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David D. Allred
allred@byu.edu

S. R. Ovshinsky

R. T. Young

G. DeMaggio

G. A. Van der Leeden

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Superconductivity at 155 K

S. R. Ovshinsky, R. T. Young, D. D. Allred, G. DeMaggio, and G. A. Van der Leeden
Energy Conversion Devices, Inc., Troy, Michigan 48084
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Transition to a superconducting zero-resistance state at 155 K is observed for the first time in bulk material. A new five-element compound has been synthesized with nominal composition $Y_1Ba_2Cu_3F_2O_y$. Fluorine plays a critical role in achieving this effect. X-ray diffraction and electron microprobe analysis indicate that the samples are multiphasic. Evidence is presented that the samples contain superconducting phases with onset temperatures considerably above 155 K. Magnetic measurements suggest a flux-trapping effect below 260 K, and diamagnetic deviations from Curie-Weiss behavior in the range 250 K $\leq T \leq$ 100 K indicate a Meissner effect in a small superconducting volume fraction.

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The accomplishment of high-temperature superconductivity is of immense scientific and technological importance. Several critical transition-temperature barriers have recently been breached since the long-standing record temperature of 23.2 K for Nb_3Ge was exceeded. The most important milestones were the announcement of $T_c \approx 30$ K in lanthanum barium copper oxide by Bednorz and Müller,[1] whose work was based upon materials developed by Michel and Raveau,[2] and the work of Chu, Wu, and others,[3] based upon the replacement of lanthanum by yttrium, which resulted in superconductivity at temperatures of approximately 95 K.

Indirect measurement techniques[4,5] have been used[6] previously to infer the existence of regions of high-T_c phases in Y-Ba-Cu-O systems. We report here for the first time the direct measurement of a zero-resistance superconducting state at 155 K. This result was observed in a new chemical system, Y-Ba-Cu-F-O.

In the quest for even higher transition temperatures, variations and replacements in the metallic portion of the compounds have not been fruitful. It was found that yttrium could be replaced by most of the rare-earth metals with achievement of approximately the same T_c.[7] Our approach has been to synthesize a new five-element compound, which has resulted in the achievement of considerably higher T_c's. In one sample, the transition to zero resistance was observed at temperatures as high as 155 K. In another sample, an abnormally rapid decline of resistivity was observed starting at room temperature, which suggests the existence of phases exhibiting superconducting onset above room temperature. We have also observed anomalies in the magnetic properties, as well as weak flux trapping below 260 K. This material contains at least four presently identified structural phases. Work is continuing to identify unambiguously the structure of the high-T_c phases. In previous papers[8] we have discussed the significant role that fluorine plays in affecting the electronic and structural properties in other multielemental materials, particularly in affecting orbital interactions. These factors[9] motivated us to synthesize the fluorinated Y-Ba-Cu-O compounds reported here.

Samples with nominal compositions $Y_1Ba_2Cu_3F_xO_y$ ($x=0$, 1, 2, 3, and 4) were prepared from two master compositions, $Y_1Ba_2Cu_3O_{6.5}$ and $Y_1Ba_2Cu_3F_4O_{4.5}$, which define the compositional extremes ($x=0$ and $x=4$). The starting reagents used to prepare the oxide and fluoroxide were (Y_2O_3, $BaCO_3$, and CuO) and (Y_2O_3, BaF_2, and CuO), respectively. Each master composition was prepared by a mixing of the sieved reagent powders, and grinding and firing of them in air in a Pt crucible at 950 °C for 8 h. After the initial firing the master compositions were reground. Samples were prepared from mixtures of the two master compositions which were pressed into $\frac{1}{2}$-in. pellets and sintered at 950 °C in flowing O_2 for 48 h, and then cooled to 200 °C over a period of 6 h. Samples were examined by x-ray powder diffraction and microprobe to determine their structure, phases, and composition. Table I summarizes the various phases and

TABLE I. Various phases and compositions of $Y_1Ba_2Cu_3F_xO_y$ from x-ray diffraction and microprobe analysis.

x	$Y_1Ba_2Cu_3O_{7-\Delta}$	$Y_1Ba_2Cu_3O_y$:F	$Y_2Ba_1Cu_1O_y$:F	$Y_1Cu_2O_y$:F	BaF_2	CuO
$x=0$	×					
$x=1$		×	×		×	×
$x=2$		×	×		×	×
$x=3$			×	×	×	×
$x=4$				×	×	×

compositions which have been identified.

