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Magnetic ordering of Gd and Cu in superconducting and nonsuperconducting $GdBa_2Cu_3O_{7-\delta}$

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An investigation of the magnetic properties of superconducting and nonsuperconducting samples of $GdBa_2Cu_3O_{7-\delta}$ has been carried out. The antiferromagnetic transition temperature for the Gd ions in the material is the same for both compounds (2.2 K) although the superconducting compound shows metallic behavior and the nonsuperconducting compound shows semiconducting behavior. This provides direct evidence for the lack of magnetic interactions mediated by conduction electrons in these materials. In the nonsuperconducting material, evidence is obtained for the presence of antiferrromagnetic ordering in the Cu sublattice at a temperature of 18 K.

The observation of superconductivity[1] in $YBa_2Cu_3O_{7-\delta}$ at temperatures in excess of 90 K has generated an unprecedented activity aimed at understanding the mechanisms responsible for the superconductivity, and in the hope of finding other materials showing similar phenomena. It was quickly realized that the complete substitution of various strongly magnetic rare-earth (RE) ions for Y caused virtually no change in the superconductivity.[2-4] This was quite unexpected in light of our usual experiences with magnetic superconductors. For example, in materials such as the Chevrel phase compounds and the R-Rh_4B_4 compounds, long-range magnetic ordering and superconductivity were found to coexist with one another, but each of the types of ordering was clearly affected by the other.[5] In the oxide superconductors, there is also magnetic ordering of the rare-earth sublattice, but at much lower temperatures ($T_m \sim 2.24$ K) than the superconducting transition temperatures ($T_c \sim 90$ K).[4,6,7] Clearly, the effect of the magnetic interactions on the superconductivity is very weak in these compounds. There is additional interest in the possibility of antiferromagnetic ordering on the Cu sublattice in both $YBa_2Cu_3O_{7-\delta}$ and $La_{1.85}Sr_{0.15}CuO_4$, clearly observed in compounds related to the latter[8,9] but not the former, and the relation that may have with the appearance of superconductivity and the nature of the pairing mechanism. For all of these reasons, detailed studies of magnetic effects in these materials are of considerable importance. In the following, we report heat capacity, magnetic susceptibility, and resistivity data on both superconducting and nonsuperconducting samples of $GdBa_2Cu_3O_{7-\delta}$. In both cases, antiferromagnetic ordering at 2.2 K due to the Gd ions is observed, with the transition temperature being unaffected by the electronic state of the compound. In the case of the nonsuperconducting sample, evidence is presented for antiferromagnetism occurring at 18 K due to the Cu ions.

Superconducting $GdBa_2Cu_3O_{7-\delta}$ was prepared by mixing appropriate amounts of $BaCO_3$, CuO, and Gd_2O_3, sintering in a pure flowing O_2 atmosphere for 10 h at 975 °C, annealing at 650 °C for 6 h, and furnace cooling. After reserving a portion of the material for subsequent measurements, the remainder was annealed in nitrogen at 850 °C for 12 h. The result of this operation is to reduce the oxygen content, and to change the crystal structure from orthorhombic to tetragonal. This change in crystal structure is due to a reordering of oxygen occupations and positions in the material, while leaving the RE lattice essentially unchanged. While the oxygen concentration has not been determined for this particular sample, neutron-diffraction measurements on a Y compound prepared in an identical manner gave $\delta \sim 0.85$. Resistivity data obtained for both samples are shown in Fig. 1. There, one sees that a sharp superconducting transition is obtained for the orthorhombic compound with $T_c = 93$ K. In agreement with other work,[2-4] this temperature is the same as that of the Y compound. The tetragonal compound is seen to be a semiconductor with very large resistivities at low temperatures and no trace of superconductivity.

Heat-capacity data have been obtained for both samples in the temperature range $T = 0.1$–20 K. The results for the superconducting sample up to $T = 5$ K are shown by the solid circles in Fig. 2. Previous heat-capacity work[4] has established that magnetic ordering (apparently to an antiferromagnetic state) occurs at $T_m = 2.24$ K for superconducting $GdBa_2Cu_3O_{7-\delta}$. It was further observed that the heat-capacity data did not fall simply to zero below T_m, but showed an additional feature which may indicate an order-order transition in the magnetic structure.[6] This is not well understood at this point, and neutron-diffraction experiments which could clarify the low-temperature state are very difficult because of the large neutron absorption cross section of the easily obtained isotopes of Gd. However, we note that this feature is very well reproduced in the current data, and it should be considered to be an intrinsic feature of the material.

