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Authors

Fisk, Z
Thompson, JD
Zirngiebl, E
et al.

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SUPERCONDUCTIVITY OF RARE EARTH-BARIUM-COPPER OXIDES

Z. Fisk, J. D. Thompson, E. Zirngiebl, J. L. Smith and S-W. Cheong

Los Alamos National Laboratory, Physics Division,
Los Alamos, New Mexico 87545

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We report the superconductivity of R-Ba-Cu-O compounds for rare earths R = Sm through Ho. The Nd and Tm compounds were not observed to be superconducting. The T_c onsets for the Eu and Gd compounds are comparable to that observed for Y-Ba-Cu-O. An approximate value for the upper critical field slope of the Gd compound is given.

The discovery of superconductivity [1] above 90 K in a polyphase sample of nominal composition $Y_{1.2}Ba_{0.8}CuO_x$ has prompted a general search for other such materials. Great interest also attaches to the question of whether or not the usual BCS description fits these new superconductors. These considerations prompted the work reported in this note.

We prepared samples of rare earth-Ba-Cu-O materials by sintering rare earth and copper oxides with $BaCO_3$ in an O_2-atmosphere at 1000°C, with repeated regrindings. For the Eu material, we found the highest fraction of superconducting phase was obtained at the nominal composition $Eu_{1.5}Ba_{1.5}Cu_2O_x$. With the exception of the Sm and Tm materials, all our data were obtained from materials prepared at this composition. Subsequently, we learned from Cava et al. [2] that the superconducting phase in Y-Ba-Cu-O has the formula $YBa_2Cu_3O_{9-\delta}$. We confirmed with Eu and Gd preparations at this stoichiometry that our superconductivity results correspond to this phase. We note, in fact, that the composition which maximized our superconducting fraction is such that:

$$Eu_{1.5}Ba_{1.5}Cu_2O_x \rightarrow 1/2\ EuBa_2Cu_3O_y + 1/2\ Eu_2BaCuO_z$$

this latter phase being the green, semiconducting one found in [2]. In addition, transmission electron microscope (TEM) diffraction patterns on individual 1000-2000 Å single crystals (from our Eu material) that possess a unit cell corresponding closely to that reported in [2] showed an amorphisization of their diffraction patterns at N_2-temperatures on a cooled grid in the TEM [3]. This can be interpreted as evidence for the superconductivity of the crystallites since their superconducting shielding currents interfere with the electron beam focussing. We also note that the maximum diamagnetism observed for our predominantly two phase samples at 7.0 K corresponds to approximately 20% of $-1/4\pi$.

We present in Fig. 1 the electrical resistance in various magnetic fields for

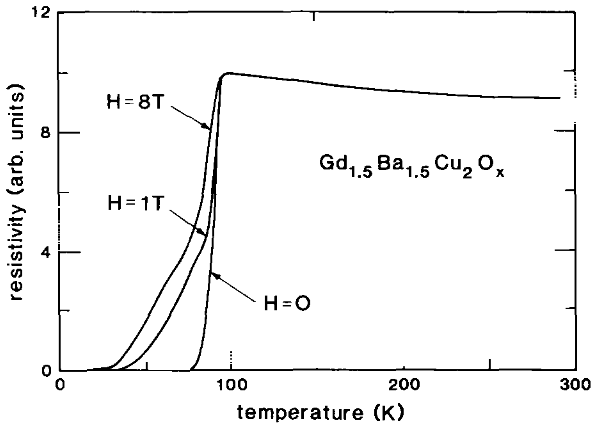

Fig. 1. Resistance as a function of temperature for $Gd_{1.5}Ba_{1.5}Cu_2O_x$ in magnetic fields of 0, 1, and 8 T. The magnetic field was applied approximately parallel to the direction of current flow in the sample. The measuring current was 0.1 mA at 223 Hz. Temperature errors due to magnetoresistance in the carbon-glass thermometer is estimated to be less than 0.1% at 1 T and 0.5% at 8 T.

$Gd_{1.5}Ba_{1.5}Cu_2O_x$. We see a reasonably sharp T_c with onset near 95 K, and some fluctuations in resistivity out to 104 K. In Fig. 2 we present some magnetic susceptibility data. Table I gives the T_c onsets observed for all the rare earth materials we have investigated. The Sm and Tm materials were prepared at a somewhat different stoichiometry before we had determined where the maximum superconducting signal was obtained.

