Nature of the magnetic order of Gd in superconducting and nonsuperconducting $GdBa_2Cu_3O_{7-\delta}$

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Low-temperature ordered states of the Gd moments in $GdBa_2Cu_3O_{7-\delta}$ have been investigated by the use of the Luttinger-Tisza method. It is shown that by taking into account the effect of the crystal field on the Gd ions, the gross features of the observed ordering can be understood if the dipole-dipole interaction is assumed to be predominant. However, the inclusion of weak superexchange interaction appears necessary. It is shown that an antiferromagnetic state with the Gd moments lying along the c axis can be stabilized if a certain condition is met for the g tensor of the Gd ions.

Since the discovery of high-temperature superconductivity in the oxide $YBa_2Cu_3O_{7-\delta}$,[1] it has been established that the Y ion can be completely replaced by various trivalent rare-earth ions (R) with no appreciable effect on the superconducting transition temperature T_c.[2,3] This may be contrasted with the situation in some ternary intermetallic compounds[4] where substitution of magnetic rare-earth ions causes a large depression of T_c. Thus it appears that in the $RBa_2Cu_3O_{7-\delta}$ oxides there is very little interaction between the magnetic rare-earth ions and the conduction electrons responsible for superconductivity. In fact, the rare-earth moments in these compounds order magnetically at low temperatures.[5-15] In particular, the highest magnetic transition temperature was measured in $GdBa_2Cu_3O_{7-\delta}$: Heat capacity and magnetic susceptibility measurements[6-8] showed the Gd moments to order antiferromagnetically at $T_N=2.24$ K, with superconductivity and magnetic order coexisting below T_N. Furthermore, $GdBa_2Cu_3O_{7-\delta}$ exhibits an unusual feature in the heat-capacity data, namely, that in addition to the regular sharp peak at T_N, a pronounced broad shoulder also appears which is centered at about 1.3 K.[7-9] This feature in the heat capacity and the value of T_N are virtually identical for both the nearly stoichiometric ($\delta<0.5$) superconducting orthorhombic phase and the oxygen-deficient ($\delta>0.5$) semiconducting tetragonal phase of $GdBa_2Cu_3O_{7-\delta}$.[9,10] Also, ^{155}Gd Mössbauer spectroscopy has provided direct evidence for an absence of conduction electrons at the Gd sites in $GdBa_2Cu_3O_{7-\delta}$.[11] This suggests that the magnetic ordering is not due to the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, which is mediated by the conduction electrons, but is rather due to dipole-dipole interaction between the rare-earth magnetic moments, and perhaps even superexchange interaction. Neutron-diffraction studies have been reported on $GdBa_2Cu_3O_{7-\delta}$ compounds with $\delta=0$ ($T_c\simeq 90$ K)[12] and $\delta=0.5$ ($T_c\simeq 40$ K).[13] Both show, at 1.5 K, an antiferromagnetic order with the Gd moments parallel to the crystallographic c axis, but while for $\delta=0$ the unit cell is doubled in all three directions; for $\delta=0.5$ the c direction is ferromagnetic. More recent neutron-diffraction studies on nonsuperconducting $GdBa_2Cu_3O_{7-\delta}$ compounds[14] with $\delta=0.86$ and 0.6 have again shown c-axis ordering with unit-cell doubling in all three directions. It has been pointed out that to a good approximation, both these configurations have the same dipole-dipole interaction energy.[12] This is due to the large separation of the Gd ions along the c axis which is approximately 3 times that along the a and b axes.[2] Also, it has been noted that simple dipole-dipole interaction would favor an antiferromagnetic order with the moments lying in the a-b plane rather than along the c axis.[15] It is, therefore, important to understand the nature of the interaction responsible for the ordering of the Gd moments in $GdBa_2Cu_3O_{7-\delta}$.

We report here a calculation of the lowest-energy configurations in both orthorhombic and tetragonal $GdBa_2Cu_3O_{7-\delta}$, assuming the interaction between the Gd moments is predominantly dipolar. In the calculation we consider the effect of the crystalline electric field (CEF) on the ground-state splitting of the Gd^{3+} ions. The ground state of the Gd^{3+} ion is $^8S_{7/2}$, so CEF effects cannot be strong. In fact, estimation of the entropy associated with the measured specific-heat anomaly yields a value close to $R\ln 8$, originating from the full Hund's-rule ground-state multiplet of the Gd^{3+} ion.[6,7] Nevertheless, CEF splittings can occur through admixtures of states with nonzero orbital angular momentum. Causa *et al.*[16] have recently reported electron-spin-resonance measurements which have indicated the existence of a CEF splitting of about 1.5 K in the ground state of Gd^{3+} ions in dilute $Gd_xEu_{1-x}Ba_2Cu_3O_{7-\delta}$. Analysis of their measured CEF parameters has further indicated the existence of an easy axis of magnetization along the z direction. [The principal axes (x,y,z) of the electric-field-gradient tensor at the Gd sites coincide with the crystallographic axes (a,b,c).] The free-ion magnetic moment of Gd is $\boldsymbol{\mu}=\mu_B g\mathbf{S}$, where $g=2$ and the magnitude of $\mathbf{S}$ represents its effective spin of $\frac{7}{2}$, i.e.,

