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LETTER TO THE EDITOR

SUPERCONDUCTIVITY ABOVE 90 K
IN MAGNETIC RARE EARTH–BARIUM–COPPER OXIDES

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We report measurements of the superconducting and magnetic behavior of GdBa$_2$Cu$_3$O$_x$ and ErBa$_2$Cu$_3$O$_x$. Superconductivity occurs below $T_c = 95$ and 93 K, respectively, for these compounds with large Meissner effects observed. The Gd-based compound has an upper critical field slope $-dH_{c2}/dT$ greater than 1.2 T/K. Both compounds exhibit Curie–Weiss behavior above $T_c$ with free-ion effective moments and small, negative temperature intercepts. In addition, the Gd-based compound orders antiferromagnetically below 2.24 K with an entropy consistent with the ordering of seven unpaired spins.

There has been an enormous amount of materials research on high $T_c$ superconductors since the report by Wu et al. [1] on superconductivity above 90 K in polyphase Y–Ba–Cu-oxide and the subsequent isolation of the superconducting phase [2]. We recently reported superconductivity in six rare earth (RE)–Ba–Cu-oxide compounds [3] (RE = Sm, Eu, Gd, Tb, Dy and Ho) and have found that $T_c$ is much the same in Y, Eu and Gd-based compounds, leading us to speculate that the magnetism of the 4f ion is somehow very ineffective at depressing $T_c$. We have performed further susceptibility, resistivity and heat capacity measurements on GdBa$_2$Cu$_3$O$_x$, which are reported here. In addition, we have prepared ErBa$_2$Cu$_3$O$_x$ and find that it also is superconducting below about 93 K.

The samples were prepared by sintering the rare earth oxide, CuO$_2$, and BaCO$_3$ in an O$_2$ atmosphere at 1000°C. The pellets were then reground and resintered at least three times to promote reaction and attainment of the desired phase, REBa$_2$Cu$_3$O$_x$.

Superconductivity occurs for the Gd-based compound below a critical temperature $T_c$ of (95 ± 3) K. Fig. 1 shows the transition to superconductivity upon cooling in an applied field (the Meissner effect) and the transition upon cooling in zero field, applying the magnetic field, and warming in the field, which shows the effect of shielding currents. We estimate that the Meissner effect amplitude corresponds to 20% of $-1/4\pi$ perfect diamagnetism and that the shielding cur-

Fig. 1. Magnetic susceptibility $\chi$ versus temperature for GdBa$_2$Cu$_3$O$_x$. A large diamagnetic response approaching 95% of $-1/4\pi$ is observed when the sample is cooled below $T_c$ in zero field and then measured upon warming in 100 G. About 20% of this diamagnetism is found when cooling in 100 G (Meissner effect). The inset shows $1/\chi$ as a function of temperature, with the measurement performed in 2 T. The effective moment agrees well with that expected from Hund's rules.
The diamagnetic signals are comparable to those observed in our earlier work [3] and are indicative of bulk superconductivity.

Resistivity measurements as a function of temperature and applied magnetic field have been performed to study the upper critical magnetic field $H_{c2}$ of GdBa$_2$Cu$_3$O$_x$; the results are shown in fig. 2. The main part of this figure shows the resistive transition in several applied fields. Because the transition broadens and changes shape in a field, we have calculated and displayed in the inset of fig. 2 two criteria for determining the transition temperature in a field: the temperature at which the resistance falls to either 0.9 or to 0.5 times $R_n$, the normal state value just above $T_c$. Employing the 0.5$R_n$ criterion, we find that $-dH_{c2}/dT$ has a value of approximately $(1.2 \pm 0.1)$ T/K. The critical field slope is much steeper, more than 3 T/K and possibly as large as 6 T/K using the 0.9$R_n$ criterion. This broad range occurs because of curvature in the data and the extreme sensitivity of the slope to the fit of a straight line. The values quoted here are consistent with those determined earlier on Gd$_{1.5}$Ba$_{1.5}$Cu$_3$O$_x$ [3].

