Magnetization and susceptibility studies of the superconductive compound $Gd_1Ba_2Cu_3O_z$

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The magnetic susceptibility and magnetization of the superconductive compound $Gd_1Ba_2Cu_3O_z$ has been studied in the temperature range from 1.5 to 270 K. The magnetic susceptibility χ of the material, which has a superconductive transition temperature T_c near 95 K, follows a Curie-Weiss law both above and below T_c with the full Gd magnetic moment $p_{\text{eff}}=7.84\mu_B$ being observed. The independence of the superconductive and magnetic behavior indicates that superconductivity in this system is highly anisotropic. This conclusion is supported by magnetization measurements below T_c, which also yield an antiferromagnetic, Curie-Weiss-like temperature Θ_M of +2.3 K.

INTRODUCTION

Very recently, a new class of superconductive materials, which are based on oxygen deficient copper oxides, has been discovered.[1,2] A representative member of these materials, which collectively exhibit superconductive transition temperatures T_c near 90 K, is the compound $Y_1Ba_2Cu_3O_z$ with $z \cong 7$. Their structure is orthorhombic, with the basal cell lengths "a" and "b" differing slightly.[3] Perpendicular to the "c" direction are sheets of atoms, containing separate layers of Cu-O, Ba-O, and oxygen-free layers of Y^{3+} ions. One remarkable feature of these materials is that when other trivalent species, especially rare-earth ions, are substituted for Y^{3+}, the T_c is only slightly affected,[4] remaining near 90 K.

In a recent investigation[5] of the Ho-based "1-2-3" compound $Ho_1Ba_2Cu_3O_z$, we found that the high-T_c superconductivity coexists with strong Ho paramagnetism. These two phenomena occur to a very large degree independently of one another, *including the temperature regime well below T_c*. These results give strong *experimental* evidence that, at least in the Ho-based compound investigated previously, the superconductivity is excluded from the layers containing Ho ions and is therefore of lower dimensionality. The picture is consistent with recent electronic band-structure calculations.[6]

The extreme anisotropy of the superconductivity can be expected to impact strongly on the physical properties of the materials and their potential applications. Consequently, it is important to establish the generality of the above conclusions by a study of other related systems, utilizing well-characterized, single-phase samples. In the work reported here, we have performed magnetic and electrical resistivity investigations of the Gd-based compound $Gd_1Ba_2Cu_3O_z$ over a temperature range of 1.5 to 270 K. While the Ho^{3+} ion is expected to have a singlet ground state in the crystal field of the compound, Gd^{3+} is an f^7 configuration S-state ion. Having zero orbital angular momentum, the Gd ion does not interact to first order with the crystalline electric field, and it retains the degeneracy of its half-integral spin $S=\frac{7}{2}$. Thus study of Gd-based material provides a particularly useful comparison with the work on $Ho_1Ba_2Cu_3O_z$.

EXPERIMENTAL ASPECTS

The samples were prepared in the same manner as previously described.[5] Basically, appropriate masses of the constituent oxides were mixed, repeatedly reacted in air at 895 °C and reground, then pressed into pellets that were sintered at 955 °C. Finally, these pellets were reground and sintered a second time at 955 °C. The material utilized in this study was single phase, as evidenced by the absence of extraneous lines in the x-ray diffraction pattern; the observed reflections were virtually identical to those reported[3] for $Y_1Ba_2Cu_3O_z$ and observed in the Ho-based material.[5] The density of the material studied was 5.1 g/cm^3, which is about 72% of the density calculated from the lattice constants.

The magnetization studies were performed in a variable-temperature vibrating sample magnetometer (VSM) equipped with a superconductive solenoid. The instrumental sensitivity was calibrated using the Meissner-state diamagnetism of a Nb sphere and cross checked with a National Bureau of Standard magnetic moment standard, a Ni sphere. For thermometry, calibrated Si diode and carbon glass resistance thermometers were used. Below T_c, isothermal magnetization curves in both increasing and decreasing fields were obtained; above T_c the susceptibility was measured in a field of 5415 Oe and corrected for demagnetizing effects, which were very small. The electrical resistivity was studied using standard four-lead ac potentiometric methods.

EXPERIMENTAL RESULTS AND DISCUSSION

In characterizing the materials, it was found that the electrical resistivity ρ was metallic in behavior, decreasing from 1580 $\mu\Omega$ cm at 295 K to 600 $\mu\Omega$ cm just above T_c. Measured resistively, the midpoint T_c was 94.7 K and zero resistivity was attained at 94.0 K. These values are typical of and quite comparable to those reported for the Ho-based material. The differences in detail are that here (a) T_c is $\simeq 3$ K higher and (b) the apparent resistivity is somewhat greater, which is attributed to a lower sample density.

