Superconductivity in argon-treated Y-Ba-Cu-O system

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We report resistivity results in argon-processed Y-Ba-Cu-O, similar to those recently reported in Eu-$Ba_2Cu_3O_{6+\delta}$, which were interpreted as possible indication of T_c above 200 K. Scanning Auger microanalysis indicated measurable argon at the surface. However, the observed results cannot be accounted for as solely due to surface effects, but may be due to an incipient metal-to-insulator transition around 220 K, and of an insulator "phase" formed on the grain boundaries and on the surface due to argon treatment.

There have been several reports of possible indications of superconductivity above 200 K in oxide superconductors. Chu[1] recently announced the observation of sharp drops in resistance of several Y, Sc, and La-based multiphase Ba-Cu oxide materials at temperatures as high as 240 K; however, the resistance drops vanished during thermal cyclings. Chen, Wenger, McEwan, and Logothetis[2] reported the detection of reverse ac Josephson effect in mixed-phase Y-Ba-Cu oxide specimens below 240 K, indicating the possible presence of T_c above 200 K. The exact processing conditions under which these high-T_c materials were made has not been adequately described. Very recently, Huang *et al.*[3] reported the observation of a sharp drop in resistance at 230 K in one argon-treated specimen of $EuBa_2Cu_3O_{6+\delta}$. The only processing information given was that the specimen was pumped at room temperature, and then exposed to argon for 48 h. They also suggest that a similar processing could prove useful for Y-Ba-Cu-O compound. We have now conducted a detailed study of argon processing in several specimens of Y-Ba-Cu-O, and obtained results very similar to that obtained by Huang *et al.*, in a reproducible fashion. Based on our observations we consider it unlikely that these results indicate a possible T_c above 200 K.

The method used in synthesizing Y-Ba-Cu-O compounds used in this study has been described elsewhere;[4] x-ray analysis indicated that the crystal structure was the typical orthorhombic phase. Most of the specimens used in this study showed a T_c of around 90 K before argon treatment. The argon treatment consisted of pumping for several hours in a vacuum of better than 10^{-5} Torr, at room temperature, followed immediately by exposure to flowing argon at room temperature again for several hours. The details for various specimens are given in Table I. All these specimens showed (qualitatively) similar resisitivity behavior with temperature (see below). The change in resistivity profile was least for specimens containing Nd.

Indium contacts were soldered to the samples for four-probe, ac resistance measurements. Figure 1 shows $R(T)$ for specimen A. The measurements, made with 50, 500, and 5000 μA currents, show a sharp superconducting transition (between 91 and 93 K) to a resistance of 2 mΩ. The resistance increases linearly to a value of 4 mΩ at

TABLE I. Details of argon treatment for various specimens.

Experiment	Specimen	Composition	Time for pumping	Time for argon exposure	Remarks
1	A	$YBa_2Cu_3O_x$	24 h	24 h	
2	A	$YBa_2Cu_3O_x$	24 h	72 h	
3	A	$YBa_2Cu_3O_x$	⋯	⋯	Resistance measured again after removing surface layer by sandpaper
4	A	$YBa_2Cu_3O_x$	⋯	⋯	Resistance measured after second rubbing with sandpaper
5	B	$YBa_2Cu_3O_x$	24 h	72 h	
6	C	$Y_{0.9}Nd_{0.1}Ba_2Cu_3O_x$	24 h	72 h	
7	D	$Y_{0.1}Nd_{0.9}Ba_2Cu_3O_x$	24 h	72 h	

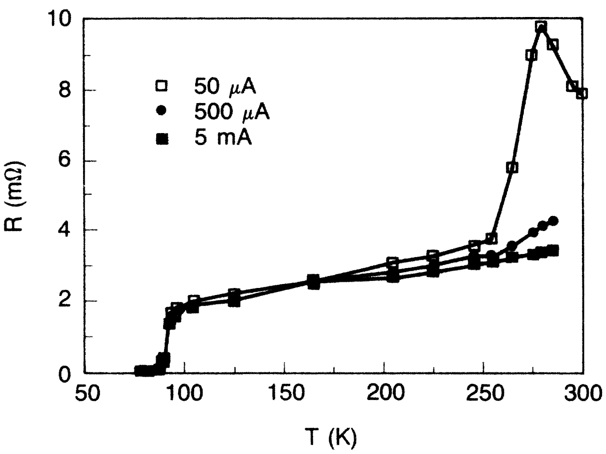

FIG. 1. Resistance vs temperature for argon-treated $YBa_2Cu_3O_{7-y}$ measured with 50, 500, and 5000 μA currents.

around 250 K where the curves for the three currents separate. The 50 μA data show a substantial resistance increase which peaks at about 275 K. The higher current data show much smaller resistance increases. The measurements were made during both warming and cooling the sample and a final 50 μA room-temperature resistance measurement, made before the removing the sample from the cryostat, agreed with the initial 50 μA resistance. The measurements were repeated on the sample after the top millimeter was sanded off as well as on several other samples. These curves had the same general behavior with the peak in the 50 μA resistance measurement varying from 275 to over 300 K.

As stated before others have attributed such large resistance changes above 200 K to extra high T_c superconducting filaments. This looks unlikely since our data show the high-temperature resistance decreasing with large currents rather than the low-temperature resistance increasing as would be expected from exceeding the critical current of the filaments. This conclusion is consistent with magnetization versus temperature measurements made on susceptometer superconducting quantum interference device (SQUID) (Fig. 2). The sample shows a virtually flat magnetic signal from 300 to 93 K where the diamagnetic onset occurs. From the magnitude of the signal at 50 K we estimate approximately 5% flux expulsion. Magnifying the curve between 200 and 300 K (inset) shows a very weak increase in the signal with decreasing temperature and no hint of diamagnetism. The points between 300 and 93 K have 10% uncertainties.

