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Magnetic and superconducting properties of $R\mathrm{Ba_2Cu_3O}_x$ compounds

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Specific-heat and dc magnetic-susceptibility measurements have been performed on $R\mathrm{Ba_2Cu_3O}_x$ (R denotes rare earth) compounds. These measurements show that the rare-earth atoms behave as local moments above the superconducting transition temperature of these compounds which can be as high or higher than in nonmagnetic $\mathrm{YBa_2Cu_3O}_x$. Further, we find coexistence of superconductivity and magnetism in R=Gd, Er, and Dy compounds and evidence for crystalline-electric-field splittings in these materials.

The discovery of superconductivity above 90 K in a Y-Ba-Cu-O compound[1] was followed soon thereafter by the report of high-temperature superconductivity in rare-earth-containing analogues.[2] That magnetic rare-earth compounds could sustain superconductivity at a critical temperature T_c and critical magnetic field as high or higher than their nonmagnetic counterparts emphasized the apparent weakness of interaction between the rare-earth local moment and the superconducting electrons. Subsequent work[3] further demonstrated that, in fact, superconductivity and magnetic order coexisted in one of those compounds $\mathrm{GdBa_2Cu_3O}_x$. Such behavior, though quite unusual, has been observed before in certain $R\mathrm{Mo_6S_8}$ (Ref. 4) and $R\mathrm{Rh_4B_4}$ (Ref. 5) materials (R denotes rare-earth) in which long-range antiferromagnetic order of the localized f electrons left essentially unperturbed superconductivity associated with the transition metal d band. Presumably, a comparable state exists in $\mathrm{GdBa_2Cu_3O}_x$; however, the nature of interactions leading to magnetic order remains an interesting question. Hall-effect measurements on $\mathrm{GdBa_2Cu_3O}_x$ indicate[6] a low concentration of conduction electrons above T_c that should be reduced even further upon cooling below T_c due to the opening of a superconducting energy gap at the Fermi energy. Consequently, Ruderman-Kittel-Kasuya-Yoshida (RKKY) interactions would be expected to be rather weak.

To characterize further these interesting new high-temperature superconductors, we have measured the magnetic susceptibility of nine $R\mathrm{Ba_2Cu_3O}_x$ compounds, both above and below T_c, from which we deduce the relative diamagnetism, effective magnetic moment μ_{eff}, and paramagnetic Curie temperature Θ. Further, from low-temperature specific-heat measurements on four of these compounds, we find that $\mathrm{GdBa_2Cu_3O}_x$ is not unique with respect to the coexistence of superconductivity and magnetic order in the $R\mathrm{Ba_2Cu_3O}_x$ series.

Samples of nominal composition $R\mathrm{Ba_2Cu_3O}_x$, with $x \simeq 7$, were prepared by conventional ceramic powder techniques starting from the rare-earth and Cu oxides and $\mathrm{BaCO_3}$. The starting materials were ground and fired three times in oxygen at 900–950 °C to form the superconducting phase, slowly cooled in oxygen after the final heat treatment, and sintered into the shape of pills for measurement. Magnetic-susceptibility measurements were performed in a Quantum Design SQUID (superconducting quantum-interference device) magnetometer over the temperature range 2–380 K. Specific-heat experiments were carried out in two separate low-mass calorimeters, one operating from 1.5 to 20 K and the other from 0.3 to 3 K.

Previous specific-heat measurements[3] on $\mathrm{GdBa_2Cu_3O}_x$ above 1.5 K showed evidence for a magnetic transition at $T_N = 2.24$ K. Assuming a linear dependence of C/T (specific heat divided by temperature) from 1.5 K to $T=0$ led to a calculated entropy associated with the transition that was 90% of the value $R\ln 8$ expected for ordering all of the Gd $J=S=\frac{7}{2}$ spins, where R is the gas constant. Shown in Fig. 1 are those earlier data together with new results obtained at lower temperatures. In the inset of Fig. 1 we see a shoulder centered near 1 K below which C/T extrapolates approximately linearly to zero. The origin of this additional structure in C/T is unknown but might arise from an incommensurate-commensurate transition in the magnetic order or is possibly due to a two- to three-dimensional ordering transition. Integrating the area under the curve in the inset now gives to within 2% an entropy of $R\ln 8$, so that the additional feature at 1 K accounts for the "missing" entropy encountered previously. That the full spin degeneracy is reflected in the entropy of the transition is consistent with the expected absence of crystal-field splitting of the $L=0$ ground state of trivalent Gd.

