1^0, q_2^0, u_1^0) or an O(4) sublattice with the potential (q_1^t, q_2^t, u_1^t):

$$T_c \approx \{T_c^0[1 - P^{(b)}(x)] + T_c^t P^{(b)}(x)\} P^{(b)}(x_c), \quad (9)$$

where T_c^t denotes the critical superconducting transition temperature in a crystal with a bistable O(4) sublattice having the potential (q_1^t, q_2^t, u_1^t), and $P^{(b)}(x_c)$ is the probability that the crystal contains a continuous sublattice of O(4) atoms bonded to a Cu(1) atom with a coordination number $N_{\text{Cu}(1)}=4$. When the vacancies of oxygen atoms are randomly distributed along the Cu(1)–O(1) chains, the relative concentrations of copper atoms with the coordination numbers $N_{\text{Cu}(1)}=4$, $N_{\text{Cu}(1)}=3$, and $N_{\text{Cu}(1)}=2$ can easily be calculated and are equal to $x_4=(1-\delta)^2$, $x_3=2\delta(1-\delta)$, and $x_2=\delta^2$, respectively, and $x=x_2+x_3$, whence it follows, in particular, that $\delta_c=1-\sqrt{1-x_c} \approx 0.13$.

To analyze $T_c(\delta)$ on the basis of Eqs. (1)–(9), we determined the parameters of the bistable potential and the character of their variation with δ on the basis of the following experimental data. An analysis of the radial distribution function showed⁹ that the distance q_2^0 between the minima lies in the range 0.1–0.13 \AA and that they are separated by a barrier at the point $q_1^0 \approx q_2^0/2$ (see Fig. 1). The height of the barrier u_1^0 was chosen so as to describe the A_g mode of the apical oxygen atom observed in the Raman spectra with a frequency $\nu \approx 500 \text{ cm}^{-1}$. Since the Cu(1)–O(4) distance decreases as δ and/or the temperature increases,^{1,3} it is clear that the universal minimum of the double-minimum potential at $\delta=0$ must be located nearer to the CuO_2 plane. The

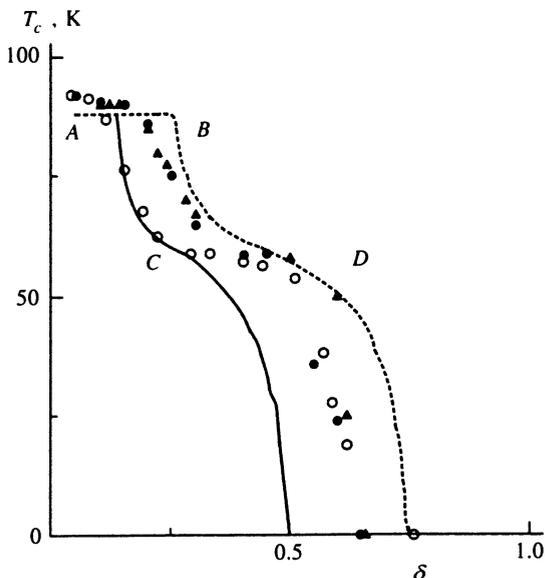


FIG. 4. Dependence of the critical superconducting transition temperature on the oxygen content in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Solid and dashed curves—calculation for disordered and completely ordered distributions of the oxygen vacancies in the basal plane, respectively; \blacktriangle , \bullet , \circ —experimental results.^{1,3,20}

changes in the parameters of the potential as δ increases from 0 to 0.6 were chosen so as to correctly reflect the experimentally observed decrease in the frequency of the A_g mode [$\Delta\nu \approx 15 \text{ cm}^{-1}$ (Ref. 8)] and shortening of the $\text{Cu}(1)\text{--O}(4)$ distance [$\Delta d \approx 0.06 \text{ \AA}$ (Ref. 1)]. The values of the parameters obtained are listed in the caption to Fig. 3, which presents the corresponding plots of $T_c(T)$.

Figure 4 presents plots of the critical temperature $T_c(\delta)$, which were calculated on the basis of the expressions (1)–(9), and experimental data for ceramic^{1,3} and crystalline²⁰ samples. We considered two limiting cases. The solid curve corresponds to a random distribution of the vacancies along the $\text{Cu}(1)\text{--O}(1)$ chains; it was assumed in the calculation (the dashed curve) that the oxygen vacancies are redistributed so that the structure with $N_{\text{Cu}(1)}=3$ does not occur ($x_3=0$), and only the structures with $N_{\text{Cu}(1)}=4$ and $N_{\text{Cu}(1)}=2$, which are characteristic of the orthorhombic and tetragonal phases, respectively, are possible.

Thus, the results presented in Fig. 4 can be interpreted in the following manner. For values of δ in the range $0 \leq \delta \leq 0.13$ the apical atoms are found with a high probability at the universal potential minimum, which is located closer to the conducting CuO_2 planes [i.e., the lower branch of the bistable frequency Ω (Ref. 5) and, accordingly, the upper branch of the function $T_c(T)$ are realized], and the set of points at which the $T_c(T)$ curves intersect with the T straight line in this range of δ form the AB plateau on the plot of $T_c(\delta)$, i.e., the 90 K superconducting phase.

