Superconducting phases with a perovskite-like structure

N. E. Alekseevskiĭ, G. M. Kuz'micheva, E. P. Khlybov, A. V. Mitin, and V. I. Nizhankovskiĭ
Institute of Physical Problems, Academy of Sciences of the USSR

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Experimental results have shown that multicomponent metal-oxide systems with bismuth have several superconducting phases. The origin of the superconducting phases with a perovskite-like structure is traced and the possibility of classifying them systematically is discussed.

Since the discovery of superconductivity in the system La–Ba–Cu–O by Bednorz and Müller[1] the search for new superconductors among metal-oxide systems has increased dramatically. The systems with yttrium and with all rare earths (except promethium), for example, have yielded superconductors of the composition

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$RBa_2Cu_3O_{7-x}$ (the 1–2–3 phase) with a critical temperature T_c of 95–100 K.[2,3] In addition, evidence of possible superconductivity at much higher temperatures has been reported by some researchers. The properties of such "superconductors" are generally unstable and are not reproducible.

On the basis of the data obtained from the study of the phase composition, the temperature dependence of the magnetic susceptibility $\tilde{\chi}(T)$, and the electrical resistivity $\rho(T)$ of multicomponent metal-oxide systems, we will trace the origin of superconducting phases with a perovskite-like structure and we will consider the possibility of classifying them systematically.

Study of samples of the system R–Ba–Cu–O (R is a rare-earth element or yttrium) has shown that the crystal structure of the phases that are formed is determined not only by the initial composition but also by the conditions under which it is found. In a Ce–Ba–Cu–O system, for example, the phase that forms most easily is the one with the structure of the cubic perovskite with the unit cell parameter $a = 4.37$ Å (this structure is shown schematically in Fig. 1a). Annealing of such a sample in a

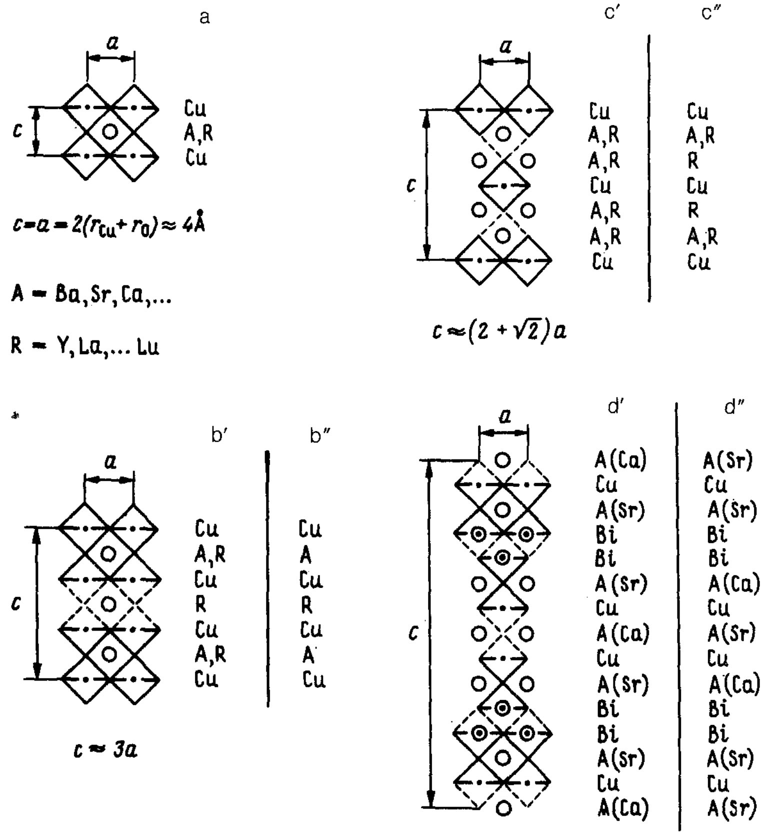

FIG. 1. Origin of the superconducting phases with a perovskite-like structure.

reducing atmosphere gives rise to the formation of a tetragonal phase with the lattice constants $a = 3.878$ and $c = 11.63$ Å. This phase apparently belongs to the structural type[4] $La_3Ba_3Cu_6O_{14-x}$ (Fig. 1b′). A prolonged heat treatment of the sample leads to additional ordering of Ce and Ba and to the appearance in the sample of an orthorhombic superconducting 1–2–3 phase (Fig. 1b″) with the lattice constants $a = 3.89$, $b = 3.92$, and $c = 11.73$ Å and with $T_c = 86$ K (Ref. 3).

The samples of the composition $(R, Ba)_2CuO_{4-x}$ crystallize in the structural type of K_2NiF_4 with the lattice constants $a = 3.7$–3.8 Å and $c = 13.3$–13.6 Å. Two phases may appear, depending on the type of ordering of the R and Ba ions with respect to the crystallographic positions: a phase with a body centered cell (Fig. 1c′) or a phase with a primitive cell. The type of ordering depends on the composition and on the conditions under which the sample is synthesized and may change as a result of the action of an external force on the sample (lowering the sample's temperature, for example), which causes a structural phase transition.