Figure 2 shows C/T as a function of temperature for $\mathrm{ErBa_2Cu_3O}_x$, where we see a pronounced specific-heat anomaly centered near 0.6 K. Linearly extrapolating C/T to zero below 0.3 K gives an entropy between 0 and 2.5 K of $1.17R\ln 2$, which is much less than $4R\ln 2$ anticipated for ordering of the $S=\frac{3}{2}$ spins of Er. Our value for the entropy is consistent with magnetic ordering in a Kramer's doublet ground state, with some small additional entropy appearing from the admixture of higher-lying multiplets. In the inset, a plot of C vs T reveals a weak, broad anomaly centered around 6 K that may be associated with the presence of a minority phase or possibly crystal-field effects. Concerning the former interpretation, we note that diamagnetic shielding experiments on this sample indicate about 90% of $1/4\pi$ diamagnetism, thereby leaving open the possibility of second phases.

The temperature dependent specific heats of

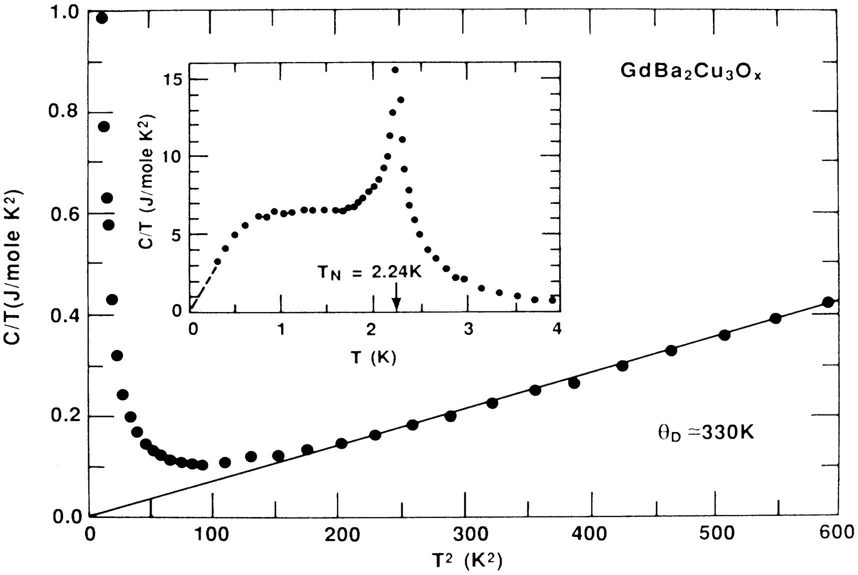

FIG. 1. Specific heat divided by temperature vs temperature squared for $GdBa_2Cu_3O_x$. The high-temperature T^3 variation in C allows an estimate of the Debye temperature $\Theta_D \simeq 330$ K. The inset shows clearly a specific-heat anomaly at 2.24 K and a shoulder centered near 1 K.

$DyBa_2Cu_3O_x$ and $HoBa_2Cu_3O_x$ (not shown) are qualitatively similar to behavior found in Fig. 2. In $DyBa_2Cu_3O_x$ we find a specific-heat anomaly centered near 0.8 K. Entropy associated with this phase transition is $1.24R\ln2$, again probably for the same reasons outlined above for $ErBa_2Cu_3O_x$, since the full magnetic entropy of $4R\ln2$ is far from being recovered. The specific heat of $HoBa_2Cu_3O_x$ increases steeply with decreasing temperature below 1 K but does not pass through a maximum above 0.3 K. This upturn may be due simply to a nuclear Schottky anomaly. These results would suggest that Ho is in a crystal-field singlet ground state.

Superconducting and magnetic properties of $RBa_2Cu_3O_x$ samples studied are summarized in Table I. The superconducting transition temperatures are those determined by the onset of diamagnetic character in the dc susceptibility, which in those cases where it was checked corresponded closely to the temperature at which the resistance fell to 90% of its normal-state value. The diamagnetic response was established by cooling the sample to 7 K in nearly zero applied field and then applying 100 G. We arbitrarily assign the strength of the response at 7 K as strong (80%–100% of perfect diamagnetism), medium (20%–80%), and weak (> 0%–20%). The percent diamagnetism as well as the effective moment were calculated assuming the nominal composition and the x-ray density of $YBa_2Cu_3O_x$.[7] The paramagnetic θ and μ_{eff} were extracted from the high-temperature ($T_c < T < 400$

