Observation of possible superconductivity at 230 K

C. Y. Huang*, L. J. Dries*, P. H. Hor†, R. L. Meng†, C. W. Chu† & R. B. Frankel‡

* Lockheed Palo Alto Research Laboratory, Palo Alto, California 94304-1191, USA

† Department of Physics, University of Houston, Houston, Texas 77004, USA

‡ Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

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 EuBa₂Cu₃O₆₊₈. Subsequent magnetic measurements on the same sample indicated a magnetic anomaly at the same temperature.

The EuBa₂Cu₃O₆₊₈ sample was synthesized by a one-step solid-state reaction of appropriate amounts of Eu₂O₃, BaCO₃ and CuO. The powders were pressed into pellets which were then heated in a reduced oxygen atmosphere (2,000 µm O₂ 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 \sim 3 mm and a cross-section of ~1×2 mm. The results at 1 mA are displayed in Fig. 1. The onset of the sharp drop in resistance (from ~1 Ω) occurs at ~238 K and the resistivity reaches the zero-baseline ($\leq 10^{-4} \Omega$ —our experimental resolution) at

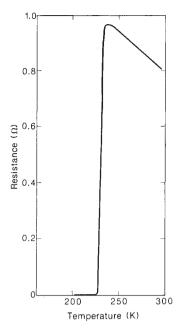


Fig. 1 Resistance plotted against temperature curve for mixedphase EuBa₂Cu₃O_{6+ δ}.

 \sim 228 K. The midpoint of the drop is at \sim 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 EuBa₂Cu₃O_{6+ δ}³. The diamagnetic magnetization at 10 K is only ~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 superconducvitity 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 10⁴). In the absence of any anomaly based on the Mossbauer measurement, which could detect both the structural and

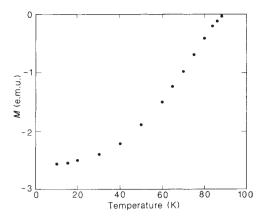


Fig. 2 Magnetization, M, at 100 G plotted against temperature, T < 90 K.

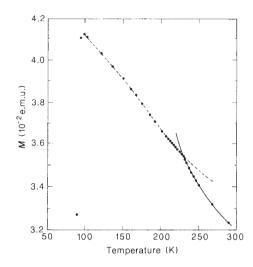


Fig. 3 Magnetization, M, at 100 G plotted against temperature, T > 90 K. The solid and dashed curves are guides for the eye.

semiconductor-metal transformations and because of no example (except 4 V_{2-x} Cr_xO_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.

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^{1.} Chu, C. W. NSF News Release and Univ. Houston News Release, 16 February 1987; The New York Times, 10 March 1987

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