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Evidence for the dependence of the magnetic ordering on the oxygen occupancy in the high-T_c superconductor $GdBa_2Cu_3O_{7-\delta}$

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Neutron-diffraction investigations have been carried out on a single crystal of $GdBa_2Cu_3O_{7-\delta}$ ($\delta \simeq 0.5$) to investigate the magnetic ordering of the Gd and Cu moments at low temperatures. $GdBa_2Cu_3O_{6.5}$ orders at $T_N = 2.2$ K with a wave vector $(\frac{1}{2}, \frac{1}{2}, 0)$. The Gd moments are antiferromagnetically coupled to their nearest neighbors in the *a-b* plane but are ferromagnetically coupled along the crystallographic *c* axis in contrast to the case of $GdBa_2Cu_3O_7$ where the coupling along this direction is antiferromagnetic. This result clearly establishes the importance of the oxygen occupancy on the magnetic ordering in $GdBa_2Cu_3O_{7-\delta}$ ($0 < \delta < 1$). No evidence for ordering of copper moments was obtained from our present results.

The discovery of superconductivity in $(La_{1-x}Sr_x)_2CuO_4$ ($T_c = 40$ K),[1] and in $YBa_2Cu_3O_{7-\delta}$ ($T_c = 90$ K)[2] has been followed by intensive theoretical and experimental study of this class of compounds. It has been observed that Y ions in the $YBa_2Cu_3O_7$ can be fully substituted by several rare-earth ions without changing the T_c values significantly.[3] The magnetic properties[4] of these compounds show that the rare-earth moments order at low temperatures. Neutron powder diffraction investigations have established[5] that Gd moments in $GdBa_2Cu_3O_7$ order antiferromagnetically at $T_N = 2.2$ K to a structure with the propagation vector $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The Gd moments are antiferromagnetically coupled both in the *a-b* plane and along the crystallographic *c* axis. In order to examine whether the oxygen deficiency δ which destroys superconductivity by going from $\delta = 0$ towards $\delta = 1$ in this compound (see e.g., Ref. 6) also plays any significant role in the magnetic ordering, we have undertaken a neutron-diffraction investigation of a single crystal of $GdBa_2Cu_3O_{6.5}$.

Single crystals of $GdBa_2Cu_3O_{7-\delta}$ have been grown by the flux method from a flux composition of $0.70\,CuO + 0.26\,BaO + 0.04\,GdO_{1.5}$. Magnetization measurement on a single crystal of dimensions $2.5 \times 2.5 \times 0.3$ mm^3 as a function of temperature with an applied magnetic field of 50 G parallel to [001] direction showed that the crystal has the superconducting transition temperature $T_c \simeq 40$ K. Thus, the value of the oxygen occupancy has been estimated[6] to be about 6.5. The same plate-shaped single crystal was mounted on the diffractometer D15 at the Institut Laue-Langevin in Grenoble. The (001) plane of the crystal (the plane of the plate) was set vertical with the [110] direction parallel to the ω axis of the diffractometer in a liquid-helium cryostat. To reduce the strong absorption by the Gd atoms, the shortest wavelength available ($\lambda = 0.85$ Å) was used. At 1.5 K, no diffraction intensity was found at the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ Bragg peak. This observation showed that the present single crystal $GdBa_2Cu_3O_{6.5}$ ($T_c \simeq 40$ K) has a different magnetic structure compared to that of $GdBa_2Cu_3O_7$ ($T_c \simeq 90$ K).[5]

