High-temperature superconductivity in metal-oxide ceramics

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A review is presented of the experimental data on the high-temperature superconductivity recently discovered in metal-oxide ceramics.

In September 1986 Bednorz and Müller of the IBM research laboratory in Zurich reported the observation of superconductivity in La-Ba-Cu ceramic oxides in the region of 30 K.[1a] By January 1987 four groups[2–5] had made announcements of high-temperature superconductivity in $(La_{1-x}M_x)_2CuO_{4-y}$ compounds with partial replacement of lanthanum by M = Ba, Sr, or Ca. Finally, in February 1987 the group of Chu[6] announced the discovery of a superconducting state in the metal oxide ceramic Y-Ba-Cu-O at the temperature $T = 93$ K(!). As is well known, the highest results of a more than 70 year search for high-temperature superconductors prior to September of 1986 were still obtained with materials having the so-called A-15 structure, among which the superconducting transition temperature $T_c = 23.7$ K in Nb_3Ge (Ref. 7) was attained more than ten years previously. In the subsequent years the continual intensive search for superconductors with higher T_c produced new classes of materials: organic superconductors, superconductors with heavy fermions, superconductors with a low carrier concentration, and so forth. However, the superconducting temperature in all these exotic materials never exceeded 15 K.

On the other hand, from the beginning of the 1970s two metal oxides were known, $Li_{1+x}Ti_{2-x}O_4$ and $BaPb_{1-x}Bi_xO_3$, with the spinel and perovskite crystal structures, in which the superconducting state appeared relatively early: $T_c = 13.7$ K in the former[8] and $T_c = 13$ K in the latter.[9] These superconductors are empirically separated into a special class of materials by the fact that their critical temperatures are approximately three times higher than all other superconductors with a comparable density of states at the Fermi surface (see the review in Ref. 10). The new metal oxides belong to the same class of materials, but they have "huge" superconducting transition temperatures and, correspondingly, huge critical magnetic fields, which, according to rough estimates, reach 10^6 Oe.

The properties of these materials, which are prepared by the techniques of ordinary ceramic technology or by hot pressing, depend strongly on the annealing conditions, the degree x of replacement of the lanthanum or yttrium by the alkaline earth elements, the oxygen deficiency y, the applied pressure, the measuring current, etc, but these properties appear to be quite stable and reproducible.

Originally, Bednorz, Müller, and Takashige reported[1a] that the resistance of La-Ba-Cu-O dropped in the interval between 35 and 13 K and that this drop was accompanied by an equally smeared-out Meissner effect, which began at 30 K (Ref. 1b) and a state of perfect diamagnetism was attained in not more than 2% of the volume.

Later it was determined that in a multiphase sample the superconducting phase is the stoichiometric phase $(La_{1-x}Ba_x)_2CuO_{4-y}$, with the tetragonal symmetry of the layered perovskite K_2NiF_4 (Refs. 2a, b, and 11), depicted in Fig. 1. Here the maximum Meissner effect (perfect diamagnetism in 30% of the volume) was reached at $x = 0.075$, and the resistance fell by 3–4 orders of magnitude in the range 35 to 22 K. The substance also exhibited a positive pressure effect, in which T_c increased to 40 K at 13 kbar.[3] It was then observed that when the lanthanum is replaced by Sr, with $x = 0.2$, the material is more uniform and the resistance falls more sharply at 37 K (Refs. 2c and 4) with a transition width $\Delta T_c = 1.4$ K [Fig. 2, (taken from Ref. 4)] and a more complete Meissner effect [60–70%, Fig. 3 (from Ref. 4)]. According to the data of a group from the People's Republic of China,[5] the resistance of the oxides La-Ba(Sr)-Cu-O is observed to begin to fall even sooner, at $T_c = 46$ and 48 K, with a transition width $\Delta T_c = 7$ K and 10 K, respectively. Replacement of lanthanum with yttrium unexpectedly brought about a drop in resistance by five orders of magnitude between 93 and 80 K [Fig. 4 (from Ref. 6a)]. Here the Meissner effect, which began at 90 K, reached 24% of that of a superconducting lead sample of the same size [Fig. 5 (Ref. 6a)]. It was determined from subsequent x-ray and neutron scattering studies that the Y-Ba-Cu-O superconducting phase has the composition $YBa_2Cu_3O_{7\pm y}$ (the so-called 1-2-3 phase[12–14]) with the structure of cubic perovskite ABO_3 and with ordered oxygen vacancies.[15–17] In this case the Ba does not replace the Y randomly, as in the case of the La

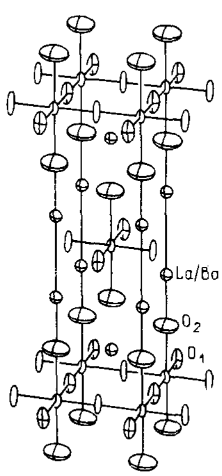

FIG. 1.