Electrical resistance was measured by means of a standard four-probe method on samples with silver-paint contacts. Rectangular bars $10\times2\times1$ mm^3 were cut from pellets for the measurements. The applied constant current ranged from 100 μA to 10 mA depending on the sample resistance. The dc magnetic susceptibility and flux trapping were studied with a SQUID magnetometer.

Of the five nominal compositions studied, only those with $x=0$, 1, and 2 show superconductivity, as measured by resistivity and magnetic susceptibility measurements. The room-temperature resistivity of samples with $x=3$ and $x=4$ is greater than 20 MΩ. The samples with $x=0$ show resistance-temperature behavior similar to that reported by others[7] for typical $YBa_2Cu_3O_{7-\Delta}$, with a modest decrease of resistivity from room temperature to the onset temperature of 95 K, reaching the zero-resistance state at 90–92 K. The $x=1$ sample showed a behavior essentially identical to that of the $x=0$ sample. Dramatically different and complex behavior was observed, however, in samples with $x=2$.

The temperature dependence of the resistance of a portion of the $x=2$ pellet is shown in Fig. 1. During the initial cooling, the sample (sample 1) completely lost its resistance at ≈ 168 K. After warming and measurement during second cooling, an increase of resistance was observed and the zero-resistance state was not reached until 148 K. An appreciable change in resistance was again observed during the second warming. The zero-resistance state remained (within our instrument noise level of $\approx 10^{-8}$ V) until 155 K. Several higher-temperature resistance transitions were also observed. The resistance anomalies seen upon warming and cooling are remarkable and may be connected with filamentary conduction.

Figure 2 shows a plot of the temperature dependence of the average resistivity for another sample (sample 2) with the $x=2$ composition. The average resistivity calculated with the assumption of uniform current density falls dramatically with temperature for this sample beginning at room temperature or above, and achieves resistivity values 5 times lower than that of single-crystal copper before the zero-resistance state is achieved at ≈ 91 K. We were able to fit the resistivity to a good approximation over the entire range by using a $T^{8.3}$ law. Since the resistivity became so low with decreasing temperature, a large current of 10 mA, or a current density of 0.5 A/cm^2, had to be applied during measurement. With the assumed multiphase filamentary type of conduction, this applied current density might have washed out more sharply defined high-T_c transitions. For comparison, the resistivity-temperature plot of pure copper[10] is also included in Fig. 2. The actual resistivity of the current-carrying phases will certainly be much less than

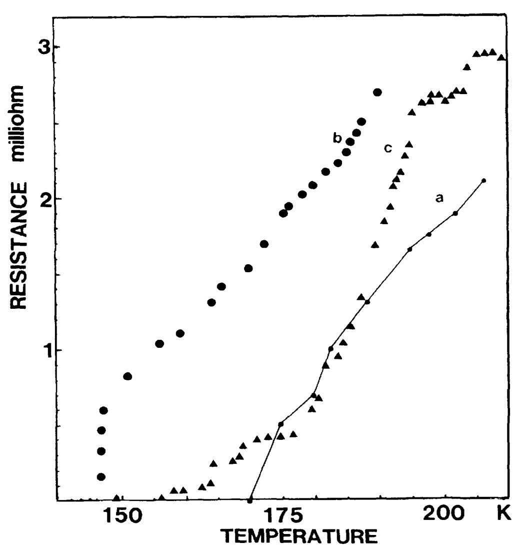

FIG. 1. Resistance vs temperature measured at constant current of 1 mA for sample 1 with nominal composition $YBa_2Cu_3F_2O_y$. Curve *a* shows the resistance upon initial cooling (line drawn to guide the eyes); curve *b*, data obtained upon second cooling; and curve *c*, data from warming after second cooling. In the superconducting state, voltage is less than 10^{-8} V, the noise level of the voltmeter. Sample dimensions are area $=1\times2$ mm^2, length $=10$ mm. This gives an average resistivity estimate of less than 2×10^{-7} Ω cm in the superconducting state.

