

Observation of possible superconductivity at 230 K

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Recently, Chu¹ announced the observation of sharp drops of up to two orders of magnitude in the resistance of several Y-, Sc- and La-based multi-phase Ba-Cu oxide samples at temperatures as high as 240 K. The resistance drops reported did not survive the thermal cyclings for magnetic measurements. Later, M. H. Cohen (personal communication) reported similar anomalies in some Y-based oxides. In the absence of zero resistivity and evidence for the Meissner effect, the sharp resistance drops have been taken only as an indication of the possible existence of superconductivity at these unusually high temperatures. More recently, Chen *et al.*² detected the reverse a.c. Josephson effect in mixed-phase Y-Ba-Cu oxide samples below 240 K, providing the strongest evidence for superconductivity to date. Here we report the observation of a sharp decrease in resistance of at least four orders of magnitude at ~ 230 K in one annealed sample of $\text{EuBa}_2\text{Cu}_3\text{O}_{6+\delta}$. Subsequent magnetic measurements on the same sample indicated a magnetic anomaly at the same temperature.

The $\text{EuBa}_2\text{Cu}_3\text{O}_{6+\delta}$ sample was synthesized by a one-step solid-state reaction of appropriate amounts of Eu_2O_3 , BaCO_3 and CuO . The powders were pressed into pellets which were then heated in a reduced oxygen atmosphere ($2,000 \mu\text{m O}_2$ partial pressure) at 925°C for 4 h and cooled at room temperature. The X-ray diffraction patterns show that the sample displays only an orthorhombic phase typical for the 1-2-3 compounds and no phase transformation has been observed from 77 K. Based on our Mossbauer measurement, no anomaly has been observed from 300 K down to 4 K. This 90-K superconductor was pumped at 300 K and then exposed to argon for 48 h. The resistance of the sample was measured using a conventional four-point probe technique. The sample has a length of ~ 3 mm and a cross-section of $\sim 1 \times 2$ mm. The results at 1 mA are displayed in Fig. 1. The onset of the sharp drop in resistance (from $\sim 1 \Omega$) occurs at ~ 238 K and the resistivity reaches the zero-baseline ($\leq 10^{-4} \Omega$ —our experimental resolution) at

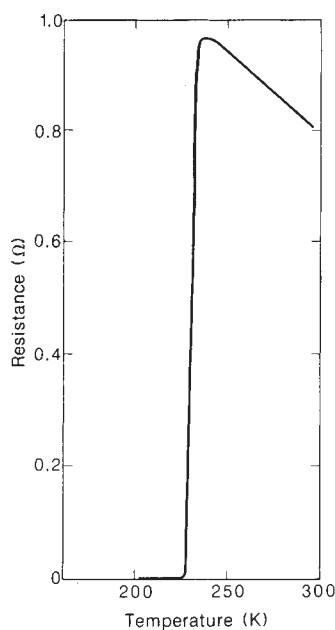


Fig. 1 Resistance plotted against temperature curve for mixed-phase $\text{EuBa}_2\text{Cu}_3\text{O}_{6+\delta}$.

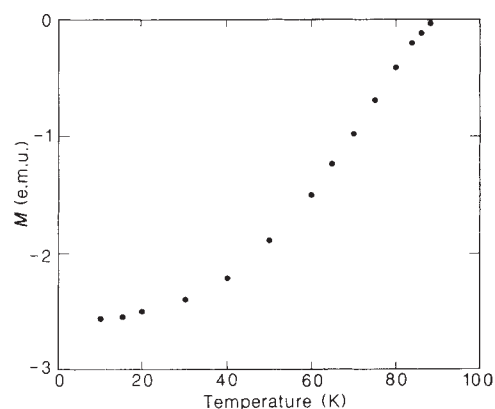


Fig. 2 Magnetization, M , at 100 G plotted against temperature, $T < 90$ K.