Scanning Auger microscope (SAM) analysis was conducted on several specimens used in this study. Compositional maps were prepared for the specimens *A* and *B* before argon treatment. Specimen *A* indicated several composition inhomogeneities and appeared to be somewhat granular, at least at some places. The specimen *B*, on the other hand, was much more homogeneous compositionwise, and also appeared to be smooth at higher magnification (×10 000), in the scanning electron microscope (SEM). After argon treatment, SAM analysis was performed at the surface in specimen *B* to detect argon. [SAM analysis of course detects composition only in the first few atomic layers (less than 100 Å in depth).] Some evidence for the presence of argon was found at the surface. The SEM observations are an indication that the resistivity effects are probably not due to granular nature of some of the specimens.

As stated before, our results do not support a claim of T_c around 220 K as suggested by Huang *et al.*[3] However, some other causes for these results such as an anomaly in terms of a semiconductor metal transition should be explored. In this connection it is interesting to note that Testardi *et al.*[5] have detected a discontinuity in static

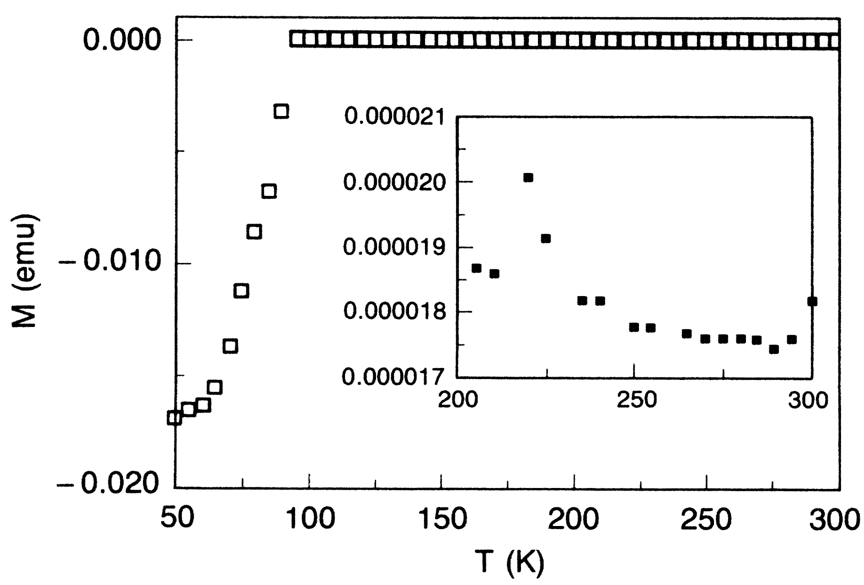

FIG. 2. Magnetization vs temperature for argon-treated $YBa_2Cu_3O_{7-y}$ showing a diamagnetic onset at 93 K and no diamagnetic shift above 200 K (inset). The points above 93 K have a 5–10% uncertainty.

dielectric constant at 220 K (observed on both cooling and heating). However, they found that anomaly at this temperature is substantially smaller or nonexistent. Jezowski *et al.*[6] have measured electrical resisitivity as well as thermal conductivity of single phase Y-Ba-Cu-O in the temperature range 5–320 K. The electrical resistivity was found to change linearly in the normal state up to the highest measured temperature. They did, however, detect a small departure from linear dependence at a temperature between 220 and 260 K. It should also be noted that a change of slope in the temperature dependence of the thermopower has also been observed around this temperature.[6]

Based on these observations, we propose that the resistance anomaly occurring in some of these specimens is most likely associated with an order-disorder transition of oxygen on or near the grain boundaries of the orthorhombic grains (showing superconducting at ~90 K). When the specimens are subjected to long-term vacuum or argon anneals (even at room temperature) oxygen content on or near grain boundaries is partially depleted, causing excess resistance to occur between grains due to this presumably tetragonal-like "phase" at or near the grain boundaries.

This shows up both as a much larger total resistance (due to insulating nature of the new "phase") and an activated temperature dependence of the resistance near 300 K due to hopping conduction between grains. In a recent study by Fiory, Gurvitch, Cava, and Espinosa,[7] which determined the temperature and composition dependence of the tetragonal-to-orthorhombic transition, it was found by extrapolation that such a transition could occur at or below room temperature for a composition of $Y_1Ba_2Cu_3O_{6.2}$. At some temperature below room temperature oxygen and oxygen vacancies order, the surface "phase" reverts to the orthorhombic structure, and the boundaries become metallic, reducing the resistance close to the intrinsic resistivity of the material; and the specimen shows a large resistivity anomaly. Thus, this may not be an indication of superconductivity but in fact may reflect a change from insulating to conducting behavior of the grain boundary. The anomaly seen in the dielectric constant and other anomalies mentioned before can be explained on the same basis.

The anomaly seen in dielectric constant (see above) in going from a very large value consistent with a ferroelectric insulator to a smaller value thus reflects the "ordering" mentioned above, and is a precursor of the metallic orthorhombic structure. If the above explanation is right, one should be able to reproduce these results without argon processing, by a suitable choice of composition and processing conditions. Our preliminary results indicate that this is indeed possible. We have been able to reproduce a resistivity profile similar to that shown in Fig. 1, without argon treatment in one specimen of Y-Ba-Cu-O.

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