The presence of local magnetic moments in superconductors is well known to be hostile to Cooper pair formation. It is remarkable that we see in our results no clear indication of such an effect in these materials. Gd, expected to

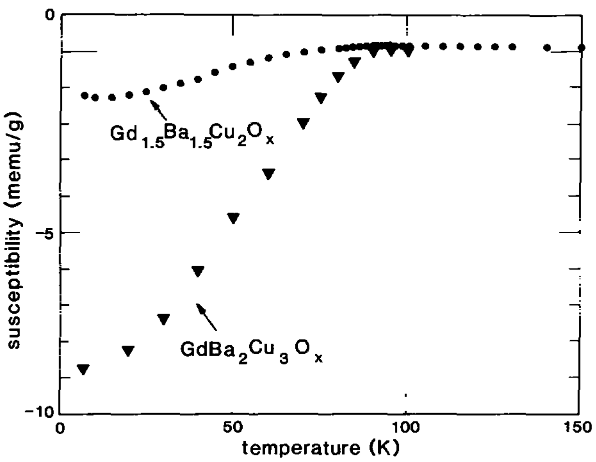

Fig. 2. dc magnetic susceptibility of $Gd_{1.5}Ba_{1.5}Cu_2O_x$ versus temperature. These data were obtained by cooling from above T_c to 7 K in zero applied field, increasing the field to 100 G, and then warming. Measurements were made with a Quantum Design SQUID magnetometer. A sign change in the slope $d\chi/dT$ occurs at 93 K and a diamagnetic response appears between 65 and 70 K. For comparison, results are shown for $GdBa_2Cu_3O_x$. Note the approximately eight times larger diamagnetism in this sample and comparable T_c. These results confirm our claim for the origin of superconductivity in $Gd_{1.5}Ba_{1.5}Cu_2O_x$.

depress T_c by the largest amount among the rare earths, has, in fact, the highest T_c. This lack of magnetic suppression is even more evident in the comparison of the Gd material with its neighbor Eu. Eu here is clearly trivalent as shown by Mossbauer measurements [4], and has, therefore, a J = 0 non-magnetic $4f^6$ ground state. The magnetic suppression on T_c should be much less for Eu here than Gd, and we see no indication of this. In the sequence of rare earth materials investigated, a dip in T_c is seen at Tb, and we have no explanation at present for this. It is possible that a magnetic transition interferes with the superconducting transition here.

Atomic size considerations are probably important in these superconductors and pressure effect measurements on T_c are clearly of interest and are in progress. The large value

Table I. Superconducting onset temperatures T_c determined from dc susceptibility measurements for rare earth-barium-copper-oxide compounds.

Compound	T (K)
$Nd_{1.5}Ba_{1.5}Cu_2O_x$	0
$Sm_{1.8}Ba_{1.2}CuO_x$	82 ± 2
$Eu_{1.5}Ba_{1.5}Cu_2O_x$	95 ± 3
$Gd_{1.5}Ba_{1.5}Cu_2O_x$	93 ± 1
$Tb_{1.5}Ba_{1.5}Cu_2O_x$	35 ± 3
$Dy_{1.5}Ba_{1.5}Cu_2O_x$	55 ± 3
$Ho_{1.5}Ba_{1.5}Cu_2O_x$	46 ± 2
$Tm_{1.8}Ba_{1.2}CuO_x$	0

of the upper critical field slope at T_c can be seen in Fig. 1 for the Gd materials and further such measurements are in progress. The large rare-earth fraction in the pure compounds leads to the expectation of magnetic order at some temperature. Superexchange interactions are probably important. We have no clue at present as to how strong this exchange might be, but it is to be expected that a signature of magnetic ordering will be observable in the upper critical field data. It is worth pointing out that magnetic suppressions of T_c are not expected to scale with T_c.

An estimate for dH_{c2}/dT ranges from -0.8 to -3.1 T/K when calculated from the 50% and 90% resistive transition temperatures, respectively. A simple argument that compares the Pauli limiting field to the oribital pair breaking field of a dirty type II superconductor suggests an upper limit on dH_{c2}/dT of about -2.7 T/K.

In summary, our results show the surprising insensitivity of T_c to the presence of local 4f-moments in the superconductors $RBa_2Cu_3O_{9-\delta}$. The Gd compound, with its large moment, has been found to have a T_c as high as any reported to date in the literature.

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