Evidence for Superconductivity above 40 K in the La-Ba-Cu-O Compound System

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An apparent superconducting transition with an onset temperature above 40 K has been detected under pressure in the La-Ba-Cu-O compound system synthesized directly from a solid-state reaction of La_2O_3, CuO, and $BaCO_3$ followed by a decomposition of the mixture in a reduced atmosphere. The experiment is described and the results of effects of magnetic field and pressure are discussed.

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Recently, Bednorz and Müller[1] have examined the electrical properties of the compound system $La_{5-x}Ba_xCu_5O_{5(3-y)}$ (LBCO). The samples were prepared by a coprecipitation method from aqueous solutions of La, Ba, and Cu nitrates in their appropriate ratios, followed by a solid-state reaction and decomposition of the precipitates at 900 °C in a reduced atmosphere. On cooling, the resistivity ρ of samples with $x \leq 1.0$ initially decreases and then rises prior to a sharp ρ drop starting at temperatures as high as ~ 35 K. For some samples, a zero-ρ state was achieved below ~ 12 K, although all were multiphased. The ρ drop was found to be shifted toward lower temperatures as the measuring current was enhanced. Possible high-temperature percolative superconductivity with a maximum onset temperature $T_{c0} \sim 35$ K was, therefore, proposed[1] in the LBCO system. The sample-preparation technique and heat-treatment conditions have been suggested[1] to play a crucial role in the observations.

We have prepared the LBCO compounds with a noncoprecipitation solid-diffusion technique and obtained[2] the same ρ drop with a $T_{c0} \sim 36$ K. The magnetic field was found to move the ρ drop to lower temperatures and can remove the zero-ρ state. The I-V curves below T_{c0} characteristic of a superconducting state were also obtained. On the other hand, ac magnetic susceptibility χ measurements indicate that no more than 2% of the sample bulk investigated displays a perfect diamagnetic state, consistent with the proposition[1] of percolative superconductivity in LBCO. Under pressure, T_{c0} increases[3] from 32 to 40.2 K at 13 kbar at a rate $\sim 0.9 \times 10^{-3}$ kbar^{-1}. Both the T_{c0} and its rate of enhancement by pressure are the highest ever detected to date in any superconductors.

All compounds investigated have the nominal compositions given by $La_{1-x}Ba_xCuO_{3-y}$ (Type I) or $(La_{1-x}Ba_x)_2CuO_{4-y}$ (Type II), with $x = 0.20$ or 0.15 and y undetermined. They were prepared by the solid-state reaction method.[4] The mixture of La_2O_3 (> 99%, Fisher Scientific), CuO (> 99%, Fluka AG) and $BaCO_3$ (reagent grade, J. T. Baker) was first heated in a reduced oxygen atmosphere of 2×10^{-5} bars at 900 °C for 6 h. The process was repeated after pulverizing of the reacted mixture. The thoroughly reacted mixture was then pressed into $\frac{3}{16}$-in.-diam cylinders for final sintering at 925 °C for 24 h in the same reduced oxygen atmosphere. Samples of dimensions $\sim 1 \times 1 \times 3$ mm were cut from the cylinders for measurements. Pt leads were attached to the samples with gold paste or pressed In contacts. The standard four-probe technique was used for ρ measurements. An inductance bridge was employed for the ac magnetic susceptibility (χ) determination. The temperature was determined with a Fe+0.07at.% Au–Chromel thermocouple, a Chromel-Alumel thermocouple, and/or a carbon-glass thermometer in various temperature ranges. They were calibrated against the Fe+0.07at.% Au–thermocouple scale[5] above 4 K, and against the Chromel-Alumel thermocouple scale[6] above 77 K. The temperature uncertainty between 25 and 50 K was estimated at ±0.2 K. A Be-Cu high-pressure clamp[7] was used to provide the hydrostatic environment with use of a fluid pressure medium. The pressure was measured with the use of a superconducting Pb manometer situated next to the samples. The magnetic field was generated in a superconducting magnet.