The superconductive transition as detected magnetically is illustrated in Fig. 1. This shows the temperature dependence of the dimensionless diamagnetic susceptibility $4\pi\chi$ developed by cooling the sample to 4 K in zero magnetic field and then applying a field of 10.8 Oe. Nearly the entire volume of the sample was screened by the induced supercurrents, with $\chi = 0.98(-1/4\pi)$. During warming, the midpoint of the transition occurred at 90.3 K and the magnetic onset temperature (corresponding to 10% remaining diamagnetism) was 95.7 K. Upon recooling in the same 10.8-Oe field, the expulsion of magnetic flux from the sample was 23% of that expected for an ideal Meissner effect. The incomplete Meissner effect is attributed to flux trapping, which is expected in these very high κ, strongly type-II superconductive materials, and which is doubtlessly enhanced by porosity existing in the sintered samples.

The dimensionless magnetic susceptibility χ of $Gd_1Ba_2Cu_3O_z$ is presented in Fig. 2 as a function of temperature T. It can be written in the Curie-Weiss form

$$\chi = \chi_0 + C/(T+\Theta) , \qquad (1)$$

where χ_0 itself is a sum of temperature-independent terms. In the figure, the symbols represent experimental values of

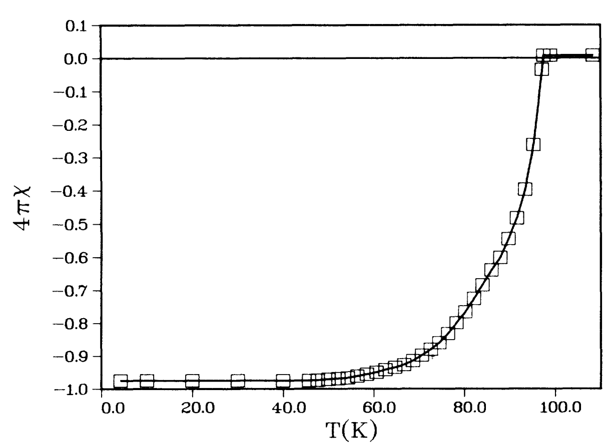

FIG. 1. For $Gd_1Ba_2Cu_3O_z$, the superconductive state diamagnetic susceptibility $4\pi\chi$ vs temperature T. The mass and volume of the single-phase sample were 0.4008 g and 0.0789 cm^3, respectively.

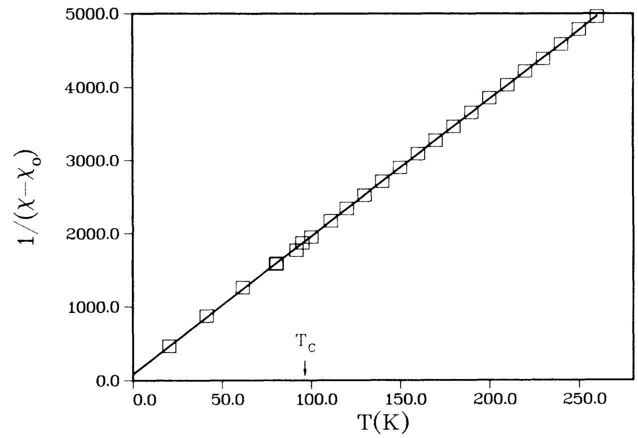

FIG. 2. Inverse of the Curie-Weiss susceptibility $(\chi-\chi_0)^{-1}$ vs T, for the same sample as in Fig. 1. The slope corresponds to an effective Gd moment $p_{\text{eff}} = 7.84\mu_B$.

$(\chi-\chi_0)^{-1}$ and the straight line is a least-squares fit of data *above* T_c to Eq. (1). Relative to the Curie-Weiss (CW) susceptibility, χ_0 is very small and has been chosen to have the same value (for an equal number of unit cells) as that found[5] for $Y_1Ba_2Cu_3O_z$. Thus, we have used $\chi_0 = 0.97\times10^{-6}$ (corresponding to a molar susceptibility of 1.4×10^{-4} cm^3 per mole of formula units). From the slope in Fig. 1, we obtain the Curie constant

$$C = (N/V)p^2\mu_B^2/3k_B = 0.0532 \text{ K} .$$

The number N of Gd ions was calculated from the sample mass and molecular weight per formula unit. The same value of the sample volume V (0.0789 cm^3) was used both in computation of χ and calculation of p, and it therefore does not affect the value of p calculated. Thus we obtain for $p = \sqrt{g^2J(J+1)}$, the effective moment per Gd spin present in the sample, a value of $7.84\mu_B$. This experimental result agrees rather well with the value $7.94\mu_B$ calculated for an f^7 $^8S_{7/2}$ Gd^{3+} ion. In addition, the fitting procedure yields a Curie-Weiss Θ of +4.3 K, where the positive sign corresponds to a net antiferromagnetic interaction between Gd moments.

