PHYSICAL REVIEW B VOLUME 35, NUMBER 13 1 MAY 1987

High-T_c superconductivity in regions of possible compound formation: $Y_{2-x}Ba_xCuO_{4-x/2+\delta}$ and $Y_{2-x}Ba_{1+x}Cu_2O_{6-x/2+\delta}$

Shiou-Jyh Hwu, S. N. Song, J. Thiel, K. R. Poeppelmeier, J. B. Ketterson, and A. J. Freeman
Materials Research Center, Northwestern University, Evanston, Illinois 60201
(Received 3 March 1987)

High-T_c superconductivity is investigated in the Y-Ba-Cu-O system. Regions of possible compound formation are $Y_{2-x}Ba_xCuO_{4-x/2+\delta}$ and $Y_{2-x}Ba_{1+x}Cu_2O_{6-x/2+\delta}$. T_c values >90 K are found for the former with $x=0.8$ (the Chu and co-workers material) and for the latter with $x=0.2$ and may imply a common superconductivity phase in both samples. Critical fields determined by resistance and low-field d_c susceptibility measurements are reported.

The discovery of high-temperature superconductivity in metallic oxides is a momentous event with possible enormous consequences for science and technology. It was only last October that Bednorz and Müller[1] reported the possible existence of superconductivity up to 35 K in the La-Ba-Cu-O layer perovskite. A number of subsequent magnetic and transport measurements confirmed this report and established a higher T_c in the La-Sr-Cu-O system.[2]

The very recent dramatic finding by Chu and co-workers[3,4] of superconductivity in the Y-Ba-Cu-O system has raised T_c well beyond 90 K: In an unpublished report,[5] they find an onset T_c of 94 K and a narrow transition (4 K) at ambient pressure. This work has literally broken the barrier to high T_c thought to be established by the limitations of the electron-phonon interaction. Since no theory to date based on electron-phonon interaction alone has predicted a T_c greater than 40 K, it is thus entirely likely that there is operative here a new mechanism of superconductivity. If so, then even higher superconducting transition temperatures than those presently achieved are also possible.

This paper confirms and extends the results reported by Wu *et al.*[3] and Chu *et al.*[5] Our investigations have centered on sample synthesis in the Y-Ba-Cu-O system near two regions of possible compound formation reported previously,[6] namely (i) $Y_{2-x}Ba_xCuO_{4-x/2+\delta}$ and (ii) $Y_{2-x}Ba_{1+x}Cu_2O_{6-x/2+\delta}$. Stable and reproducible transport and magnetic susceptibility measurements with an onset resistance transition temperature above 93 K and onset of diamagnetism at 92 K are reported for samples with $x=0.8$ in system (i), the Chu-Wu[3,5] composition, and $x=0.2$ in system (ii). We find that the sample in (ii) shows a much narrower resistance transition than does the sample in (i). While the results are preliminary, our findings do reflect two points: First, sample preparation is important and, second, compositions other than those reported by Chu and co-workers[3,4] are superconducting.

Our results on three representative samples are summarized below. Two were prepared by the solid-state reaction of Aldrich Y_2O_3 (99.99%), $BaCO_3$ (99.999%), and CuO (99.999%) in the relative molar amounts 0.6:0.8:1.0, respectively, as in the work of Chu and co-workers.[1-3] Sample A was heated in air at 900 °C for 12 h and then reground. It was then heated at 1100 °C in air with two grinds at 7-h intervals. The x-ray diffraction pattern of sample A had the three strongest diffraction peaks at $d=2.986$, 2.921, and 2.821 Å. It did not show a superconducting transition. Sample B was heated in air at 900 °C for 9 h and then reground. It was then heated to 1000 °C in air for 15 h with one grind after 7 h. The x-ray diffraction pattern of sample B was very similar to that of sample A. Sample B, however, did show superconducting behavior (see below).

A third sample, sample C, was prepared with the relative molar ratios of Y_2O_3:$BaCO_3$:CuO of 0.9:1.2:2.0. This sample mixture was heated in air to 900 °C for 11 h and then reground. It was then heated at 1100 °C for 7 h, ground, and then heated at 1000 °C for 10 h. The x-ray diffraction pattern of sample C was substantially different from that of samples A and B. Sample C, like sample B, was superconducting (see below).