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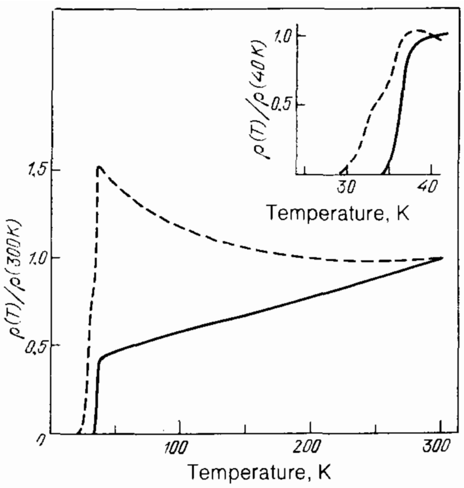

FIG. 2.

compounds, but is ordered in the sequence Ba-Ba-Y-Ba-Ba-Y along the *c* axis. It has subsequently been observed that in the 1-2-3 compounds $MBa_2Cu_3O_7$ the yttrium can be replaced by almost any of the rare earth elements M = Ho (Ref. 18), Dy, Er, Sm, Lu, and others, as well as Sc (Refs. 19, 22) while the critical temperature varies only slightly, in the range from 85 to 100 K.

The multicomponent metal oxide compounds are a product of a solid state chemical reaction, for which the conditions are produced after mixing powders of the corresponding oxides and carbonates [for instance La(OH), $SrCO_3$, and CuO (Ref. 4), La_2O_3, and $BaCO_3$ (Ref. 2b), and Y_2O_3, $BaCO_3$, and CuO (Ref. 6)] in the required concentration and sintering the mixture for several hours to several days at around 1000 K, sometimes with grinding during this process. Experiments were also carried out on samples annealed in a controlled oxygen pressure.[2d] Materials prepared in this way turn out to be nonuniform, with an uncontrolled density, and composed of randomly oriented anisotropic polycrystalline grains with a characteristic dimension of $\sim 1\,\mu$m. Therefore the observed superconductivity is undoubtedly of a percolation nature, as is indicated by the broad superconducting transition, by the Meissner effect, which is even broader and is shifted to lower temperatures (see Figs. 2–5), and also by the weak currents that destroy the superconductivity.[4]

It is also possible that these materials are media with multiple Josephson junctions. This possibility, in particular, is indicated by the marked increase in the resistance in the

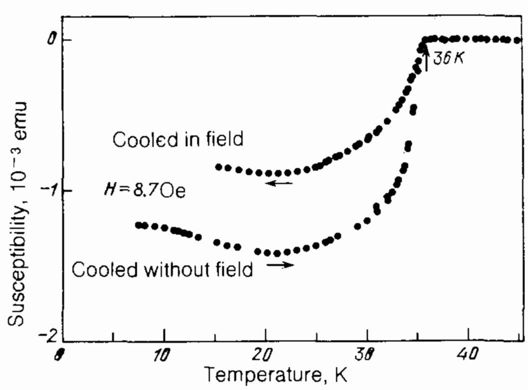

FIG. 3.

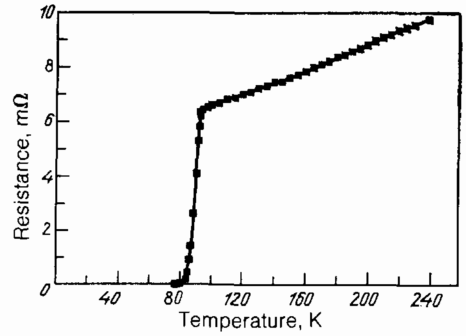

FIG. 4.

pre-transition region when the measuring current is decreased.[5]

The properties of the undoped La_2CuO_4 matrix, as well as of the compounds of La-M-Cu-O above room temperature were thoroughly studied prior to the discovery of high-temperature superconductivity.[20,21]

At $T > 248$ °C the La_2CuO_4 crystal exists in a tetragonal phase of the K_2NiF_4 type, with a unit cell volume of 190 Å^3, and exhibits metallic properties.[13]

As can be seen from Fig. 1, this structure contains perovskite layers of CuO in which the Cu_6O octahedra share a common vertex; these layers are separated by layers of La-O. In stoichiometric La_2CuO_4 the octahedra are elongated along the *c* axis by a factor of 1.226.[11]

At $T = 248$ °C there is a structural transition to phase with orthorhombic symmetry, possibly associated with the Jahn-Teller character of the Cu^{+2} ($3d^9$) ion, for which in a cubic crystal field the ground state has a hole in the twofold degenerate e_g orbital. Below 50 K La_2CuO_4 shows a sharp increase in resistance, and remains an insulator down to 4 K.[1]