In the range of concentrations $0.2 < \delta < 0.5$ the superconducting properties of the crystal are determined by the bistable sublattice of apical $\text{O}(4)$ atoms, for which the universal potential minimum is located closer to the $\text{Cu}(1)$ atom

(see Fig. 1). In this case the functions $T_c(T)$ become single-valued (see Fig. 3). It follows from a comparison of the behavior of the experimental plots of $T_c(\delta)$ with the theoretically calculated plots that the experimentally observed plateau CD (the 60 K phase) is caused by redistribution of the oxygen vacancies in the basal plane and is associated with the thermodynamic instability of the structure with the coordination number $N_{\text{Cu}(1)}=3$. In fact, in the range of concentrations $0.2 < \delta < 0.5$ the experimental points migrate from the theoretical (solid) curve to the dashed curve, which was calculated for the absence of the structure with $N_{\text{Cu}(1)}=3$. As the cooling rate during growth of the sample is increased, the dependence of $T_c(\delta)$ should shift toward the solid curve, which describes a random distribution of the vacancies, in agreement with the experimental results^{1,3} (the cooling rate in Ref. 3 was higher than that in Ref. 1). We note that the experimental points for the crystalline samples are closer to the solid curve. This is because redistribution of the oxygen vacancies in crystalline samples with a low concentration of such vacancies is unlikely (they have a long diffusion path).

The further increase in the concentration of oxygen vacancies at $\delta > 0.5$ causes practically all the $\text{Cu}(1)$ atoms in the crystal to have a coordination number $N_{\text{Cu}(1)} < 4$. Under these circumstances $P^{(b)}(x_4) \rightarrow 0$, and the crystal passes into the tetragonal phase, which does not exhibit superconductivity.

5. CONCLUSIONS

Thus, the formation of two superconducting phases [the AB and CD plateaus on the plot of $T_c(\delta)$] is associated with the realization of two possible states of the bistable oxygen sublattice consisting of $\text{O}(4)$ atoms: the AB plateau forms when the vibrations of the sublattice atoms occur with a higher probability in the universal minimum, which is closer to the CuO_2 plane, and the CD plateau forms when the oxygen vacancies in the basal plane are redistributed as a result of the thermodynamic instability of the structure with the coordination number $N_{\text{Cu}(1)}=3$, and the sublattice with the universal minimum located further away from the CuO_2 begins to dominate. The cut-off values of the ranges of oxygen contents for which the 90 K and 60 K superconducting phases are observed are determined by the percolation threshold for the problem of the bonds in a cubic lattice.

This research was supported by the Fund for Fundamental Research of the Republic of Belarus.

¹R. J. Cava, A. W. Hewat, E. A. Hewat *et al.*, *Physica C* **165**, 419 (1990).

²J. Grybos, D. Hohlwein, T. Zeiske *et al.*, *Physica C* **220**, 138 (1994).

³J. D. Jorgensen, B. W. Veal, A. P. Paulikas *et al.*, *Phys. Rev. B* **41**, 1863 (1990).

⁴H. A. Blackstead and J. D. Dow, *Pis'ma Zh. Éksp. Teor. Fiz.* **59**, 262 (1994) [*JETP Lett.* **59**, 283 (1994)].

⁵A. P. Saiko, V. E. Gusakov, and V. S. Kuz'min, *Pis'ma Zh. Éksp. Teor. Fiz.* **56**, 425 (1992) [*JETP Lett.* **56**, 411 (1992)].

⁶A. F. Goncharov, V. N. Denisov, I. P. Zibrov *et al.*, *Pis'ma Zh. Éksp. Teor. Fiz.* **48**, 453 (1988) [*JETP Lett.* **48**, 497 (1988)].

⁷S. D. Conradson and I. D. Raistrick, *Science* **243**, 1340 (1989).

⁸G. Ruani, C. Taliani, M. Muccini *et al.*, *Physica C* **226**, 101 (1994).

⁹J. Mustre de Leon, S. D. Conradson, I. Batistić, and A. R. Bishop, *Phys. Rev. Lett.* **65**, 1675 (1990).

- ¹⁰M. Zoli, *Physica C* **229**, 99 (1994).
- ¹¹A. P. Saïko, V. E. Gusakov, and V. S. Kuz'min, *Pis'ma Zh. Éksp. Teor. Fiz.* **57**, 108 (1993) [*JETP Lett.* **57**, 116 (1993)].
- ¹²A. P. Saïko, V. E. Gusakov, and V. S. Kuz'min, *Fiz. Nizk. Temp.* **19**, 1367 (1993) [*Low Temp. Phys.* **19**, 970 (1993)].
- ¹³A. P. Saïko, and V. E. Gusakov, and V. S. Kuz'min, *Fiz. Nizk. Temp.* **20**, 968 (1994) [*Low Temp. Phys.* **20**, 764 (1994)].
- ¹⁴A. P. Saïko, V. E. Gusakov, and V. S. Kuz'min, *Fiz. Nizk. Temp.* **20**, 1191 (1994) [*Low Temp. Phys.* **20**, 937 (1994)].
- ¹⁵A. D. Bruce and R. A. Cowley, *Structural Phase Transitions*, Taylor and Francis, London, 1981 (Russ. transl. Mir, Moscow, 1984).
- ¹⁶A. P. Saïko, V. E. Gusakov, and V. S. Kuz'min, *Dokl. Akad. Nauk Belarus.* **37**, 38 (1993).
- ¹⁷V. Z. Kresin, *Phys. Lett. A* **122**, 434 (1987).
- ¹⁸V. E. Gusakov, in *Abstracts of 4th International Conference on Materials and Mechanisms of Superconductivity HTSC*, Grenoble, 1994, p. 140.
- ¹⁹B. I. Shklovskii and A. L. Efros, *Electronic Properties of Doped Semiconductors*, Springer-Verlag, Berlin, 1984.
- ²⁰I. V. Aleksandrov, A. B. Bykov, I. P. Zibrov *et al.*, *Pis'ma Zh. Éksp. Teor. Fiz.* **48**, 449 (1988) [*JETP Lett.* **48**, 493 (1988)].

Translated by P. Shelnitz