Gadolinium is well known to strongly depress superconductivity in many metallic hosts because of the Cooper pair-breaking effect of its seven unpaired 4f spins [4]. In the rare earth–barium–copper-oxide systems, however, the effect of the Gd moments on superconductivity must be very small indeed as the $T_c$ of the Gd-based compound is essentially the same as in the Y-based material, which has no f electrons. To try to understand better the interaction of the Gd 4f's with the superconductivity, we have performed dc susceptibility $\chi$ and heat capacity $C$ measurements. The inset of fig. 1 shows the inverse susceptibility above $T_c$ plotted versus $T$. A good Curie–Weiss fit is obtained with the parameters $\rho_{\text{eff}} = 7.9\mu_B$, essentially the Gd free-ion value, and $\theta = -4.8$ K, which indicates weak antiferromagnetic correlations. The specific heat results in fig. 3, plotted as $C/T$ versus $T^2$ show a linear behavior above about 200 K (≈ 14 K), corresponding to a lattice contribution to the specific heat characterized by a $\theta_D$ of $(330 \pm 20)$ K. In general, the Debye law is only expected to be valid for $T \leq \theta_D/50$, or about 6.5 K. The fact that the above quoted value is in good agreement with that measured on the related system La$_{1.8}$Ba$_{0.2}$CuO$_4$ [5] may well be fortuitous. The upturn in $C/T$ below about 100 K (10 K) is actually the high temperature part of a magnetic ordering peak as shown in the inset of fig. 3, here
plotted versus $T$ with a compressed vertical scale. The maximum in $C/T$ occurs at 2.24 K; the maximum in $C$ is estimated to be not more than 0.01 K higher. The entropy under the transition peak integrated from 1.6 K, the lowest measured value, up to 4 K is 10.15 J/mol K. Extrapolating $C/T$ linearly from 1.6 K to zero gives an additional contribution of 5.2 J/mol K, for a total of about 0.9Rln 8, the expected entropy for magnetic ordering in Gd with seven unpaired spins. Although the above extrapolation is admittedly a rather long one, it appears to be quite reasonable.

Work is in progress to extend these measurements to lower temperatures and to determine the magnetic field dependence of $T_N$.

Susceptibility measurements at 1.8 K show no evidence of remanence or paramagnetic signals, thus implying that the order is not of a ferromagnetic nature. In addition, resistivity measurements show no reentrant behavior at 1.5 K. We thus conclude that the order is of an antiferromagnetic type which coexists with superconductivity, similar to the situation found in some rare earth–molybdenum–sulfide compounds [6].

We speculate that the weakness of interactions among the Gd ions, reflected in the low ordering temperature in this compound, may arise because of three mechanisms: 1) the relatively dilute concentration (about 8 at%) of the Gd ions in this structure tends to reduce their direct interactions; 2) the low carrier concentration implies a reduced number of conduction electrons available for carrying the RKKY interaction; and, 3) the large superconducting energy gap consistent with $T_c = 95$ K may interfere with the formation of magnetic correlations. All these mechanisms would work to reduce the magnetic ordering temperature.

We have also performed magnetic susceptibility and resistivity measurements on ErBa$_2$Cu$_3$O$_x$, and find it to be superconducting below 93 K. Our results are shown in fig. 4. The effective moment is 9.52μ_B and the Curie–Weiss θ value is −8.8 K, indicating slightly stronger correlations for the Er than for the Gd-based compound. The zero field cooled shielding currents correspond to 85–90% of the sample volume being superconducting; field cooled Meissner flux expulsion corresponds to about 10% of perfect diamagnetism. These results are very similar to those for the Gd compound.

The resistance measurements in the inset of fig. 4 show an onset $T_c$ of approximately 93 K but with superconducting fluctuations to much higher temperatures.

In conclusion, we report superconductivity in GdBa$_2$Cu$_3$O$_x$ and ErBa$_2$Cu$_3$O$_x$ as evidenced by Meissner effect and resistance anomalies near 95 K. The upper critical field slope for the Gd compound is greater than 1.2 or 3 T/K depending on the criterion chosen to determine $T_c$. Finally, the Gd compound orders antiferromagnetically at 2.24 K with an entropy consistent with Rln 8, corresponding to seven spins per Gd ion.

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