SUPERCONDUCTIVITY OF RARE EARTH-BARIUM-COPPER OXIDES

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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 Tc 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_7. 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_7 + 1/2 Eu_2BaCuO_2

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 amorphization 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 -1/4v.

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

![Graph showing resistance as a function of temperature for Gd_{1.5}Ba_{1.5}Cu_2O_x](image)

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 Tc 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 Tc 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.

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Fig. 2. dc magnetic susceptibility of Gd$_{1.5}$Ba$_{1.5}$Cu$_2$O$_x$ 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$_2$Cu$_3$O$_y$. 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$_2$O$_x$.

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>T (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd$<em>{1.9}$Ba$</em>{1.5}$Cu$_2$O$_x$</td>
<td>0</td>
</tr>
<tr>
<td>Sm$<em>{1.9}$Ba$</em>{1.5}$Cu$_2$O$_x$</td>
<td>82 ± 2</td>
</tr>
<tr>
<td>Eu$<em>{1.9}$Ba$</em>{1.5}$Cu$_2$O$_x$</td>
<td>95 ± 3</td>
</tr>
<tr>
<td>Gd$<em>{1.9}$Ba$</em>{1.5}$Cu$_2$O$_x$</td>
<td>93 ± 1</td>
</tr>
<tr>
<td>Tb$<em>{1.9}$Ba$</em>{1.5}$Cu$_2$O$_x$</td>
<td>35 ± 3</td>
</tr>
<tr>
<td>Dy$<em>{1.9}$Ba$</em>{1.5}$Cu$_2$O$_x$</td>
<td>55 ± 3</td>
</tr>
<tr>
<td>Ho$<em>{1.9}$Ba$</em>{1.5}$Cu$_2$O$_x$</td>
<td>46 ± 2</td>
</tr>
<tr>
<td>Tm$<em>{1.9}$Ba$</em>{1.5}$Cu$_2$O$_x$</td>
<td>0</td>
</tr>
</tbody>
</table>

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$_c$2/dT ranges from -0.8 to -3.1 T/K when calculated from the 50% and 90% resistive transition temperatures, respectively. A simple argument that compares the Pauli limiting field to the orbital pair breaking field of a dirty type II superconductor suggests an upper limit on dH$_c$2/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$_{2}$Cu$_{3}$O$_{y}$. 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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References

3. J. F. Smith and D. M. Parkin. private communication.