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Nature of the Magnetic Order of Cu in Oxygen-Deficient $NdBa_2Cu_3O_{6+x}$

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Neutron-diffraction measurements have been taken on single crystals of $NdBa_2Cu_3O_{6+x}$ to explore the nature of the magnetic order as a function of oxygen concentration x. The Cu-O planes are known to order antiferromagnetically at T_{N1}, with $T_{N1}(x \approx 0) = 450$ K. At lower temperatures we find that the oxygen-deficient Cu planes also order magnetically [$T_{N2}(x \approx 0.1) = 80$ K], with a large ordered moment of $0.46\mu_B$ and a simple antiferromagnetic sequencing along the c axis. Both ordering temperatures decrease with increasing x, with T_{N2} being much more sensitive to x than T_{N1}.

The magnetic properties of the superconducting oxide class of material have been of particular interest both because of the intrinsic interest in magnetism and because of the possibility that the magnetic fluctuations are responsible for the superconducting pairing.[1] The $RBa_2Cu_3O_{6+x}$ (R = rare earth) system is known to order antiferromagnetically[2-4] for small x ($x \lesssim 0.4$), where the system is tetragonal and nonsuperconducting. The magnetic structure consists[3,4] of a simple antiparallel arrangement of Cu spins both within the Cu-O planes as well as along the tetragonal c axis, while the oxygen-deficient Cu planes possess no net moment. The three-dimensional ordering can be quite high [$T_{N1}(x \approx 0) = 450$ K], indicating that the magnetic interaction energies are large, and in addition it is expected[5] that quite strong 2D magnetic correlations persist within the Cu-O planes to even higher temperatures. The 3D transition temperature is very sensitive[2] to the oxygen concentration x, decreasing rapidly with increasing x and approaching zero for $x = 0.4$.

Very recently, a second magnetic phase transition has been observed by Kadowaki *et al.*[6] and independently by us, in which oxygen-deficient Cu planes (which contain the Cu-O chains) also order magnetically. We have investigated the nature of this ordering and the effect of oxygen concentration on T_{N2}. We find that at small x and low T the basic magnetic structure consists of a simple antiferromagnetic arrangement of spins both within the planes and along the c axis. In particular, we find an unexpectedly large magnetic moment on the Cu chain sites. At intermediate temperatures the spin arrangement is a superposition of the high-T and low-T con-

figurations. We also find that *both* transition temperatures decrease with increasing x, with the lower transition T_{N2} being much more sensitive to x than the higher transition T_{N1}.

The neutron measurements were carried out at the National Bureau of Standards Research Reactor with standard triple-axis instruments. Unpolarized diffraction data were collected with an incident energy of either 14.8 or 13.7 meV with use of a pyrolytic-graphite PG(002) monochromator. Polarized-neutron measurements were then taken to establish that the new peaks are magnetic in origin, and this procedure has been described previously.[4] Angular collimations before and after the monochromator and analyzer (when used) were 40' (FWHM) in all cases, and pyrolytic-graphite filters were employed to suppress higher-order wavelengths. The single-crystal samples were grown by our slowly cooling a flux of BaO, CuO, and PbO from 1220°C. One crystal was a square plate weighting 9.5 mg, and has been studied previously.[4] The oxygen concentration was determined by Rutherford backscattering techniques to be approximately 6.35, which agrees quite well with the x obtained from the observed value of T_{N1}.[2] A second crystal from a different growth boule was found to have an oxygen concentration $x \approx 0.1$, based again on the measured T_{N1}. The volume of the crystal was about 7 times that of the small crystal. A standard helium cryostat or Displex was used for the low-temperature measurements, while a vacuum furnace was employed for the measurements above room temperature. Most of the diffraction measurements were taken in the (*hhl*) scattering plane.

We first discuss the spin configuration of the high-temperature magnetic phase, which has already been investigated in detail.[3,4] The nearest-neighbor spins within the Cu-O planes align antiparallel, with the spin direction in the tetragonal plane. There are two Cu-O planes per unit cell in the (unique) c-axis direction, and nearest-neighbor spins in adjacent planes are also aligned antiferromagnetically to produce a $+ - + - + -$ arrangement of spins in this direction. This spin arrangement gives rise to magnetic Bragg peaks of the type $(h/2, k/2, l)$ where (h, k, l) are integers. The l index is integral since there are two Cu-O planes in the chemical unit cell, and the magnetic and chemical unit cells are then the same in this direction.

