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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 $GdBa_2Cu_3O_x$ and $ErBa_2Cu_3O_x$. 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 $GdBa_2Cu_3O_x$, which are reported here. In addition, we have prepared $ErBa_2Cu_3O_x$ 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, $REBa_2Cu_3O_x$.

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-
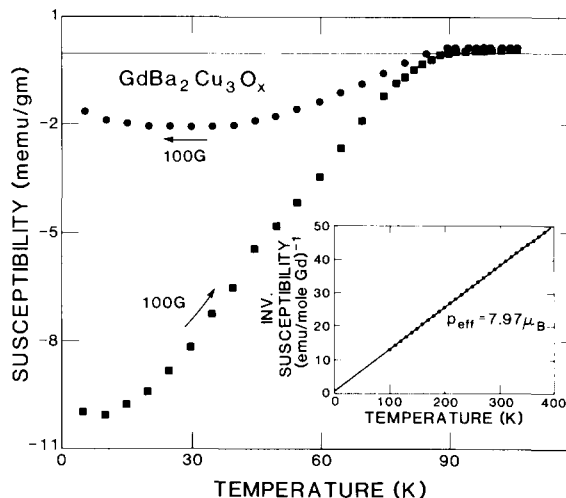

Fig. 1. Magnetic susceptibility χ versus temperature for $GdBa_2Cu_3O_x$. A large diamagnetic response approaching 95% of $-1/4\pi$ is observed when the sample is cooled below T_c in zero field and then measured upon warming in 100 G. About 20% of this diamagnetism is found when cooling in 100 G (Meissner 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.

rents correspond to about 90 to 95% of the specimen volume. These 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 0.5R_n criterion, we find that $-dH_{c2}/dT$ has a value of approximately (1.2 ± 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 0.9R_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 χ and 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 $p_{eff} = 7.97\mu_B$, 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^2 (≈ 14 K), corresponding to a lattice contribution to the specific heat characterized by a θ_D of (330 ± 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^2 (10 K) is actually the high temperature part of a magnetic ordering peak as shown in the inset of fig. 3, here
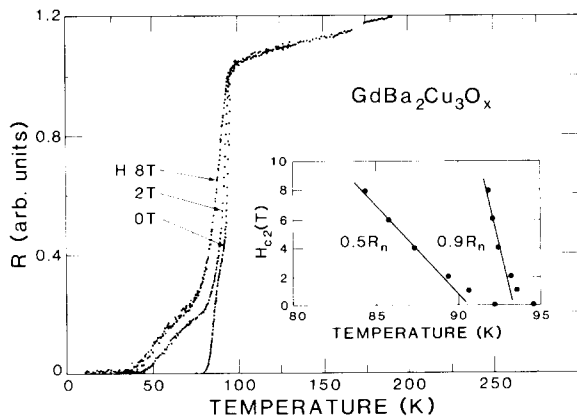

Fig. 2. Resistance versus temperature for GdBa$_2$Cu$_3$O$_x$ in various applied magnetic fields. A current density of approximately 5 mA/cm^2 was used in these measurements. The inset gives the temperature dependence of the upper critical field H_{c2} determined from the temperatures at which the resistance fell to 90 and 50% of its normal state value.
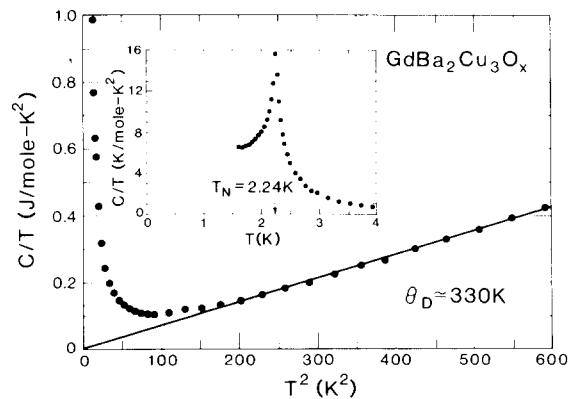

Fig. 3. Specific heat C divided by temperature versus temperature squared for GdBa$_2$Cu$_3$O$_x$. The high temperature linear part of this plot yields a Debye temperature of approximately 330 K. The rapid rise in C/T at low temperatures signals the onset of antiferromagnetic order at $T_N \approx 2.24$ K. The inset shows the ordering feature plotted as C/T versus T with a greatly compressed vertical scale.

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 $0.9R\ln 8$, 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 $ErBa_2Cu_3O_x$, and find it to be superconducting below 93 K. Our results are shown in fig. 4. The effective moment is $9.52\mu_B$ 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
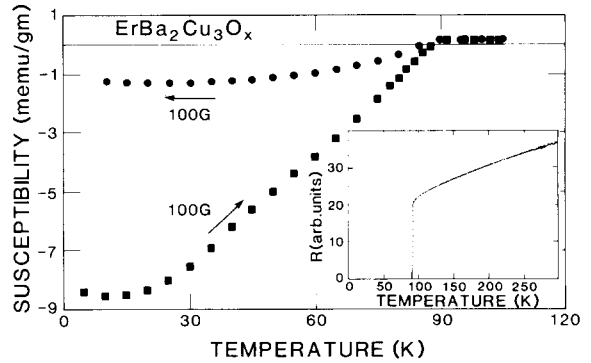

Fig. 4. Magnetic susceptibility as a function of temperature for $ErBa_2Cu_3O_x$, measured upon warming in 100 G and cooling in 100 G. The temperature dependence and magnitude of the diamagnetism and Meissner effect are comparable to those shown in fig. 1 for $GdBa_2Cu_3O_x$. The inverse susceptibility of $ErBa_2Cu_3O_x$ measured at 2 T gives a linear dependence upon T above T_c with an effective moment of $9.52\mu_B$ and a Curie–Weiss $\theta = -8.8$ K. The inset shows the resistance dropping to zero at 89 K with an onset $T_c \approx 93$ K but with superconducting fluctuations present at much higher temperatures.

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 $GdBa_2Cu_3O_x$ and $ErBa_2Cu_3O_x$ 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 $R\ln 8$, corresponding to seven spins per Gd ion.

Acknowledgements

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