As seen in Fig. 2 the Curie-Weiss behavior observed above T_c continues in the temperature region well below T_c. The experimental susceptibility data for $Gd_1Ba_2Cu_3O_z$ in the superconductive state lie quite close to the CW line extrapolated from temperatures above 100 K. This shows that the material's superconductivity exists to a high degree independently of the rare-earth paramagnetism. If the wave function of the superconductive pairs were to overlap the rare-earth moments, then one would expect some significant change in behavior relative to the Y-based compounds, which do not contain layers of local magnetic moments. Whatever the pairing mechanism, some effect would be likely: With BCS-like singlet pairing, the magnetic ions would act as pair breakers; if triplet pairing were effective, then some interaction between the resulting spin-1 pairs and the rare-earth moments would be expected. Since there is no indication as yet for any type of modified superconductive behavior relative to the Y-based "1-2-3" compound, the experimental evidence is that the layered magnetic ions have almost no effect on the mechanism responsible for superconductivity. Thus we deduce that the superconductivity itself is highly anisotropic. This is consistent with values[3,7] of the Ginzburg-Landau coherence length ξ ranging from 0.9–2.2 nm, which are comparable with the unit cell height "c," 1.17 nm. Since ξ must be obtained by applying theory for isotropic superconductors to very anisotropic materials, the semiquantitative agreement is not unreasonable. We further surmise that since the superconductive pairs are confined between the rare-earth (RE) layers with spacing c (as already discussed), the coherence length will be only a few tenths of a nm in the c direction and considerably greater in the basal plane of the orthorhombic material where there are extended electronic states.[6]

At low temperature, the field dependence of the isothermal magnetization $M(H,T)$ of the $Gd_1Ba_2Cu_3O_z$ becomes noticeably nonlinear. This can be seen in Fig. 3, a plot of magnetization M at $T=4.2$ K versus applied magnetic field H, where data were acquired in increasing and decreasing fields. To obtain the points shown, the field sweep was periodically stopped and the magnetization was allowed to relax to its static value, since a dynamic response in the signal was observed. The nonlinearity of the magnetization envelope, which was greatest at low temperatures and gradually disappeared with increasing temperature, is due to magnetic saturation of the system of interacting Gd spins. For noninteracting moments with angular momentum J, the variation of $M(H,T)$ is given by the Brillouin function $B_J(g\mu_B JH/k_B T)$. Here we allow for interactions among spins by modifying the temperature argument of B_J, so that

$$M(H,T)=(N/V)g\mu_B JB_J[g\mu_B JH/k_B(T+\Theta_M)] , \qquad (2)$$

as was employed previously.[5] For the saturation magnetization [the prefactor in Eq. (2)], results from the susceptibility work have been used, with $g\equiv 2$. The broken curve in Fig. 3 is the result of this model expression with an effective temperature $(T+\Theta_M)=6.5$ K; i.e., $\Theta_M=+2.3$ K. Similar results have been obtained for data at other temperatures. Thus it is evident that the Gd-ion subsystem is highly responsive magnetically. It is equally clear that the material also is superconductive, as evidenced by the hysteretic difference in the data taken in increasing versus decreasing field. It is equally evident that the two phenomena, field-induced paramagnetism and superconductivity, exist literally "side by side" in the compound, and are nearly independent of one another. Given the layering of the rare-earth moments in the "1-2-3" structure, we take this as experimental evidence that the superconductivity is highly anisotropic and restricted to Cu-O layers or perhaps weakly intercoupled linear arrays perpendicular to the long c axis in the crystal.

One can extract estimates of the critical current density J_c from the difference in magnetization in increasing versus decreasing magnetic field, assuming applicability of the critical state model.[8] For the data in Fig. 3, values of 5.0 to 4.0×10^3 A/cm^2 were obtained for applied magnetic field of 25 to 75 kOe, respectively. The J_c values, which are comparable to those observed in $Ho_1Ba_2Cu_3O_z$, decreased by a factor of 10 when the temperature was elevated to 40 K.