Powder x-ray diffraction patterns at room temperature showed that almost all samples were multiphased. Type-I samples consisted of K_2NiF_4 ($\sim 90\%$) and unidentified ($\leq 10\%$) phases, while type-II ones were mainly K_2NiF_4 phase within our resolution of 5%. The $\rho(T)$ similar to that previously reported[1] was obtained for both $x = 0.2$ and 0.15. For some Type-II samples, ρ starts to drop at $T_{c0} \sim 36$ K and becomes zero below 20 K as shown in Fig. 1. Typical results of a Type-I sample,[3] at ambient pressure, are shown in the following few figures. Figure 1 displays the magnetic field effect on $\rho(T)$. It is clear that the rapid ρ drop is suppressed and the zero-ρ state at 4 K can be destroyed by magnetic fields. Below 18 K, a diamagnetic shift is clearly evident and reaches a maximum of 2% of the signal of a superconducting Pb sample of the same size as shown in Fig. 2. The inset shows the I-V characteristic at zero pressure for the sample at 4.2 K. The zero-ρ state is removed as current exceeds a critical value which increases

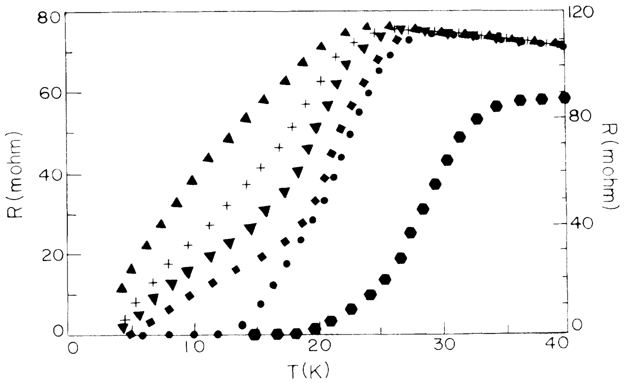

FIG. 1. The $\rho(T)$ of a type-I sample in different magnetic fields in kilogauss: Circles, 0; lozenges, 4.5; inverted triangles, 15; plusses, 30; and triangles, 58.5. Hexagons, Type-II sample in zero field and pressure.

with decreasing temperature. All these strongly demonstrate that the ρ drop is associated with a nonbulk superconducting transition in support of the previous suggestion.[1]

Under hydrostatic pressure, ρ at 300 K is suppressed and the ρ drop is broadened slightly, but with an overall shift toward higher temperatures as shown in Fig. 3. T_{c0} increases rapidly with pressure as shown in Fig. 4. At 13 kbar, T_{c0} is ~40.2 K. Above 13 kbar, the sample was damaged because of a shear strain introduced accidentally by application of pressure below $-20\,^{\circ}\mathrm{C}$, as evidenced by the appearance of a rapid ρ increase following the ρ drop at T_{c0} on cooling and the irreversibility of ρ after the pressure was reduced.

It has been shown[8] that for a dirty superconductor, pair conductivity due to superconducting fluctuations above the transition temperature T_c can be large and exhibits a "Curie-Weiss" behavior. This can lead to a downward deviation of ρ from its normal-state value and

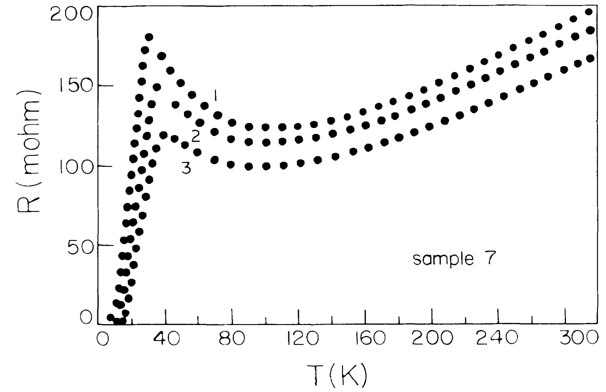

FIG. 3. $\rho(T)$ of a type-I sample at different pressures: Curve 1, 0 kbar; curve 2, 6.6 kbar; and curve 3, 13.3 kbar.