The temperature dependence of the $(\frac{1}{2} \frac{1}{2} 2)$ peak, which has the strongest intensity in this phase, is shown in Fig. 1(a) for the small crystal. At this oxygen concentration the magnetic order develops at $T_{N1} \simeq 230$ K. At low temperatures, however, we see that the intensity of the $(\frac{1}{2} \frac{1}{2} 2)$ peak shows a downturn, indicating that the spins are either undergoing a spin freezing, or a change in structure. Figure (1b) shows that in fact in the same temperature region where the $(\frac{1}{2} \frac{1}{2} 2)$ shows the downturn, new Bragg peaks develop at positions where all three indices are half-integral. Hence a new spin configuration develops in this sample for temperatures
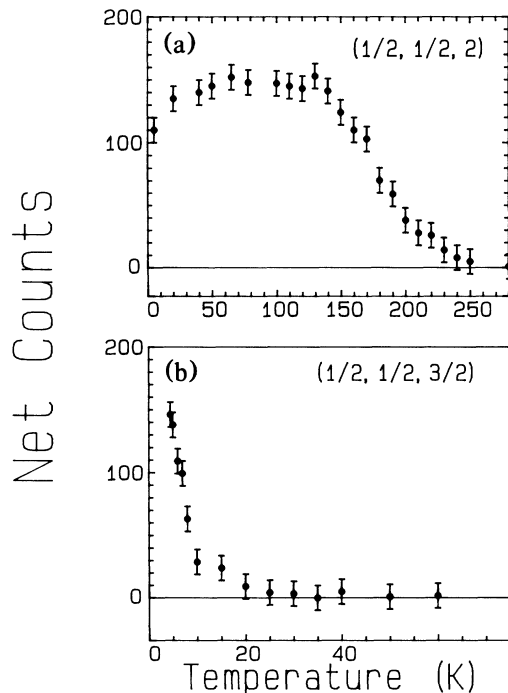
below $T_{N2} \simeq 10$ K, with a component to the magnetic structure which is twice the chemical unit cell along the c axis. However, note that at the lowest T measured the intensity of the $(\frac{1}{2} \frac{1}{2} 2)$ peak is still comparable to the $(\frac{1}{2} \frac{1}{2} \frac{3}{2})$ peak, which turns out to have the largest intensity for the new structure. Hence below 10 K the intensities of both types of peaks are finite, and the spin configuration is a superposition of the two types of order (l half-integral, and integral). In the present sample we have $T_{N1} \approx 230$ K, and $T_{N2} \approx 10$ K. Such half-integral peaks were first observed[6] in a single crystal of $YBa_2Cu_3O_{6.2}$, with $T_{N1} \approx 400$ K and $T_{N2} \approx 40$ K.

Our central result is shown in Fig. 2, where the intensities of the $(\frac{1}{2} \frac{1}{2} 2)$ and the $(\frac{1}{2} \frac{1}{2} \frac{3}{2})$ peaks for the larger single crystal are plotted. The upper transition temperature is measured to be $T_{N1} = 430 \pm 5$ K, which corresponds[2] to an oxygen concentration $x \approx 0.1$. The downturn in the intensity, however, commences at much higher temperatures than for the large-x sample. This downturn is accompanied again by the development of reflections at positions such as $(\frac{1}{2} \frac{1}{2} \frac{3}{2})$ as shown in the bottom part of the figure. In this case, however, the intensity of the $(\frac{1}{2} \frac{1}{2} \frac{3}{2})$ peak becomes much larger than the maximum intensity of the $(\frac{1}{2} \frac{1}{2} 2)$. Moreover, the intensity of the $(\frac{1}{2} \frac{1}{2} 2)$ peak is practically zero in this sample in the low-temperature limit.[7] We remark that
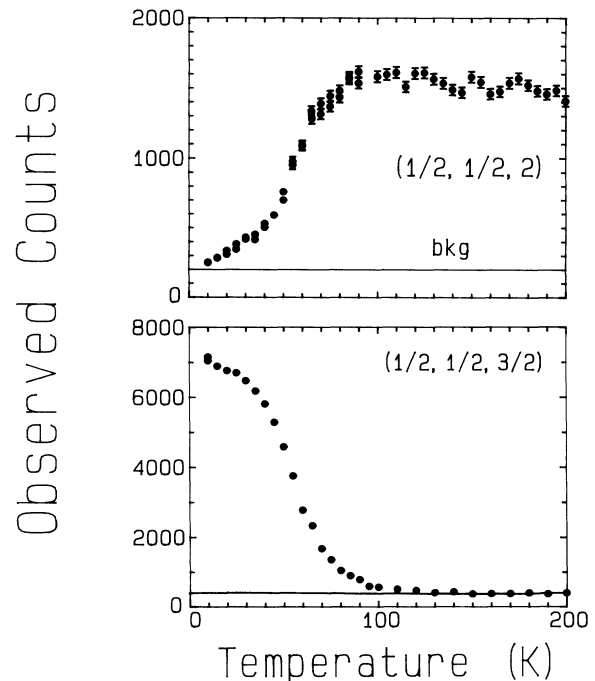