Further search revealed a small peak at $(\frac{1}{2}, \frac{1}{2}, 0)$. The intensity of this reflection drops to zero at about 2.2 K confirming its magnetic origin. The intensities of 10 magnetic reflections together with those of a few nuclear reflections were measured at 1.5 K. In order to obtain reasonable counting statistics each magnetic peak had to be measured for about 5 h. The magnetic intensities were corrected for absorption by the method of Gaussian integration and also for the Lorentz factor and were placed on an absolute scale using two nuclear reflections. Inspection of the intensities thus obtained showed that the magnetic structure factors were maximum for $l = 0$ and decreased monotonically with increasing l. This suggests that the moment direction is parallel to the crystallographic *c* axis. The observed magnetic intensities were divided by the square of the form factor[7] of Gd^{3+} and $q^2 (q^2 = \sin^2\alpha$, where α is the angle between the moment direction and the scattering vector) to give the square of the corresponding magnetic moment. The value of the magnetic moment obtained from the mean of all reflections was $6.9(7)\mu_B$ which corresponds well with that expected for the Gd^{3+} ion. The observed and calculated magnetic structure factors are listed in Table I together with the goodness of fit parameter χ^2. The structure factors were also calculated for a model (model 2) in which the moments were confined to the *a-b* plane. The best fit obtained with such a model is for the orientation of the Gd moments which make an angle of 33° to the *a* axis. However, this model gave a much worse fit compared to the model with the *c*-axis orientation (model 1). The large value of χ^2 (27) for model 1 is probably due to underestimation of the errors in the structure factors, the standard deviations indicated in Table I being obtained just from the counting statistics. The actual errors are much larger and arise from the uncertainty in the absorption corrections due to irregularities in the shape of the crystal

TABLE I. Observed and calculated magnetic structure factors for $GdBa_2Cu_3O_{6.5}$. Model 1 is the preferred structure with the moments in the c direction. Model 2 is the best fit with the moments in the a-b plane. The magnetic structure factors are in units of 10^{-12} cm/unit cell. The goodness of fit parameter χ^2 is given by $\chi^2=[1/(n_{obs}-n_{pars})]\sum_{obs}[(I_{obs}-I_{calc})^2/(\Delta I_{obs})^2]$, where n_{obs} and n_{pars} are the numbers of observations and parameters.

				F_{calc}	
h	k	l	F_{obs}	Model 1	Model 2
$\frac{1}{2}$	$\frac{1}{2}$	0	1.49(3)	1.79	0.50
$\frac{3}{2}$	$\frac{1}{2}$	0	1.35(7)	1.46	1.45
$\frac{1}{2}$	$\frac{3}{2}$	0	1.92(4)	1.47	0.73
$\frac{1}{2}$	$\frac{1}{2}$	1	1.13(8)	1.60	1.34
$\frac{3}{2}$	$\frac{1}{1}$	1	1.43(6)	1.41	1.48
$\frac{1}{2}$	$\frac{3}{2}$	1	1.42(5)	1.42	0.86
$\frac{1}{2}$	$\frac{1}{2}$	2	1.21(9)	1.25	2.00
$\frac{1}{2}$	$\frac{1}{2}$	3	1.14(9)	0.94	2.23
$\frac{3}{2}$	$\frac{1}{2}$	3	1.28(12)	1.13	1.63
$\frac{1}{2}$	$\frac{3}{2}$	3	1.42(7)	1.13	1.32
	χ^2			27	238