The open circles in Fig. 2 show the data for tetragonal, nonsuperconducting $GdBa_2Cu_3O_{7-\delta}$. It is seen that the magnetic transition occurs at precisely the same temperature in both samples. Furthermore, the secondary feature at lower temperatures is also preserved, with only a minor difference in the two data sets in the vicinity of one degree. Thus, the magnetic structure is unchanged in spite of the fact that the material has gone from metallic to semiconducting behavior, and has at the same time lost its superconductivity. Since the magnetism is independent of

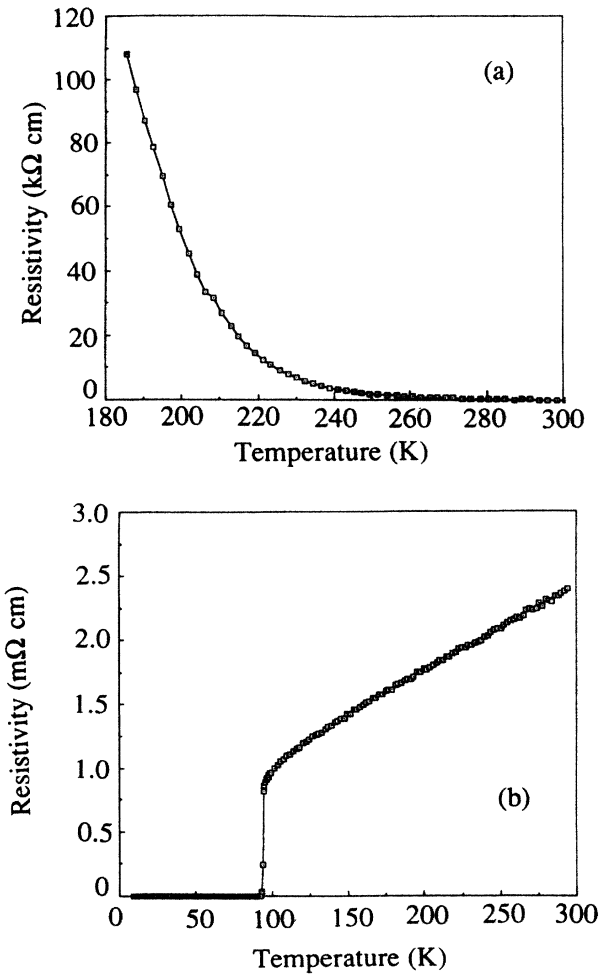

FIG. 1. Resistivity data for $GdBa_2Cu_3O_{7-\delta}$ in (a) the tetragonal, nonsuperconducting state and (b) orthorhombic, superconducting state.

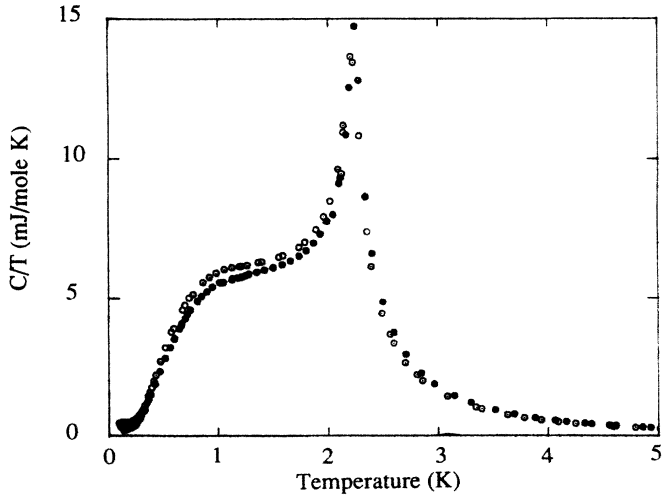

FIG. 2. Heat-capacity data for $GdBa_2Cu_3O_{7-\delta}$. The closed circles correspond to the superconducting compound and the open circles correspond to the nonsuperconducting compounds.