Because of the superconductive hysteresis evident in Fig. 3, the value of Θ_M obtained, +2.3 K, is uncertain by about 20%. In order to corroborate this result, a second Gd-based sample was synthesized with a shorter processing time, so as to degrade its superconductive properties. The resistive T_c and x-ray diffraction pattern differed very little from those for the previously discussed sample, but the magnetically determined superconductive transition was broader. Because the superconductive hysteresis also diminished considerably, the model function, Eq. (2), was more easily fit to the data. This can be seen in Fig. 4, which shows a plot of M vs H at 20 K. In this case, the solid line is drawn using $\Theta_M=+2.6$ K and fits the experi-

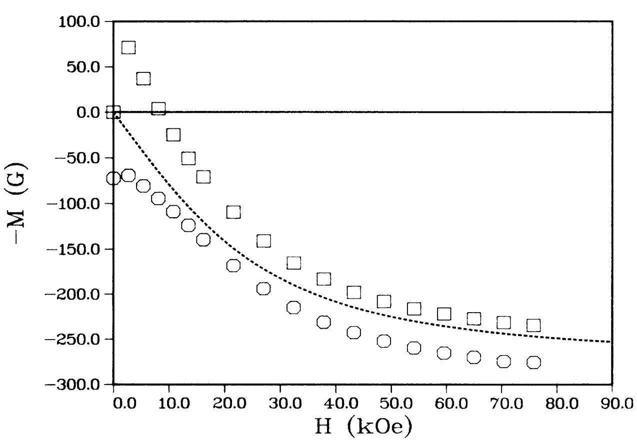

FIG. 3. The magnetic field dependence of the static magnetization $-M$ at 4.2 K, taken in increasing (□) and decreasing (○) magnetic field. The continuous curve is a Brillouin function drawn for an effective temperature $(T+\Theta_M)=6.5$ K. (Same sample as Fig. 1.)

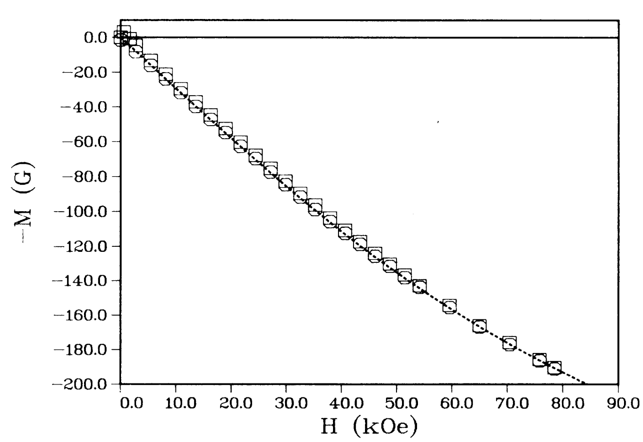

FIG. 4. The field dependence of $-M$ at 20.0 K, in increasing (□) and decreasing (○) field. The Brillouin function (continuous curve) is drawn for an effective temperature $(T+\Theta_M)=22.6$ K. The mass and volume of this less hysteretic sample were 0.5887 g and 0.947 cm^3, respectively.

mental ponts quite well at high field values.

The positive sign of the Θ_M values indicates that there is a net antiferromagnetic interaction in the $Gd_1Ba_2Cu_3O_z$ compound. Since crystal-field effects are expected to be relatively unimportant for the $^8S_{7/2}$ ion, these results point toward an antiferromagnetic transition with a Néel temperature T_N near 2 K. This conclusion is consistent with recent reports[9] of specific-heat anomalies between 2.0 and 2.3 K. It was not possible to observe directly the proposed transition in the magnetization data which extended down to 1.5 K, due to the substantial field-dependent superconductive diamagnetism of the sample in modest applied fields. From magnetic dipoles, the local field due to near-neighbor Gd-Gd interactions is $\sim$6 kOe; in an applied field of the same magnitude, the component of sample magnetization arising from the superconductivity at low temperature changes rapidly with H. This precluded a detailed observation of any antiferromagnetic changes near 2 K in this work. Expressed in units of temperature, the magnetic interaction energy between Gd dipoles within the nearly square planar array is very comparable with the magnitude of Θ_M. If purely dipolar in origin, an ordering of spins in the plane perpendicular to the c axis is likely, perhaps with linear arrays of aligned spins (along the shorter base of the unit cell) alternating in direction. This speculation must, of course, be substantiated by microscopic measurements such as neutron scattering.

To conclude, we find that superconductivity and field-induced paramagnetism in $Gd_1Ba_2Cu_3O_z$ exist largely independently of one another, similar to the case of the Ho-based compound with the same structure. Evidence from both the magnetic susceptibility and magnetization lead one to conclude that the superconductivity is highly anisotropic. Furthermore, the results are suggestive of coexistent antiferromagnetism near 2 K in $Gd_1Ba_2Cu_3O_z$ materials. Other superconductive aspects of these materials will be presented elsewhere.

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