to the possible appearance of a ρ peak at T_{c0} in LBCO. However, the $\rho(T)$ for some samples near and below T_{c0} does not vary with temperature in such a fashion,[9] particularly in view of the relatively sharp transition of the type-II sample shown in Fig. 1. In addition, magnetic field is expected to suppress fluctuations. However, the gradual decrease of ρ near and below T_{c0} persists in magnetic fields. Apart from the diamagnetic ac χ shift detected by us, the most recent observations[10] of diamagnetic dc χ shift below ~28 K clearly show that T_{c0} can be reasonably taken as the onset temperature of a superconducting transition and that the broad ρ drop is attributed to a wide distribution of T_c's. Therefore, it is reasonable to assume that superconductivity at temperature above 40 K has been observed by us in LBCO under pressure.

An ac diamagnetic χ shift generally consists of contributions from the diamagnetism of the superconducting component and the shielding effect of the normal and superconducting components of a sample. The ac χ shift can set only the upper limit of the superconducting

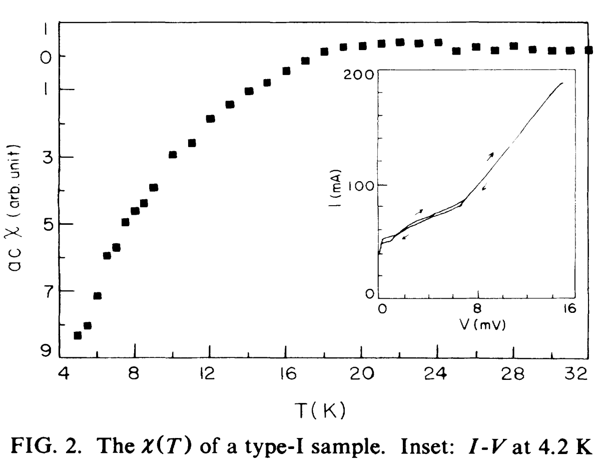

FIG. 2. The $\chi(T)$ of a type-I sample. Inset: I-V at 4.2 K

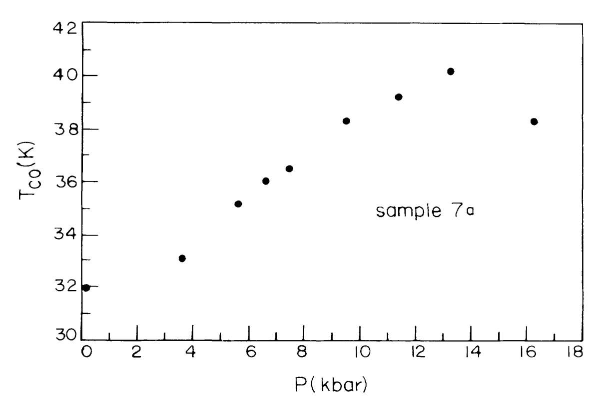

FIG. 4. $T_{c0}(P)$ of a type-I sample. The sample was damaged at 16.3 kbar.

volume fraction of a sample. We found that as the amount of the K_2NiF_4 phase increases, the ac diamagetic χ shift increases with a narrower transition and a higher T_{c0} shown in Fig. 1. However, the small ac χ shift in contrast to the presence of the major K_2NiF_4 phase in our samples suggests that the superconductivity observed may be associated with either a yet unidentified new minor phase or interfaces in the LBCO compounds due to mixed valence or concentration fluctuations. It should be mentioned that the oxygen-deficiency–octahedron layer structure of the K_2NiF_4 phase can also provide conditions for interfaces. More studies are required for clarification.