Samples B and C were pressed (at 1.3-kbar fluid pressure) in the form of disks 1 cm in diameter and 1.5 mm thick. The disks were annealed in one atmosphere of pure O_2 at 1000 °C for 1.5 h. After annealing the samples were shaped into specimens with a 1 mm×3 mm rectangular cross section which were 7-mm long. Four leads were attached with silver paint (two for potential and two for current). Samples were mounted on a specially designed transport probe which is inserted (via a vacuum load lock) into the sample chamber of a model VTS-50 susceptometer (SHE Corp., San Diego, California); this instrument operates in the temperature range 0–400 K and 0–5 T. A current of 1 mA was used for resistance measurements and voltages were determined with a Keithley model 181 Nanovoltmeter. The temperature of the probe could be read either with the thermometer in the VTS unit or with a carbon glass thermometer mounted on the probe.

Susceptibility measurements were carried out in the above-mentioned VTS-50 cryostat. The sample was contained in a quartz basket which was suspended by a cotton thread from the VTS sample translator drive. The temperature and field dependence of the susceptibility of the basket were previously determined and their effect was negligible in the present experiments. The susceptometer was calibrated by National Bureau of Standards Al and Pt standard samples.

Two superconducting samples were studied in this work: sample B, which has the nominal composition

$Y_{1.2}Ba_{0.8}CuO_4$, had resistivities of 3.9×10^{-2} Ω cm and 2.8×10^{-2} Ω cm at 300 and 104 K, respectively; sample C, with a nominal composition $Y_{1.8}B_{1.2}Cu_2O_6$, had resistivities of 4.9×10^{-2} Ω cm and 2.6×10^{-2} Ω cm at 300 and 97 K, respectively.

Figure 1 shows the temperature dependence of the measured resistance of sample B at two fields: $H=0.0$ and 3.0 T, and sample C at field $H=0.0$ T. At zero field the 10%, 50%, and 90% resistance changes correspond to 88.5, 91.2, and 94.5 K, respectively. At zero field the 10%, 50%, and 90% resistance changes for sample C occur at 91.6, 93.3, and 94.2 K, respectively. The transition width is 2.6 K. As often occurs, and as seen in Fig. 1, the width of the transition is increased in the presence of an applied magnetic field. The ratio of the resistance in the normal state to that in the superconducting state is greater than 10^4; this ratio was limited by noise associated with our dc resistance technique.

In Fig. 2 we plot the temperature of the 50% and 90% resistance shift for sample B as a function of the corresponding magnetic field. The slope $dH_{c2}/dT_c=-1.25$ T/K can be used to estimate the zero temperature upper critical field using the expression

$$H_{c2}(T=0)=-0.693(dH_{c2}/dT_c)T_c(H=0)\ ,$$

for which we obtain approximately 80 T. This is at the lower point of the range reported by Wu *et al.*[3] As is well known, higher critical fields are associated with shorter electron mean-free paths.

The susceptibility of sample B is shown in Fig. 3. The lower curve shows the data obtained when the sample was rapidly cooled to 5 K in a zero field (less than $\frac{1}{2}$ Gauss) and then had a field of 12 G applied; the temperature was then slowly increased and the data collected. The upper curve shows the behavior obtained when the direction of the temperature sweep was reversed on reaching 110 K and the sample subsequently cooled; clearly, the flux exclusion is less complete on cooling, even at 12 Oe. Since the density of this material is not available we can only estimate the superconductivity fraction at 20%–30%.

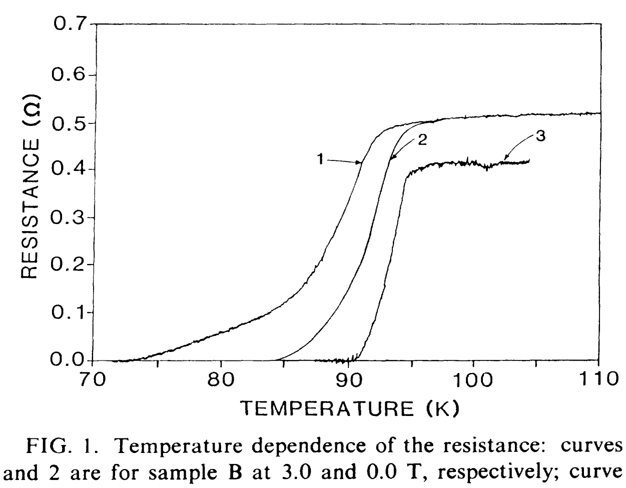

FIG. 1. Temperature dependence of the resistance: curves 1 and 2 are for sample B at 3.0 and 0.0 T, respectively; curve 3 shows sample C at 0.0 T. In the fully developed superconducting state the resistance is smaller than in the normal state by a factor greater than 10^4.