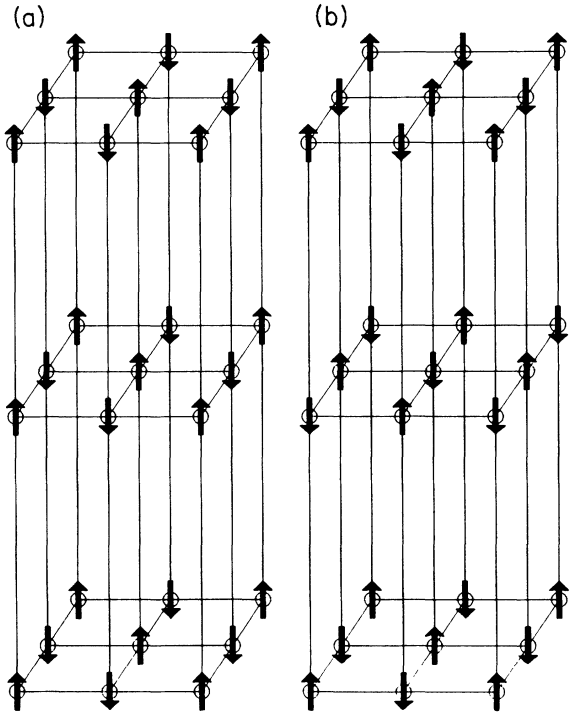

FIG. 1. Schematic representation of the magnetic structures of (a) superconducting $GdBa_2Cu_3O_{6.5}$ ($T_c\simeq 40$ K) and (b) superconducting $GdBa_2Cu_3O_7$ ($T_c\simeq 90$ K). Only the Gd atoms and the directions of their moments are shown.

with a very high absorption coefficient ($\mu\simeq 40$ cm^{-1} for $\lambda=0.85$ Å).

The orientation of the magnetic moments on the Gd ions in $GdBa_2Cu_3O_{6.5}$ corresponding to the above results is illustrated in Fig. 1. In the same figure we also show the moment orientations for $GdBa_2Cu_3O_7$ determined by McK Paul *et al.*[5] The magnetic moments in both structures are coupled antiferromagnetically in the a-b plane. However, the magnetic coupling between the Gd ions along the c axis is antiferromagnetic in the case of superconducting $GdBa_2Cu_3O_7$ whereas in the case of the superconducting $GdBa_2Cu_3O_{6.5}$ it is ferromagnetic. This surprising result indicates that the magnetic coupling along c is very sensitive to the oxygen occupancy. It should also be noted that the change in the oxygen occupancy is also responsible for stabilizing either the superconducting or the nonsuperconducting ground state.

The three-dimensional magnetic ordering in $GdBa_2Cu_3O_{7-\delta}$ and its dependence on the oxygen occupancy raise once again the question of the mechanism of the magnetic interaction between the rare-earth (R) ions in $RBa_2Cu_3O_{7-\delta}$ along the c axis in which direction they are separated by about 12 Å. Mössbauer (isomer shift) investigations[8] show that the electronic charge density at the Gd nucleus is negligibly small. This suggests that the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction is rather weak in this compound. Several authors[8,9] have pointed out the importance of dipolar interactions in these compounds which have low Néel temperatures. However, dipolar interaction cannot by itself explain the coupling between rare-earth ions separated by about 12 Å along the c axis. Energy calculations[5] assuming dipolar interactions alone lead to a Néel temperature of only about 0.2 K for $GdBa_2Cu_3O_7$ which is much lower than the actual ordering temperature of 2.2 K. Moreover, dipolar interaction cannot explain the dependence of the sign of the magnetic exchange along the c axis on the oxygen occupancy which is found in the present experiment. Meyer *et al.*[8] point out that if dipolar interactions were dominant in the a-b plane, one would expect a structure with the coupling between near neighbors ferromagnetic along the a axis, antiferromagnetic along b, and with the Gd-moment direction along the a axis. However, both neutron and Mössbauer investigations show that the coupling along both a and b axes is antiferromagnetic and that the Gd moments are oriented along the c axis. The same authors[8] also assert that if the magnetic interaction along the c axis were dominantly dipolar, one would expect ferromagnetic coupling in that direction. Such ferromagnetic coupling is found for the superconducting $GdBa_2Cu_3O_{6.5}$ (with $T_c\simeq 40$ K), but not for $GdBa_2Cu_3O_7$ (with $T_c\simeq 90$ K). This observation suggests that superexchange via the oxygen atoms must be invoked to understand the magnetic ordering in these compounds.