The large positive continuous effect of pressure on superconductivity in LBCO compounds, $\sim 0.9\times10^{-3}$ kbar^{-1}, is unprecedented, in the absence of a pressure-induced phase transition (although the next largest pressure effect, but negative, occurs interestingly in a defected perovskite superconductor $SrTiO_{3-x}$). On the other hand, such a large positive pressure effect on T_{c0} is consistent with the picture of interfacial superconductivity[11] between a metal and a semiconductor where pressure[12] can fine tune the coupling of the two components, the Fermi energy of the metallic part and the energy gap of the semiconducting part. The possible pressure-induced valence change cannot be ruled out. On the basis of the present experimental data, the surface effects on superconductivity appear to play an important role in superconductivity whether in a mixed phase or in the layered K_2NiF_4 phase. It was pointed out previously[13] that high-temperature superconductivity in oxide systems always occurs near the metal-insulator phase boundaries (i.e., mixed-phase region) and the oxides always consist of oxygen octahedrons. LBCO apparently is another such system. Oxides of this type tend to be ferroelectric in general. The large dielectric constant of ferroelectric modes may provide a channel for the enhanced electron-pairing interaction required for high-temperature superconductivity. Therefore, we believe that superconductivity well above 40.2 K is achievable by the application of pressure and the optimization of the sample conditions of LBCO. It should be noted that the T_{c0} drop above 13 kbar is due to damage induced by a shear strain as mentioned earlier.

In conclusion, we have observed evidence for nonbulk superconductivity above 40 K in an LBCO compound system under hydrostatic pressure, and the largest positive pressure effect on superconductivity. Interfacial superconductivity due to mixed phases or concentration fluctuation and noninterfacial superconductivity arising from mixed-valence effects in this system are consistent with existing experimental results, although a definitive conclusion is yet to be made based on further studies. The results also suggest that superconductivity at temperature greatly exceeding 40 K is achievable in LBCO and related systems through fine tuning of the sample parameters by physical and chemical means.

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Note added, 6 January 1987—Detailed examination of the results on the sample in Ref. 2 indicated that the sample exhibited a $T_{c0}\sim70$ K and the sharp R drop occurred at ~60 K, although the zero-R state was not reached. We, in collaboration with M. K. Wu at the University of Alabama at Huntsville, also found that the replacement of Ba by Sr produces a $T_{c0}\sim42$ K at ambient pressure.

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[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2] One sample exhibited a $T_{c0}>56$ K but was later destroyed and could not be reproduced. The sample characteristics were found to depend also on thermal history, in addition to samples and their preparation conditions.

[3] Pressure effects of the Type-II samples with $T_{c0}\sim36$ K will be published later.

[4] C. Michel, L. Er-Rakho, and B. Raveau, Mat. Res. Bull. **20**, 667 (1985).

[5] R. L. Rosenbaum, Rev. Sci. Instrum. **39**, 890 (1968).

[6] *OMEGA Complete Temperature Measurement Handbook and Encyclopedia* (OMEGA Engineering, Inc., Stamford, CT, 1986), p. T-43.

[7] C. W. Chu, T. F. Smith, and W. E. Gardner, Phys. Rev. Lett. **20**, 198 (1968).

[8] R. E. Glover, Phys. Lett. **25A**, 542 (1967); L. G. Aslamazov and A. I. Larkin, Phys. Lett. **26A**, 238 (1968); M. Strongin, D. F. Kammerer, J. E. Crow, R. S. Thompson, and H. L. Fine, Phys. Rev. Lett. **20**, 922 (1968); L. R. Testardi, W. A. Reed, P. C. Hohenberg, W. H. Haemmerle, and G. F. Brennert, Phys. Rev. **181**, 800 (1969). We thank M. Strongin for pointing out this possibility.

[9] P. H. Hor *et al.*, unpublished.

[10] K. Kitazawa (17–40%); A. Müller (0.7%), private communications.

[11] D. Allender, J. Bray, and J. Bardeen, Phys. Rev. B **3**, 1020 (1973); T. H. Geballe and C. W. Chu, Comments Solid State Phys. **9**, 115 (1979).

[12] C. W. Chu and M. K. Wu, *High Pressure in Science and Technology,* edited by C. Homan, R. K. MacCrone, and E. Whalley (North-Holland, New York, 1984), p. 3.

[13] C. W. Chu, S. Huang, and A. W. Sleight, Solid State Commun. **18**, 977 (1976).