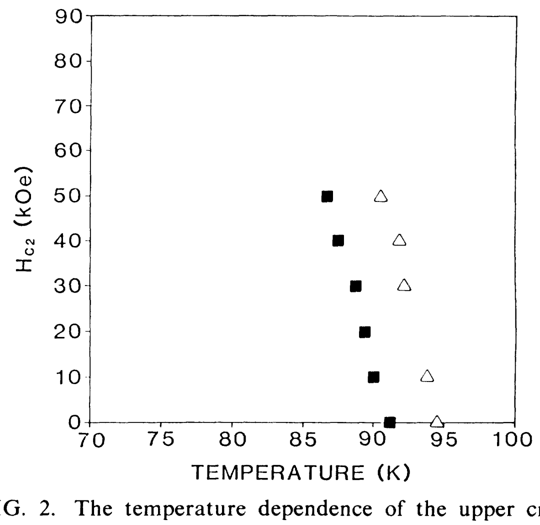

FIG. 2. The temperature dependence of the upper critical field. The filled squares show the data corresponding to a 50% drop and the open triangles to 10% drop in resistance.

Our knowledge of the subsolidus phases in the Y-Ba-Cu-O system, their nucleation, and stability are fragmentary. The synthesis of pure and mixed phase materials will be an important area of research in relationship to superconductivity in these mixed metal oxide systems. Our results indicate that a phase common to both compositions studied may be the superconducting component.

While the origin of superconductivity in this material is not clear, there are a number of factors in common with the earlier $La_{2-x}M_xCuO_4$ system. In both, there are strong Cu d–Op interactions[7] and the addition of divalent

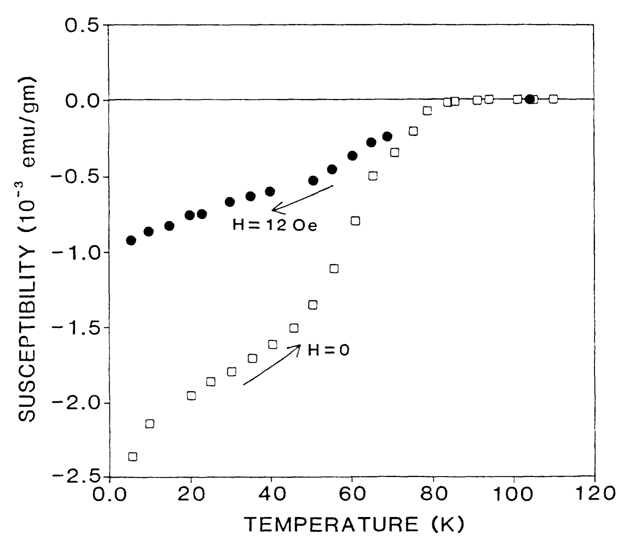

FIG. 3. The temperature dependence of the magnetic susceptibility of sample B. The open squares show the susceptibility of a sample cooled to 5 K at zero field; a field of 12 G is then applied, and the temperature is increased in increments to 110 K. The filled circles show the data on recooling the sample from 110 K.

M ions brings about Cu^{2+}-Cu^{3+} charge fluctuations. In the La system, frozen phonon calculations[8] for the optical breathing mode showed that there was a large electron-phonon interaction matrix element, a high frequency (110 meV) with a high Θ_D ($\sim$1200 K), and large charge fluctuations between the Cu sites. What may be important for superconductivity is the possible resonant coupling to, and enhancement of, the natural (M induced) ground state Cu^{2+}-Cu^{3+} fluctuations between in-plane Cu atoms. Whether similar effects are operative in the Y-Ba-Cu-O systems remains to be seen.

This work was supported by a National Science Foundation grant through the Northwestern University Materials Research Center.

[1]J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).
[2]C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang, Phys. Rev. Lett. **58**, 405 (1987); R. J. Cava, R. B. Van Dover, B. Batlogg, and E. A. Rietman, *ibid.* **58**, 408 (1987); S. Uchida, H. Takagi, K. Kitzawa, and S. Tanaka, Jpn. J. Appl. Phys. **26**, L1 (1987).
[3]M. K. Wu, J. R. Ashburn, C. J. Thorng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).
[4]P. H. Hor, L. Gao, R. L. Meng, Z. J. Huang, Y. Q. Wang, K. Forster, J. Vassiliou, C. W. Chu, M. K. Wu, J. R. Ashburn, and C. J. Thong, Phys. Rev. Lett. **58**, 911 (1987).
[5]C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, J. Bechtold, D. Campbell, M. K. Wu, J. Ashburn, and C. Y. Huang (unpublished).
[6]C. Michel and B. Raveau, Rev. Chem. Miner. **21**, 407 (1984).
[7]J. J. Yu, J.-H. Xu, and A. J. Freeman, Phys. Rev. Lett. **58**, 1035 (1987).
[8]C. L. Fu and A. J. Freeman (unpublished).