The $\tilde{\chi}(T)$ curves of the two-phase samples with 1–2–3 structures and K_2NiF_4 have two break points caused by the transitions of these phases to the superconducting state at $T_c \approx 90$ K and $T_c \approx 40$ K, respectively.[3] The phases which we are considering here are based, as one can easily see, on the cubic perovskite motif.

The Bi–Ca–Sr–Cu–O system, on the basis of which superconductors with $T_c = 110$–120 K can be synthesized, as has been reported, has recently been studied extensively.[5] The systems Bi–Ca–Sr–Cu–O, Bi–Ba–Sr–Cu–O, Bi–Sb–Ca–Sr–Cu–O, Tm–Be–Cu–O, Bi–Pb–Ca–Sr–Cu–O, R–Bi–Ca–Sr–Cu–O, and R–Al–Bi–Ca–Sr–Cu–O, which we have studied, have shown that they can form phases with a cubic perovskite structure (in a Bi–Ba–Sr–Cu–O system with $a = 4.28$ Å, for example) and phases which may be viewed as derivatives of the cubic perovskite. In the Bi–Ca–Sr–Cu–O system the most strongly single-phase samples with a maximum concentration of the superconducting fraction ($T_c = 90$–100 K) are synthesized from the initial composition $Bi_2(Ca, Sr)_6Cu_4O_{13+x}$. The x-ray data imply that such samples are characterized by either a body-centered cell or a primitive cell whose lattice constants a and c are close to those which are given for the 4–6–4 phase of the composition $Bi_4(Ca, Sr)_6Cu_4O_{16+x}$ ($a = 3.816$ Å and $c = 30.5$ Å). The onset of the superconducting transition at 110–120 K is attributed to this phase.[5] Two probable types of ordering of the Ca and Sr in these phases are illustrated in Fig. 1,d′ and d″. Additionally, we have identified the phases with the following characteristic sets of lattice constants:

1) $a = 3.831$; $b = 3.878$; $c = 11.63$ Å .
2) $a \approx b = 4.18 \div 4.28$; $c = 13.60 - 13.70$ Å.
3) $a \approx b = 3.80 - 4.11$; $c = 24.10 - 24.66$ Å.

In the first case the diffraction photograph of the sample of the system Bi–Ca–Sr–Cu–O is the same as that of the 1–2–3 phase of the system R–Ba–Cu–O (Fig. 1b″), and the $\tilde{\chi}(T)$ curve has only one slope change corresponding to $T_c \approx 90$ K (curve b in Fig. 2). The $\tilde{\chi}(T)$ curves of some of the samples have two slope changes near 50 K and 90 K (curve a in Fig. 2). The temperature dependence of the electrical

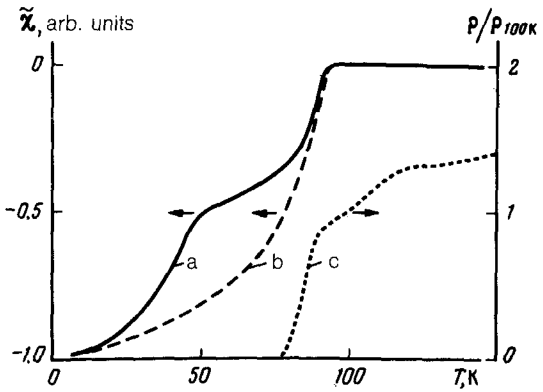

FIG. 2. Temperature dependence of the magnetic susceptibility $\tilde{\chi}$, measured in an alternating field (curves a and b), and of the electrical resistivity ρ (dashed curve) for three samples of the system Bi–Ca–Sr–Cu–O.

resistivity also has two slope changes (curve c in Fig. 2). It can be assumed that in addition to the 4–6–4 phase with $T_c = 110$–120 K, which was described in Ref. 5, the systems with bismuth have at least two superconducting phases with $T_c = 30$–50 K and $T_c = 60$–100 K. These phases, which are structural derivatives of the cubic perovskite, can undergo a transition, as in the case of the 1–2–3 phases, from the tetragonal to the orthorhombic phase. The critical temperature T_c of these phases depends on the degree of the *b–a* orthorhombic distortion.[3]

The identification and classification of perovskite-like phases, with allowance for the particular features of their structure, are some of the ways in which an understanding of the superconductivity mechanism of these systems can be gained. Analysis of the origin of the structures shows that a kind of "polymerization" of the original cubic perovskite, similar to that reported for superconducting molybdenum chalcogenides by Potel *et al.*,[7] can be produced by making more complex the unit cell of the superconducting phases. Such a polymerization, moreover, is accompanied in several cases by the emergence of additional order in the arrangement of A and R ions. In such structures the intensity of the low-frequency modes may increase with increasing parameter *c*, which should, in principle, cause T_c to increase. The stability of the lattice is, however, expected to decrease in this case. Superconductivity with $T_c > 150$ K could conceivably be related to unstable phases of this sort, specifically causing poor reproducibility and degradation of their properties with time.

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