$$\mu=\mu_B g[S(S+1)]^{1/2}=7.937\mu_B .$$

As the temperature is reduced towards the region where kT is comparable with the overall splitting (~ 1.5 K) of the energy levels, i.e., the region just somewhat below T_N in our case, the population of the upper levels will then be decreased, leading to anisotropy in the g value, as well as

to a smaller effective spin.[17] In our coordinate system this g tensor is diagonal with the principal values g_{xx}, g_{yy}, and g_{zz}. For the tetragonal phase of $GdBa_2Cu_3O_{7-\delta}$ we use the notation $g_{\parallel} \equiv g_{zz}$ and $g_{\perp} \equiv g_{xx} = g_{yy}$. Since the orthorhombic distortion in the superconducting phase is quite small,[2] we can use for simplicity in this case the values of $g_{\parallel}$ and $g_{\perp}$ to a good approximation. As the temperature dependence of these g values is not known experimentally, our prediction of the kind of low-temperature ordering will be given as a function of the $g_{\perp}/g_{\parallel}$ ratio. As we have already mentioned, z is an easy axis of magnetization in the Gd compound.[16] Therefore, due to the thermal population of the CEF-split Gd^{3+} levels, it is reasonable to assume that the $g_{\perp}/g_{\parallel}$ ratio would grow smaller as the temperature is lowered.

The calculation of the low-temperature ordering was carried out using the method of Luttinger and Tisza[18] for minimizing the dipole-dipole interaction energy, as later generalized for the case of anisotropic spins.[19] The Gd lattice is divided into eight sublattices, all the dipoles on a given sublattice being parallel to one another. The dipole-dipole interaction energy may then be written as a quadratic form of the directions of the dipole moments. The minimum eigenvalue of the quadratic form and its corresponding eigenvector are, respectively, the minimum dipole-dipole energy and the lowest-energy configuration. In the calculation we used the following lattice parameters:[2] $a = 3.8397$ Å, $b = 3.8987$ Å, and $c = 11.703$ Å for the orthorhombic phase; and $a = b = 3.8770$ Å and $c = 11.810$ Å for the tetragonal phase. Dipolar lattice sums were evaluated within a sphere of radius 500 Å. In order to also allow for the possibility that the lowest-energy configuration would turn out to be ferromagnetic, the energies of ferromagnetic arrangements were corrected for demagnetization for a long thin needle, as explained in Ref. 20.

The lowest-energy configurations for the case $g_{\perp} = g_{\parallel}$, i.e., when CEF effects are not important, have been found to be antiferromagnetic with the moments along the x direction, as shown in Figs. 1(a) and 1(b). Their energies are given in Table I for both the orthorhombic and tetragonal phases. The configurations of lowest energy with moments lying along the z direction have also been found to be antiferromagnetic and are shown in Figs. 1(c) and 1(d). As shown in Table I, their energies are higher than those in the x direction. However, by varying the $g_{\perp}/g_{\parallel}$ ratio, we have found that the energies of the z-axis configurations become lower than those of the x direction when

$$g_{\parallel} > \alpha g_{\perp} , \tag{1}$$

with $\alpha = 1.400$ for the orthorhombic phase or $\alpha = 1.388$ for the tetragonal phase. Neutron-diffraction measurements[12-14] indicate that at 1.5 K the Gd moments are along the z direction. Thus, when lowering the temperature, thermal population of the CEF-split Gd^{3+} levels should result in condition (1) being satisfied for temperatures $T < T_a$, where $T_a > 1.5$ K. If T_a is higher than T_N (which is 2.24 K), then the ordered state just below T_N will be indeed antiferromagnetic with moments in the z direction. However, if T_a is between T_N and 1.5 K, then the ordered state just below T_N will be antiferromagnetic with moments in the x direction. Then, as the temperature is lowered, a magnetic order-order transition should take place from the x-direction configuration to that in the z direction, which could provide an explanation for the low-temperature shoulder in the heat capacity data of