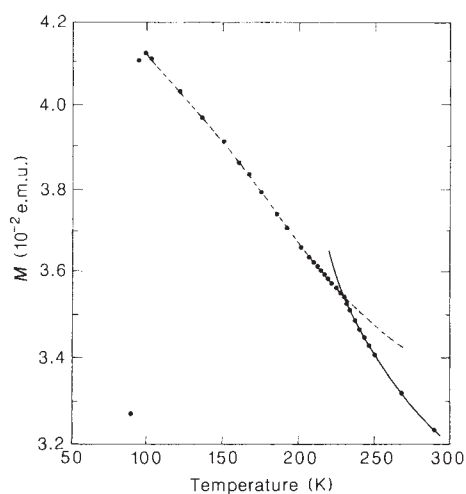


Fig. 3 Magnetization, M , at 100 G plotted against temperature, $T > 90$ K. The solid and dashed curves are guides for the eye.

~ 228 K. The midpoint of the drop is at ~ 230 K. A similar sharp drop in resistance at 0.1 mA was reproduced the following day. (The smaller current was used to avoid damaging the sample as we had done previously.) We interpret this sharp drop as a superconducting transition. However, the zero-resistance phenomenon at 230 K disappeared after several thermal cyclings, even though a small kink appeared at ~ 230 K. The kink disappeared completely after four weeks and the sample became an average 90-K superconductor. We point out that we have prepared several samples in the same manner as described but none has exhibited zero resistance at 230 K, even though some of them have somewhat higher superconducting transition temperatures.

To confirm the nature of this transition, it was necessary to measure the magnetization, M . The same sample was taken to the National Magnet Laboratory at Massachusetts Institute of Technology (MIT) one week later to use the SHE Model 905 SQUID magnetometer. Figure 2 shows the magnetization data below 90 K taken at 100 G. The temperature dependence shows that the superconducting transition is rather broad in comparison with a good, unpumped 90-K sample of $\text{EuBa}_2\text{Cu}_3\text{O}_{6+\delta}$ ³. The diamagnetic magnetization at 10 K is only $\sim 33\%$ of that of perfect diamagnetism.

The high-temperature data measured at 100 G are shown in Fig. 3. The magnetization at 300 K is proportional to the applied field up to 5×10^4 G, demonstrating that the sample is paramagnetic. On cooling, the magnetization of the sample increases with decreasing temperature, expected for a paramagnet. But at 230 K, the rate of increase suddenly decreases, suggesting the onset of a diamagnetic component due to the Meissner effect in the magnetization. This onset temperature coincides with the occurrence of the resistance drop as shown in Fig. 1. The appearance of both 'zero resistance' and diamagnetism strongly suggests the onset of superconductivity at ~ 230 K. The observed magnetic anomaly is reversible. We have been able to reproduce this anomaly even at 900 G. Although the diamagnetic signal is clear, its small magnitude suggests that the 230-K superconductivity may arise from 'percolated' superconducting linear chains occupying only a small fraction of the sample (a few parts in 10^4). In the absence of any anomaly based on the Mossbauer measurement, which could detect both the structural and

semiconductor-metal transformations and because of no example (except⁴ $\text{V}_{2-x}\text{Cr}_x\text{O}_3$ over a limited x range) exhibiting a semiconductor-metal transition on cooling, we rule out the interpretation of this anomaly in terms of a semiconductor-metal transition. The diamagnetic component has persisted through several thermal cyclings for more than three weeks.

The observations reported here, and in refs 1 and 2, appear to require the existence of a new structural or compositional phase which is different from the 1-2-3 90-K compound, independent of the trivalent element involved. We would also like to point out that the superconducting phase reported here may not be the same as those reported in refs 1 and 2. More experiments are necessary to obtain this high-temperature superconducting phase.

C.Y.H. would like to thank C. J. Lobb for stimulating discussions. The work at Lockheed is supported by Lockheed Independent Research funds and that at Houston by NSF, NASA and the Energy Lab of the University of Houston. The Francis Bitter National Magnet Laboratory is supported by NSF.

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