Superconductivity above 90 K in the compound $YBa_2Cu_3O_x$: Structural, transport, and magnetic properties

P. M. Grant, R. B. Beyers, E. M. Engler, G. Lim, S. S. P. Parkin, M. L. Ramirez, V. Y. Lee, A. Nazzal, J. E. Vazquez, and R. J. Savoy

IBM Almaden Research Center, San Jose, California 95120

We report the structural, transport, and magnetic properties of the principal phase responsible for superconductivity in the recently discovered Y-Ba-Cu-O compounds with transition temperatures greater than 90 K.

After many years of intense search for superconductors with transition temperatures significantly higher than 20 K, a literal explosion of success has occurred in past months. Beginning with the discovery by Bednorz and Müller[1] of a 30-K transition in $La_{2-x}Ba_xCuO_{4-y}$, a rapid series of advances has occurred culminating in recent reports by Wu *et al.*;[2] Chu *et al.*;[3] Tarascon, Greene, McKinnon, and Hull;[4] and Zhao *et al.*[5] of an onset temperature greater than 90 K in multiphase material produced from various mixtures of Y, Ba, and Cu compounds subsequently oxidized at high temperature.

In this paper, we report identification of the phase responsible for the superconducting behavior, and detail its preparation, characterization, transport, and magnetic properties. We also report the value of the lower critical field, and estimate the thermodynamic critical field and κ (penetration depth to coherence length ratio).

Few details have been reported on the synthesis of above–90 K superconductors. We explored a variety of preparative conditions and obtained our best results as follows: Ultrapure (99.999%) Y_2O_3, $BaCO_3$, and CuO powders were rigorously mixed in atomic ratios of [Y]/[Ba]/[Cu] $= 1.2/0.8/1.0$, and heated in flowing oxygen at 900 °C for 24 h. The resulting green insulating powder was reground and reheated for another 24 h. A darker green powder was obtained which was pressed into pellets (typically 1 cm in diameter and 1–2 mm thick), and sintered at 1000 °C in air for 2 h. The oven was allowed to cool down slowly to room temperature over a period of 8 h yielding dark grey pellets. In comparison to the $La_{2-x}Sr_xCuO_{4-y}$ system, the Y-Ba-Cu-O materials are considerably more sensitive to preparative details and we observed a wide range of related transition temperatures throughout the course of this work.

Examined under optical microscopy, typical sample material prepared as described above displayed intermixed green and black particles. Electron microprobe, x-ray diffraction, and transmission electron microscopy (TEM) were used to analyze these particles. Electron microprobe showed that the nominal composition of the green material was $Y_{0.2}Ba_{0.1}Cu_{0.1}O_{0.5-0.6}$ and that of the black phase $Y_{0.1-0.2}Ba_{0.1-0.2}Cu_{0.2-0.3}O_{0.5-0.6}$. Energy-dispersive analysis on individual crystals in the TEM detected the same Y-Ba compositions as the microprobe. Both the microprobe and the TEM composition analyses found that the green crystals were uniform from grain-to-

grain, whereas the black crystals showed significant composition variations. This variation in the black crystals may be due to inhomogeneities in a single phase or to the presence of more than one phase.

Preliminary analysis by Chu and co-workers[6] indicates that the green phase is orthorhombic and the black phase cubic or tetragonal. However, they found that presence of the black phase is necessary for superconductivity, whereas the green phase by itself does not superconduct. Consequently, we focused on identifying the major phase in the black material. X-ray diffraction spectra of powder samples indicated that this phase was pseudotetragonal (orthorhombic) with lattice parameters $a = 3.89$ Å, $b = 11.69$ Å, and $c = 3.82$ Å. Convergent-beam electron diffraction in conjunction with x-ray diffraction identified the space group as *Pmm*2. The proposed unit cell is shown in Fig. 1, an oxygen-defect perovskite structure with ordering of the Y and Ba atoms, and it is consistent with our compositional and structural data. We note that this finding contrasts with Chu *et al.*,[3] who suggest that perovskite phases might not be present. Also note that our structure is potentially much more three dimensional[7]
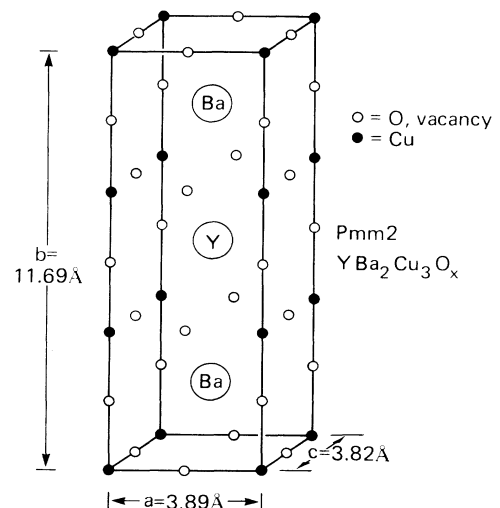