FIG. 1. Magnetic intensities for the $NdBa_2Cu_3O_{6.35}$ crystal with the larger concentration of oxygen. The onset of magnetic order is at 230 K as revealed by the intensity of the $(\frac{1}{2} \frac{1}{2} 2)$ peak. The downturn in intensity at low temperatures is accompanied by new Bragg peaks at positions such as $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ as shown in (b).

FIG. 2. Magnetic intensities for the $NdBa_2Cu_3O_{6.1}$ crystal with a small oxygen concentration. Here the downturn of the $(\frac{1}{2} \frac{1}{2} 2)$ peak begins at much higher temperature and the intensity at low T is very small, while the intensity of the $(\frac{1}{2} \frac{1}{2} \frac{3}{2})$ peak dominates the low-T scattering. T_{N1} for this crystal is 430 K.

TABLE I. Upper and lower transition temperatures for three values of x.

Sample[a]	T_{N1} (K)	T_{N2} (K)
$NdBa_2Cu_3O_{6.1}$	430	80
$YBa_2Cu_3O_{6.2}$[b]	400	40
$NdBa_2Cu_3O_{6.35}$	230	10

[a]Reference 8.
[b]Reference 6.

our polarized-beam results demonstrate that the $(\frac{1}{2}\ \frac{1}{2}\ \frac{3}{2})$ peak is indeed magnetic in orgin. Hence for this smaller value of x we have $T_{N2} \approx 80$ K, which is much higher than for the first crystal. A comparison of the transition temperatures for the three crystals studied so far is given in Table I. We see that both transitions decrease with increasing x.

Since the half-integral and whole-integral l peaks correspond to separate Fourier components, we may solve the components of the spin structure separately and then superpose them. Of course, for the $x \approx 0.1$ crystal at low T the whole-integral peaks are very small, and we neglect them initially in describing the ground-state configuration of this crystal.[7] We have tried to fit a number of spin models to the magnetic data, and have arrived at the following basic model for the ground state as shown in Figs. 3(a) and 3(b). The $T=0$ structure consists of a simple collinear arrangement of spins, with the spin direction in the tetragonal plane. The nearest-neighbor spins within the Cu-O planes (designated M_P, for planes) are again aligned antiparallel as they are in
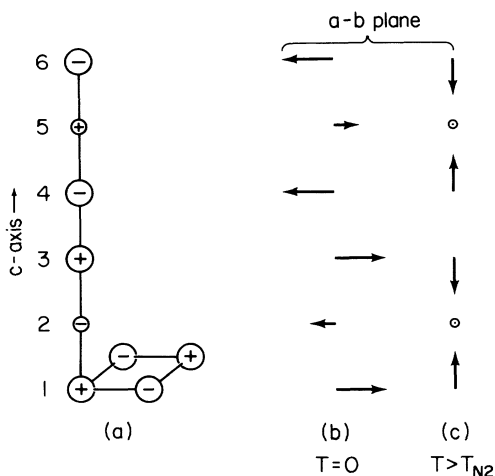

FIG. 3. Basic spin structure for the Cu spins. At $T=0$ there is a moment on the Cu ions in the oxygen-deficient planes (layers 2 and 5), and the spin configuration is shown in (a) and (b). For $T_{N2} < T < T_{N1}$ the net moments are found only on the Cu-O planes as shown in (c). At intermediate temperatures $0 < T < T_{N2}$ the spin configuration is a (noncollinear) superposition of (b) and (c).