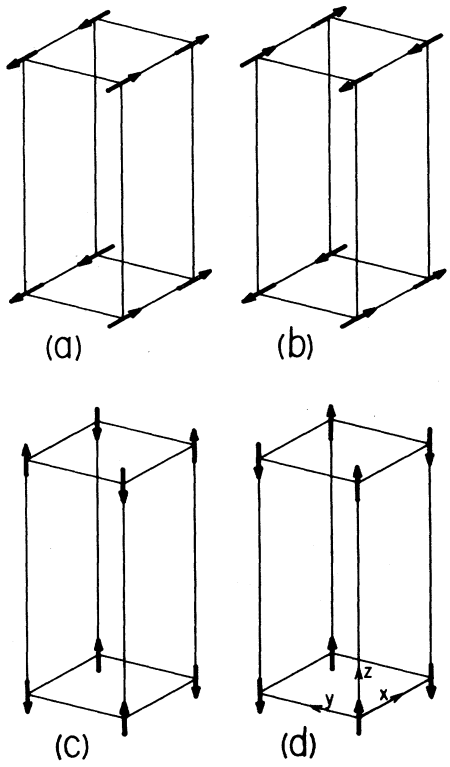

FIG. 1. Low-energy arrangements of the Gd moments in both orthorhombic and tetragonal $GdBa_2Cu_3O_{7-\delta}$. Each arrangement was assumed to have eight sublattices, all the dipoles on a given sublattice being parallel to one another. In the tetragonal phase there also are similar arrangements to (a) and (b) with the same energy but with moments along the y direction.

TABLE I. Gd dipolar energies in units of K for the antiferromagnetic (a), (b), (c), and (d) arrangements shown in Fig. 1, for both the orthorhombic and tetragonal phases of $GdBa_2Cu_3O_{7-\delta}$. The energies of the arrangements in Figs. 1(a) and 1(b) are the same to five significant figures. The y-axis ordering is similar to (a) and (b) in Fig. 1, but with moments along the y direction. The g value was assumed here to be isotropic, and the moments were assumed to have the free-ion value of $7.937\mu_B$.

Ordering	Dipolar energy (K) Orthorhombic	Tetragonal
x axis (a) and (b)	−1.7580	−1.7173
y axis (a) and (b)	−1.6992	−1.7173
z axis (d)	−0.8972	−0.8913
z axis (c)	−0.8970	−0.8911

$GdBa_2Cu_3O_{7-\delta}$.[7-9] However, from their CEF analysis, Causa *et al.*[16] have concluded that the low-temperature shoulder is not influenced much by the crystal field, indicating that there is only a single ordering process in the entire temperature range measured, and therefore we must have $T_a > T_N$, namely, condition (1) is satisfied even for some range of temperatures above T_N.

The z-direction lowest-energy configuration shown in Fig. 1(d) is in agreement with that observed in Ref. 13 for the $\delta=0.5$ compound. The configuration shown in Fig. 1(c), on the other hand, agrees with that observed in Refs. 12 and 14 for $\delta=0$, 0.6, and 0.86. It has almost the same dipole-dipole energy as that of Fig. 1(d). More precisely, as seen in Table I, its energy is higher by only about 0.2 mK. This energy difference between the two z-direction configurations remains approximately the same also when the g factor is anisotropic. Pure dipolar coupling cannot explain this dependence of the ordering on the oxygen deficiency δ. Thus, there should be an additional mechanism, presumably superexchange, which accounts for this behavior. It should be noted that the change in δ is also responsible for stabilizing either the superconducting or the nonsuperconducting phase. It has recently been indicated that the excess oxygen for $\delta < 0.5$ can be stabilized through lower-valent peroxide ions.[21] Therefore, it could be variation of superexchange paths with oxygen occupancy as well as with oxygen valency which changes the sign of the interplane interaction. Such superexchange paths in the nonsuperconducting phase could also be different from those in the superconducting phase. It is also possible, as Mook *et al.*[14] argue, that there is some inaccuracy in the structure determination of Ref. 13, or that small impurities may have altered their magnetic structure. In conclusion, we have seen that the gross features of the Gd magnetic ordering can be understood by assuming the predominant interaction to be dipolar, taking crystal-field effects into account. However, the addition of a very small amount (> 0.2 mK) of superexchange interaction energy appears to be crucial in order to account for the change of preference between the two possible lowest-energy configurations.

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