Figure 2 shows the temperature dependence of the sublattice magnetization determined from the variation with temperature of the neutron scattering intensity of $\frac{1}{2}\frac{1}{2}0$ reflection. It is compared with the behavior to be expected for two- and three-dimensional systems (full and dashed curves) given by

$$M=M_0\exp\left(\frac{T-T_N}{T_N}\right)^{\beta},$$

with $T_N=2.2$ K and $\beta=0.125$ for the two-dimensional

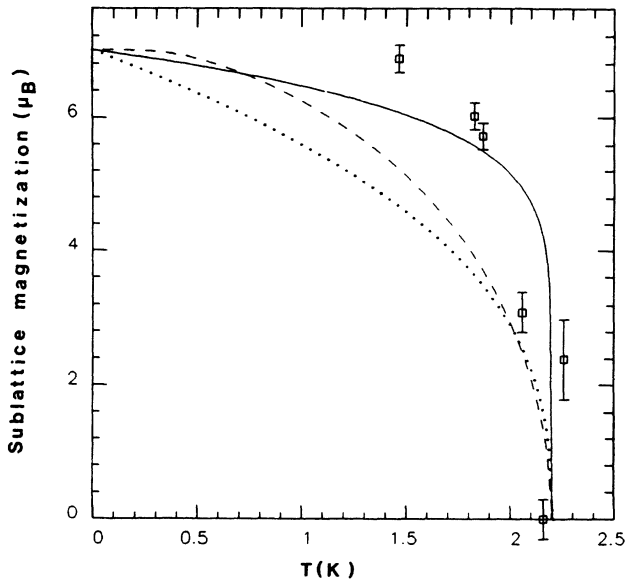

FIG. 2. Temperature dependence of the sublattice magnetization in $GdBa_2Cu_3O_{6.5}$ obtained from the intensity of the $\frac{1}{2}\frac{1}{2}0$ reflection. The continuous and the dashed curves correspond to two- and three-dimensional behavior, respectively. The dotted curve gives the Brillouin function for $S=\frac{7}{2}$.

and $\beta=0.365$ for the three-dimensional case. M_0 is the saturation value of the magnetic moment at $T=0$ which is about $6.9(7)\mu_B$ obtained from the magnetic intensities at $T=1.5$ K. The Brillouin function for $S=\frac{7}{2}$ (dotted curve) is also plotted. The plotted points are in fair agreement with the curve for the two-dimensional system. Meyer *et al.*[8] from their study of the magnetic properties of two samples of $GdBa_2Cu_3O_{7-\delta}$ with $\delta=0$ and $\delta>0.5$ conclude that the magnetic interactions in these compounds are nearly two dimensional. They determined a value of the critical exponent $\beta=0.14$ typical of a two-dimensional system. Lynn *et al.*[9] have found two-dimensional ordering in $ErBa_2Cu_3O_7$ between 0.5 and 0.3 K. $ErBa_2Cu_3O_7$ finally orders[10] three dimensionally at about $T=0.2$ K but apparently the magnetic interaction along the c axis is rather stronger in the gadolinium compounds so that long-range three-dimensional order sets in at 2.2 K.

We have not observed any evidence for ordering of the Cu moments in our present investigations. We were unable to associate the differences between the observed and calculated magnetic structure factors with magnetic scattering from the copper ions. The intensities of the $\frac{1}{2}\frac{1}{2}0$ and $\frac{1}{2}\frac{1}{2}1$ reflections drop to zero at 2.2 K showing that any copper moments contributing to these reflections only order at or below this temperature. However, it is still possible that the Cu moments order with a different propagation vector although we were unable to detect any magnetic intensity in the $\frac{1}{2}00$ and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ reflections at 1.5 K. However, the absence of magnetic ordering of the Cu moments in the present single crystal $GdBa_2Cu_3O_{6.5}$ ($T_c\simeq 40$ K) is not surprising. Although magnetic ordering of the Cu moments has been observed in the nonsuperconducting $YBa_2Cu_3O_{6+x}$,[11] so far no evidence of the magnetic ordering in the superconducting $YBa_2Cu_3O_{7-\delta}$ exists.

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