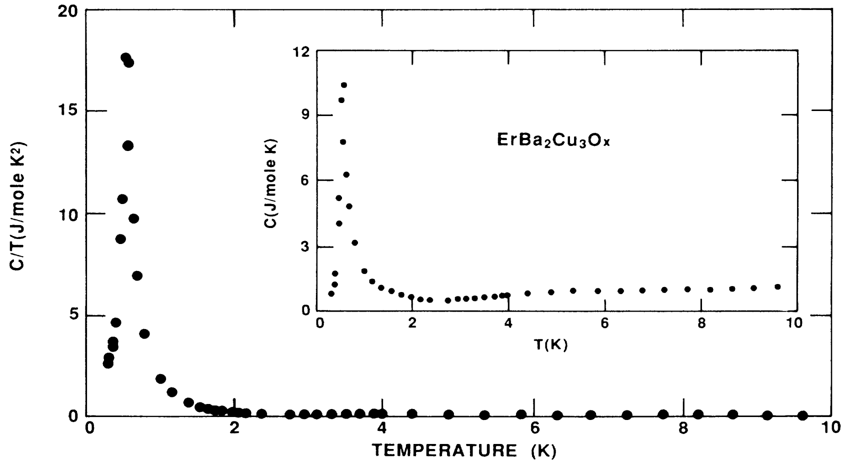

FIG. 2. Specific heat divided by temperature as a function of temperature for $ErBa_2Cu_3O_x$. A sharp maximum in C/T at 0.6 K signals a magnetic transition. The inset, specific heat vs temperature, shows a broad, weak feature centered near 6 K. Very similar behavior is found in $DyBa_2Cu_3O_x$.

TABLE I. Summary of magnetic and superconducting properties of $R\mathrm{Ba_2Cu_3O}_x$ compounds. μ_{eff} values in brackets correspond to those expected from Hund's rules for R^{3+}.

Rare earth	T_c (K)	Diamagnetism (relative to $1/4\pi$)	μ_{eff} (μ_B)	Θ (K)	T_N (K)
Nd	47 ± 1	Medium	3.60 [3.62]	-107	$\cdots$
Sm	65 ± 1	Weak	$J \simeq 0$		
Eu	90 ± 1	Strong	$J = 0$		
Gd	96 ± 1	Strong	7.97 [7.94]	-4.8	2.24, ~ 1
Tb	35 ± 1	Weak	8.65 [9.72]	-45.6	$\cdots$
Dy	92 ± 1	Medium	10.56 [10.63]	-8.4	0.8
Ho	93 ± 2	Medium	10.62 [10.60]	-8.9	< 0.3
Er	92 ± 2	Strong	9.52 [9.59]	-8.8	0.6
Yb	91 ± 1	Strong	5.35 [4.54]	-68.1	$\cdots$

K) dc susceptibility measured in a field of 2 kG. We see in Table I that μ_{eff} is in good agreement with Hund's-rules moments for R^{3+} (in brackets) except in the cases of $\mathrm{SmBa_2Cu_3O}_x$, $\mathrm{TbBa_2Cu_3O}_x$, and $\mathrm{YbBa_2Cu_3O}_x$. We note that Sm, Tb, and Yb are known to have more than one valence state and that second phases are present in these samples. In all cases Θ is negative, signifying the presence of antiferromagnetic correlations. An open question is the nature of interactions that drive the magnetic transition at such low temperatures. Possibly in these crystallographically anisotropic materials, not all of the Fermi surface is involved in superconductivity. In this case, weak RKKY interactions could provide the mechanism. However, more likely is superexchange[2,3] or dipolar[8] interactions. Further experiments are required to distinguish among these possibilities.

To conclude, the rare-earth atoms in $R\mathrm{Ba_2Cu_3O}_x$ materials behave as weakly antiferromagnetically correlated local moments that have little if any effect on superconductivity.[2,3,8-12] Specific-heat measurements, combined with electrical resistance and ac susceptibility data, show that magnetic order and superconductivity coexist in at least $\mathrm{GdBa_2Cu_3O}_x$, $\mathrm{DyBa_2Cu_3O}_x$, and $\mathrm{ErBa_2Cu_3O}_x$ and that crystal fields play an important role in determining the ground-state degeneracy. Finally, we note that the ordering temperatures in these three compounds scale qualitatively as $S(S+1)$, where S is the local moment spin.

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