FIG. 1. Unit cell of the oxygen-defect perovskite $YBa_2Cu_3O_x$.

than the layered perovskite K_2NiF_4. Figure 1 is an ideal-ized structure and is not intended to indicate precise atomic cell coordinates nor oxygen site occupation. It is likely that oxygen and copper atoms in the middle third of the cell will be compressed due to the larger size of the Ba ions relative to yttrium. We also note that, unlike the sit-uation for the layered perovskite systems, here the alkaline-earth metal Ba does not play the role of an oxi-dizing dopant. The transport properties of oxygen-defect perovskite structures have been discussed by Michel and Raveau[8] and are shown to be very sensitive to oxygen con-tent which can vary over surprisingly large ranges. More-over, as oxygen content increases, the Cu^{3+}-to-Cu^{2+} mixed-valence ratio increases, a condition speculated by Bednorz and Müller[1] as necessary for high-temperature superconductivity. Studies of samples with the same nom-inal compositions as the black and green materials are in progress to refine our proposed structure and to identify additional phases. Details will be published later.[9]

Proceeding on the insights gained above, two constitu-ent mixtures were prepared according to the atomic ratios [Y]/[Ba]/[Cu] $=2/1/1$ and $1/2/3$, respectively, and heated at 925 °C in flowing O_2 for 12 h. Separate green and black powders were obtained as expected, given our previ-ous analysis. Pellets were then formed and sintered at 950 °C for 12 h under a variety of conditions. The $2/1/1$ stoichiometry was always insulating and always green. The black $1/2/3$ material became conducting when an-nealed under O_2 flow, while annealing under argon alone yielded only insulating material. The rate of removal from the oven was found to be critical in obtaining both high T_c and narrow transition widths. The x-ray pattern of the black material was consistent with the structure given in Fig. 1 as the major phase.

Figure 2 shows the resistance data on two samples of black material quenched at different rates from the final oxygen anneal. Data were taken by the four-probe tech-n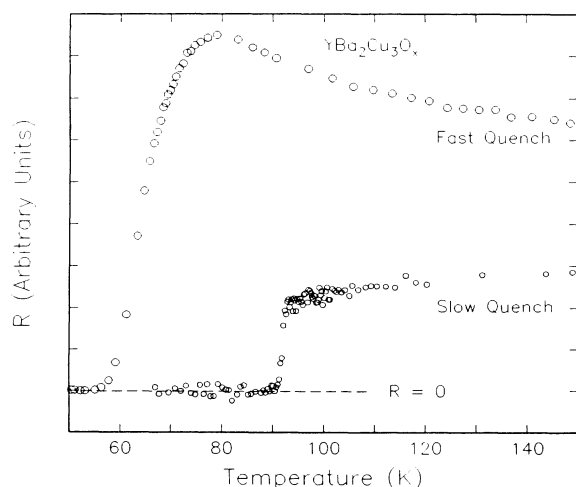ique using silver paste contacts painted around the sam-ple and lock-in detection with current densities kept less than 10 $\mu A/cm^2$. The sample itself was cemented directly onto a Lake Shore diode (calibrated to ± 0.5 K) with GE varnish assuring that both the thermometer and sample were in equilibrium at all temperatures. The rapidly quenched sample displayed below 200 K a negative resis-tivity coefficient ending in what is possibly a weak-localization peak around 80 K after which superconduc-tivity dominates, resulting in zero resistance near 57 K. The behavior of the slowly quenched cooled sample is markedly different. The normal-state resistance near the transition was very low, perhaps three to four times under that of samples prepared by former methods. The onset occurs at 92.5 K and reaches zero resistance at 90 K.