Replacement of trivalent La^{+3} by the divalent alkaline earth ions Ba^{+2}, Sr^{+2}, or Ca^{+2} stabilizes the tetragonal phase while maintaining its metallic properties. It is very probable that trivalent Cu^{+3} ions, which are not subject to the Jahn-Teller effect, are formed. A similar variable valence of Ti and Bi is known in the Li-Ti-O and Ba-Pb-Bi-O metal oxides. Thus, the replacement of La by alkaline earth ions in this case leads to the formation of an electronic state (i.e., a hole in the d band of copper) between the Jahn-Teller and the non-Jahn-Teller ions, Cu^{2+} and Cu^{3+}, which have different local environments. We cannot rule out the possibility that the variable valence near the Fermi surface, accompanied by a strong electron-phonon interaction, induces the high-temperature superconductivity. In any case, the high

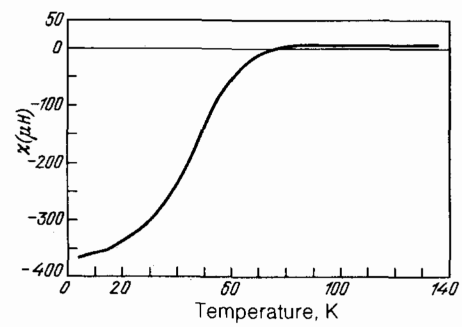

FIG. 5.

oxygen nonstoichiometry, which changes the Cu^{+3}/Cu^{+2} concentration, has a critical effect on the conductivity of the oxides [see Fig. 6 (from Ref. 2c)].

The variable valence of copper and the magnitude of the oxygen deficiency are apparently very important in the 1-2-3 materials. As has already been noted, in the cubic perovskite structure there are oxygen vacancies in the compound $YBa_2Cu_3O_7$ such that the copper ions which are adjacent to vacancies are surrounded by four or five oxygen atoms. With this composition 2/3 of the copper ions are in the Cu^{+2} state, 1/3 are in the Cu^{+3} state, and these states are uniformly distributed over the lattice.[15]

Figure 2 shows the temperature dependence of the resistance of $La_{1.8}Sr_{0.2}CuO_4$, annealed in air (the dashed curves $\rho_{300\,K} \approx 2200\ \mu\Omega\cdot cm$) and in oxygen ($\rho_{300\,K} \approx 5500\ \mu\Omega\cdot cm$).[4] The important effect of an oxygen atmosphere in the annealing of $La_{1.85}Ba_{0.15}CuO_4$ is demonstrated in Fig. 6 (from Ref. 2c).

These results show that in the technology that is presently used the degree of oxidation determines in an essential way the uniformity of the material and, consequently, its electrical conductivity. (Moreover, a group from the People's Republic of China[5] has reported on the instability of samples that are stored in air). On the other hand, the properties of the superconducting phase depend to a considerably lesser extent on the degree of oxidation.

We note also that the persistent observation that the onset of the superconductivity transition is unstable and depends on the method of sample preparation, while at the same time the termination of the transition is known to be stable, has led some investigators to hypothesize the existence of an even higher-temperature, but, possibly, metastable superconducting phase. Such a possibility is indicated, in particular, by the recent appearance of unpublished reports of measurements of the resistance of single crystals, where a sharper transition has been observed with an onset at a considerably lower temperature.

The temperature dependence of the resistance for the record material as of March 1987, $(Y_{0.6}Ba_{0.4})_2CuO_4$, measured directly in a liquid nitrogen dewar,[6a] is shown in Fig. 4. Below 80 K the resistivity is below the "instrumental zero," and does not exceed $3\cdot 10^{-8}\ \Omega\cdot cm$.[6a] In contrast to La-Ba-Cu-O, the position and the width of the superconducting transition in the yttrium-based ceramic is practically independent of the pressure.[6b]