the conductivity of the compound, it is clear that magnetic interactions mediated by conduction electrons [Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions] are unimportant. Lattice sum calculations for this material show that dipolar energies can range from 1.5–3.3 K, depending on the magnetic structure that is assumed, in good agreement with the magnetic transition temperature. The remarkable result that follows is that the magnetic ions in this material are virtually isolated from the rest of the lattice, existing as a sublattice which interacts magnetically only through dipolar interactions, and that those interactions are responsible for the magnetic ordering that occurs. This is in agreement with recent band-structure calculations for $YBa_2Cu_3O_{7-\delta}$ which show very low conduction electron density at the Y site.[10] This also supports recent Mössbauer work on the Gd site of the orthorhombic compound which found hyperfine interaction parameters that were very ionic, and not characteristic of those found in metallic systems.[11] This isolation of the magnetic moments from the conduction electrons provides an explanation of the insensitivity of the superconductivity

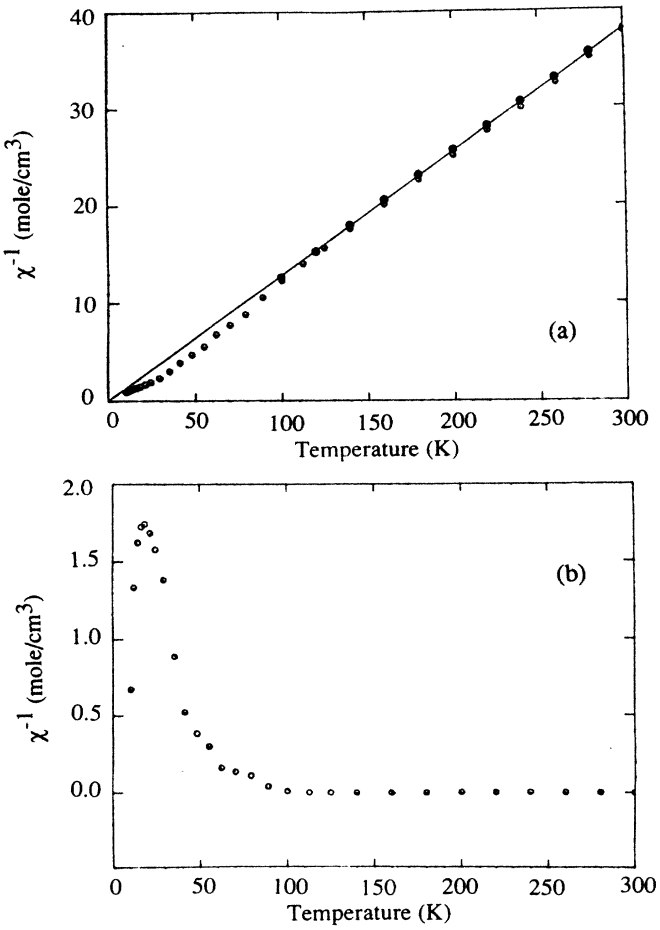

FIG. 3. (a) Magnetic-susceptibility data for $GdBa_2Cu_3O_{7-\delta}$. The closed circles correspond to the superconducting compound and the open circles correspond to the nonsuperconducting compounds. (b) Magnetic susceptibility for the nonsuperconducting data after subtraction of the Gd paramagnetic contribution, according to Eq. (1).

to magnetic ion substitution, since the conductions electrons effectively do not see the pair-breaking magnetic ions.

Magnetic-susceptibility data for the two compounds is given in Fig. 3(a). Above 100 K, the susceptibility is dominated by the Gd paramagnetism, and the solid line shows the Curie law for free-ion Gd. In order to more completely characterize the susceptibility, we have analyzed the data in the high-temperature region with a modified Curie law,

$$\chi = \chi_0 + N\mu_{\text{eff}}^2/3k_B(T-\Theta). \quad (1)$$

Since Gd is an S-state ion, and therefore not subject to crystal-field effects, we have fixed the moment to the free-ion value, $\mu_{\text{eff}} = 7.94\mu_B$, and fit Eq. (1) to the data to obtain the other parameters. This gives $\chi_0 = 2.4\times10^{-5}$ and 9.4×10^{-5} emu/mole and $\Theta = -0.9$ and 2.3 K for the orthorhombic (superconducting) and tetragonal (nonsuperconducting) compounds, respectively. The χ_0 values are small compared to other measurements in these types of superconductors, but the values are not very reliable since the susceptibility is so strongly dominated by the Gd paramagnetism. We also can see here that the Θ values are uncorrelated with the antiferromagnetic ordering temperature of the Gd ions.