Figure 3 summarizes our magnetometry results on the slow-quench-cooled sample of Fig. 2. We show the di-amagnetic shielding obtained by cooling in zero field[10] and then applying a 20 mT field (lower curve), followed by warming in this field and subsequent cooling, resulting in the observed Meissner effect (upper curve). Our low-temperature diamagnetic shielding is almost complete, nearing 100% when demagnetization and porosity correc-tions are applied. We do not understand at present the small deviation between 40–70 K. The Meissner effect saturates very quickly to around 20%. Both effects have a very sharp onset and agree precisely with the temperature for zero resistance seen in Fig. 2. The magnitude of both effects is the largest yet reported and indicates that the bulk of the sample superconducts. It would be difficult to account for these values on the basis of interfacial effects alone. We have measured the field dependence of the magnetization at 4 K and find the lower critical field, $H_{c1} \simeq 400$ Oe defined at the point of departure from linear dependence. Using $H_{c2} \simeq 100$ T at $T=0$ K as estimated by Chu et al.,[3] with the relations[11] $H_{c1} = (H_c \ln \kappa)/1.414\kappa$ and $H_{c2} = 1.414 \kappa H_c$, where H_c is the $T=0$ K thermo-dynamic critical field and κ the ratio of penetration depth to coherence length, we find $H_c \simeq 9600$ Oe and $\kappa \simeq 70$. From the expression $\gamma^{1/2} \simeq H_c(0)/T_c$, and the results of Finnemore et al.[12] on the layered perovskite system, we

FIG. 2. Resistivity vs temperature for black material of ma-jor phase given in Fig. 1 as obtained under rapid and slow cool-ing conditions; that is, rate of removal from the furnace after final anneal. Both curves are to the same scale.
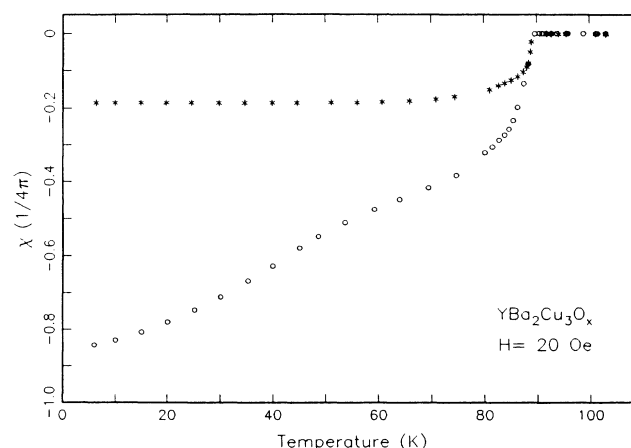
FIG. 3. Magnetometry data for the slowly cooled material of Fig. 2: Susceptibility vs temperature showing diamagnetic shielding (lower curve) and Meissner effect (upper curve).

infer that the electronic specific-heat coefficient γ will not be very different in the Y-Ba-Cu-O compounds. More complete details will be published later.[13]

In summary, we have determined the superconducting phase in the Y-Ba-Cu-O quaternary system and measured its transport and magnetic properties. But why is its transition temperature so high? It is unlikely that the electronic density of states will be much different than in the layered perovskites as the transport bands in both are formed from $Cu(3d)$—$O(2p)$ bonds. However, by virtue of being an oxygen-defect perovskite, $YBa_2Cu_3O_x$ may have a considerably wider range of Cu^{3+}-Cu^{2+} mixed-valence electronic states. As pointed out by Cava, van Dover, Batlogg, and Rietman,[14] doping with an alkaline-earth metal alone can only control the Cu oxidation state within certain limits. We believe that it is the ability of $YBa_2Cu_3O_x$ to sustain a large range of mixed valency, as demonstrated by its sensitivity to oxidation and quenching conditions, that is responsible for its high and variable transition temperature, and that even higher temperatures might be achieved by exploring similar materials.

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