In spite of the fact that subsequent estimates[22] have improved the zero of resistance to $10^{-12}\ \Omega\cdot cm$ (and according to some data, even $10^{-17}\ \Omega\cdot cm$), direct measurements of the discontinuity in the resistance are quite difficult because of the extreme nonuniformity and the excess oxidation on the sample surface, and in many respects depend on the nature of the contacts.[2d] A direct indicator of the superconducting phase may be considered the Meissner effect accompanying a discontinuity in the resistance, as has been observed by all groups. The temperature dependences of the magnetic susceptibility, characteristic of a percolation type II superconductor, shown in Figs. 3 and 5, were obtained by various methods for $La_{1.8}Sr_{0.2}CuO_4$ (by cooling in a magnetic field of 8.70 Oe and in the absence of a field)[4] and for $YBa_2Cu_3O_7$ (Ref. 6). The change with temperature of the upper critical field, measured at the 50% drop of the resistance is found to be relatively large: $-dH_c/dT\,|_{T=T_c} \approx 0.5 - 2T/K$.[1b,2d,3,6,8] According to Refs. 1b and 2c, the curve of $H_{c2}(T)$ for La-Sr(Ba)-Cu-O for small H_{c2} has a marked positive curvature that decreases with decreasing temperature such that at 30 K the dependence $H_{c2}(T)$ is nearly linear. From these results we can suppose that the uniform superconducting phase is characterized by giant critical magnetic fields. According to Ref. 2d, a crude extrapolation yields an estimate for H_c of 50-60 T for La-Sr(Ba)-Cu-O. In any case, at the boiling point of liquid neon ($T_{Ne} = 27$ K) it cannot be less than 12 T and at the temperature of liquid helium (4.2 K) it cannot be less than 25 T. An estimate of H_{c2} for Y-Ba-Cu-O (Ref. 6) is even higher, up to 80 T. There are even more optimistic extrapolations which estimate H_{c2} to be as high as 200 T. Let us recall for purposes of comparison that the critical field for Nb_3Ge is of the order of 40 T and the highest critical field known, that for $PbMo_6S_8$, does not exceed 60 T. The estimate of H_{c1} for La-Ba(Sr)-Cu-O gives a value of the order of 0.05 T.[2d,3] Preliminary data on the magnetic properties of the 1-2-3 compounds based on the rare earth elements indicate the interesting possibility that ferromagnetism and superconductivity coexist in these materials.[18,22]

At the time that this paper was prepared, studies of the

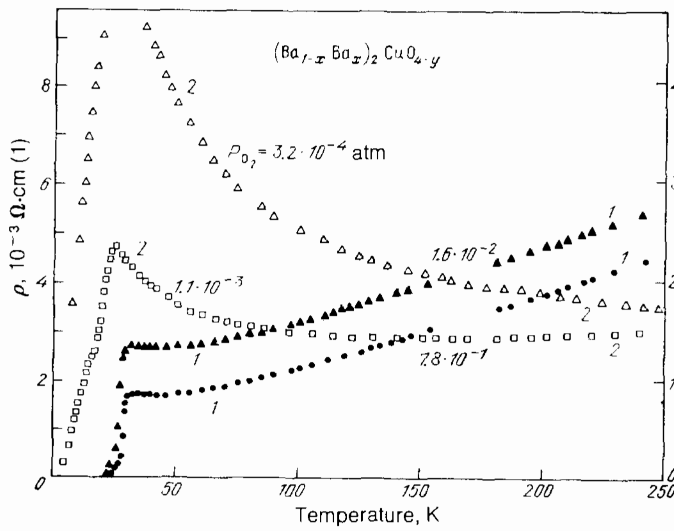

FIG. 6.

physical properties of the superconducting phase were not very reliable. Direct measurements of the energy gap in the electron spectrum, carried out by various groups using various methods, disagree considerably. In the work that has been published, optical methods of measuring the gap of La-Ba(Sr)-Cu-O are the most completely described.[23–25] In spite of the disagreement among the results, we can say that width of the gap measured by these methods is somewhat smaller than the value $2\Delta < 3.5T_c$ predicted by the BCS theory. Other standard methods—tunneling measurements and NMR—give less reliable results.

Because of the general interest in high-temperature superconductivity, both as a fundamental physical phenomenon and as a phenomenon of enormous practical importance, we may expect in the near future very careful investigations of the structural and physical properties of the presently existing materials and the appearance of new and more technologically applicable superconductors. Therefore the results that have been discussed here will surely be obsolete when this paper is published.

Indeed, after the discovery by Bednorz and Müller until March of this year the critical temperature has risen an average of 15 K/month. (Let us compare this rate with the increase in T_c during the previous heroic period which began with the discovery of high-temperature superconductivity in type A-15 compounds in 1954 and lasted almost 20 years (see e.g., Ref. 26), during which time the critical temperature increased uniformly from 18 to 23 K). Today, in view of the paucity of experimental data, we must consider as unresolved the alternatives: can the observed high-temperature superconductivity be explained by the standard BCS theory (possibly with a strong electron-phonon interaction), or have we encountered a new superconductivity mechanism? For this reason I have deliberately refrained from discussing the possible theoretical explanations of the pheonomenon that are currently being put forth and that are clearly outdistancing the experimental investigations.

The increasing stream of experimental studies gives confidence that in the near future we will have a sufficient data base for elucidating the nature of high-temperature superconductivity.

I wish to express my appreciation to D. I. Khomskiĭ for help in a critical analysis of the stream of published data on the superconducting metal oxides.

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