Below 100 K, the susceptibility of the orthorhombic compound is not shown because of the onset of superconductivity. However, the nonsuperconducting, tetragonal compound shows a significant deviation from the Gd Curie law. Note that this does not represent remanent superconductivity since the susceptibility is increased (i.e., more paramagnetic), rather than decreased (more diamagnetic). Since Gd is an S-state ion with orbital angular momentum $L=0$, it is not subject to crystal-field interactions. Therefore, the Gd contribution to the susceptibility should be given by Eq. (1) at all temperatures, and so can be subtracted from the total susceptibility. When this is done, the data shown in Fig. 3(b) show a peak typical of antiferromagnetic ordering. From a Curie-Weiss plot of the data above the peak, we estimate a magnetic moment of $\sim 0.4\mu_B$/f.u.

The peak in the susceptibility occurs at one order of magnitude higher temperature than the Gd magnetic ordering temperature. While one cannot rule out a higher-temperature Gd ordering which does not occur in the orthorhombic compound, the most reasonable explanation is that this represents antiferromagnetic ordering in the Cu sublattice. The large neutron absorption cross section of Gd prohibits a direct confirmation of this ordering, but there are several ways in which this may be further explored. In view of the insensitivity of the Gd magnetism to electronic structure, we presume that the Cu ordering is completely independent of the ion occupying the Gd site. Thus, similar magnetic effects should be observed in Y compounds, and this possibility is being investigated. In analogy with present information on the antiferromagnetism of La_2CuO_4 (Ref. 8) we expect the magnetic transition temperature to be strongly dependent on oxygen content, and hence on the details of heat treatments. This is also being pursued.

In summary, we have shown that the antiferromagnetic ordering of Gd ions in $GdBa_2Cu_3O_{7-\delta}$ is independent of the presence or absence of superconductivity and is unchanged in both insulating and metallic systems. This provides direct proof that the magnetic interactions occur only through dipolar terms, and that the influence of conduction-mediated processes such as the RKKY interaction is unimportant. Consequently, reductions in T_c due to magnetic pair breaking are not important for these materials. Furthermore, magnetic-susceptibility data in nonsuperconducting $GdBa_2Cu_3O_{7-\delta}$ give strong evidence for the presence of antiferromagnetic ordering in the Cu sublattice. This observation puts these materials in a much more parallel position with the La_2CuO_4 derived superconductors, where Cu magnetic phenomena now appear to be well established.[8]

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[1] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 408 (1967).

[2] P. H. Hor, R. L. Meng, Y. Q. Wang, L. Gao, Z. J. Huang, J. Bechtold, K. Forster, and C. W. Chu, Phys. Rev. Lett. **58**, 1891 (1987).

[3] J. W. Willis, Z. Fisk, J. D. Thompson, S.-W. Cheong, R. M. Aiken, J. L. Smith, and E. Zirngiebl, J. Magn. Magn. Mater. **67**, L139 (1987).

[4] D. W. Murphy, S. Sunshine, R. B. van Dover, R. J. Cava, B. Batlogg, S. M. Zahurak, and L. F. Schneemeyer, Phys. Rev. Lett. **58**, 1888 (1987).

[5] *Superconductivity in Ternary Compounds,* edited by O. Fischer and M. B. Maple, Topics in Current Physics, Vols. 32 and 34 (Springer, New York, 1982).

[6] S. E. Brown, J. D. Thompson, J. O. Willis, R. M. Aiken, E. Zirngiebl, J. L. Smith, Z. Fisk, and R. B. Schwarz, Phys. Rev. B **36**, 2298 (1987).

[7] B. D. Dunlap, M. Slaski, D. G. Hinks, L. Soderholm, M. Beno, K. Zhang, C Segre, G. W. Crabtree, W. K. Kwok, S. K. Malik, I. K. Schuller, J. D. Jorgensen, and Z. Sungaila, J. Magn. Magn. Mater. **68**, L139 (1987).

[8] D. Vaknin, S. K. Sinha, D. E. Moncton, D. C. Johnston, J. M. Newsam, C. R. Safinyaand, and H. E. King, Jr., Phys. Rev. Lett. **58**, 2802 (1987).

[9] Y. Yamaguchi, H. Yamauchi, M. Ohashi, H. Yamamoto, N. Shimoda, M. Kikuchi, and Y. Syono, Jpn. J. Appl. Phys. Lett. **26**, L447 (1987).

[10] S. Massidda, J. Yu, A. J. Freeman, and D. D. Koelling, Phys. Lett. A **122**, 198 (1987).

[11] E. E. Alp, L. Soderholm, G. K. Shenoy, D. G. Hinks, D. W. Capone II, K. Zhang, and B. D. Dunlap, Phys. Rev. B **36**, 8910 (1987).