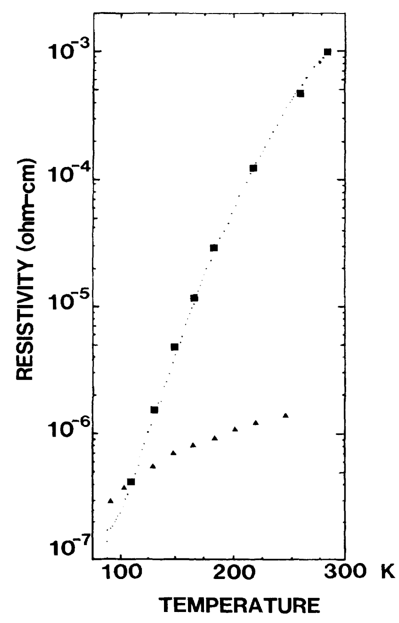

FIG. 2. The logarithm of the average resistivity of sample 2 of $YBa_2Cu_3F_2O_y$. Average resistivity was calculated on the assumption of uniform current density. Resistivity was found to follow T^n, where $n\approx8.3$; these points are indicated by squares. The ideal resistivity of pure copper (Ref. 10) is also plotted (triangles).

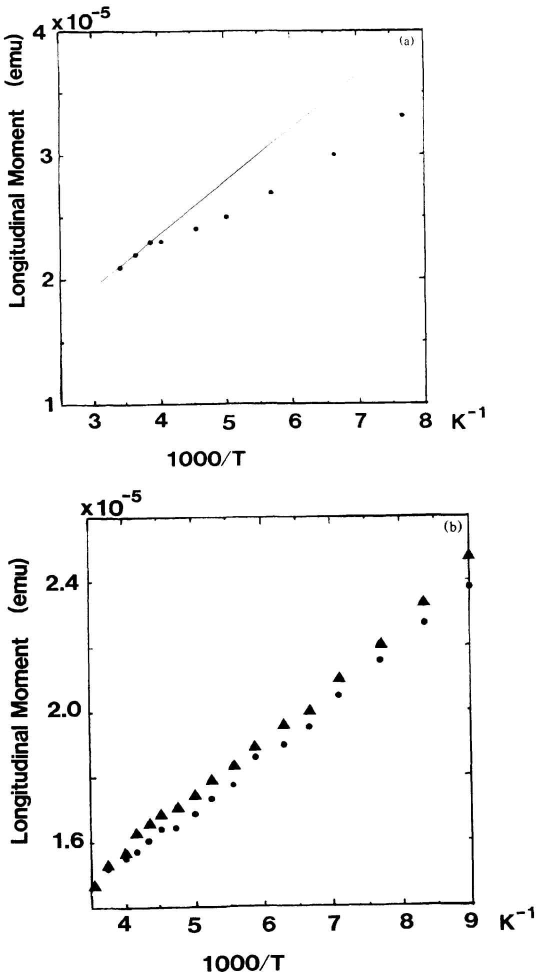

FIG. 3. Longitudinal moment vs $1000/T$ for $YBa_2Cu_3F_2O_y$. (a) Measurements made with use of 100-G field. Note the diamagnetic deviation from a Curie-Weiss law below 250 K. (b) Weak magnetic hysteresis at 20 G. Data for warming after zero-field cooling are indicated by circles and data from cooling with field applied are indicated by triangles.

the calculated average. The fact that the average resistivity of the multiphase ceramic material at a temperature of 91 K is 5 times lower than copper provides another indication of the existence of higher-temperature superconducting phases.

The magnetic measurements in Fig. 3 suggest that only a very small volume fraction of the sample is superconducting at these high temperatures. Figure 3(a) plots the magnetic moment as a function of temperature in a magnetic field of 100 G. The diamagnetic deviation from the Curie-Weiss law at temperatures below 250 K is an indication of the Meissner effect in this small volume fraction. A large diamagnetic response below 90 K is also observed but not plotted here. Weak magnetic hysteresis is observed as shown in Fig. 3(b), where the data on warming after zero-field cooling are indicated by circles and the data on cooling with field applied, by triangles. The facts that (1) the data of warming and cooling measurements coincide from room temperature until 260 K and deviate below this temperature and (2) the paramagnetism is stronger in the cooling process provide additional verification of the existence of high-temperature superconducting phases.

In summary, a zero-resistance state at 155 K has been observed in the fluorinated Y-Ba-Cu-O system and phases with even higher T_c have also been observed. The abnormally rapid decline of resistivity starting at room temperature suggests the existence of phases exhibiting superconducting onset above room temperature. The high-temperature phases are in the process of being identified. In the samples reported here, the volume fraction of the high-T_c materia. is very small as indicated by the magnetic data. Since a zero-resistance state requires a percolation path, the small-volume-fraction superconducting phase appears to be in a filamentary form. Work continues both to identify clearly the structure of the high-T_c phase or phases and to optimize materials synthesis to increase their yield.

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