TABLE II. Magnetic intensities at low temperatures for the single crystal of $NdBa_2Cu_3O_{6.1}$ with $T_{N1} \approx 430$ K. The $(\frac{1}{2}\ \frac{1}{2}\ \frac{3}{2})$ peak has been defined to have an observed intensity of unity for convenience, and the magnitudes of the moments have been chosen so that the ratio of the $(\frac{1}{2}\ \frac{1}{2}\ \frac{3}{2})$ and $(\frac{1}{2}\ \frac{1}{2}\ \frac{5}{2})$ is correct.

(hkl)	I_{obs}	I_{calc}
$\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$	0.05 ± 0.01	0.03
$\frac{1}{2}\ \frac{1}{2}\ \frac{3}{2}$	$\equiv 1.00 \pm 0.04$	1.00
$\frac{1}{2}\ \frac{1}{2}\ \frac{5}{2}$	0.21 ± 0.01	0.21
$\frac{1}{2}\ \frac{1}{2}\ \frac{7}{2}$	< 0.04	0.02
$\frac{1}{2}\ \frac{1}{2}\ \frac{11}{2}$	0.28 ± 0.02	0.32
$\frac{3}{2}\ \frac{3}{2}\ \frac{1}{2}$	< 0.04	0.04
$\frac{3}{2}\ \frac{3}{2}\ \frac{3}{2}$	0.30 ± 0.02	0.47
$\frac{3}{2}\ \frac{3}{2}\ \frac{5}{2}$	0.05 ± 0.01	0.08

the high-temperature magnetic phase. However, along the c axis the oxygen-deficient Cu moment (designated M_C, for chains) is nonzero, and aligned antiparallel to the spins in the Cu-O layers. The doubling of the unit cell along the c axis direction results because the sense of the spins is reversed in going from one chemical unit cell to another as shown in the figure.

A comparison of the calculated and observed intensities is given in Table II, where we see that the overall agreement is quite good. We remark, though, that with the present set of data it is not possible to rule out small variations in the spin structure such as might be produced by canting, for example. However, the low-temperature structure shown in Figs. 3(a) and 3(b) is substantially different from the one proposed by Kadowaki et al.,[6] where they have layers 1, 2, and 3 aligned parallel, and layers 4, 5, and 6 also coupled ferromagnetically, with the two groups of layers antiparallel. Their model, for example, would predict that the $(\frac{1}{2}\ \frac{1}{2}\ \frac{3}{2})$ and $(\frac{1}{2}\ \frac{1}{2}\ \frac{5}{2})$ peaks have approximately the same intensity, while the observed ratio of intensities (in the present case) is 5. They also obtained a very small moment on the Cu chain ions of $0.012\mu_B$, but this small moment originates because their data do not extend much below T_{N2}.

The values of the ordered moments we obtain at low temperatures are $M_P = (0.97 \pm 0.09)\mu_B$ for the Cu-O planes (assumed equal), and $M_C = (0.46 \pm 0.06)\mu_B$. This compares with $M_P \approx 0.6\mu_B$ for the maximum moment found[4] above T_{N2}, with the spin structure shown in Fig. 3(c). The essential difference between the two structures is of course the moment M_C which develops below T_{N2}. We note that at intermediate temperatures $(0 < T < T_{N2})$ the spin configuration is a superposition of the "pure" configurations shown in 3(b) and 3(c), which results in a noncollinear structure. A noncollinear structure is essential if we make the physically reasonable assumption that the magnitudes of the moments on the two Cu-O planes are the same.

The conventional viewpoint for the $RBa_2Cu_3O_{6+x}$ class of materials is that the Cu valence in the $Cu-O_2$ planes is 2+, with an associated magnetic moment, while the Cu "chain" layers contain Cu^{1+} which is nonmagnetic. The unexpectedly large value of M_C which we have observed on the Cu chain layers demonstrates that the Cu^{1+} state is not an appropriate description of the electronic configuration of the chain layers in these materials: There must be strong hybridization of the (band) electronic wave functions within all three Cu planes. We believe that it is this strong hybridization and the consequent electron correlations which are the genesis of the very high three-dimensional magnetic ordering temperature, and perhaps the high superconducting transition temperature as well.

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[7]The $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ intensity is clearly not saturated in Fig. 1. However, preliminary measurements just completed at lower temperatures show that the behavior of the two samples is identical.

[8]There is some uncertainty in the absolute values of x for samples prepared under different conditions. We have used the values of T_{N1} to obtain an effective oxygen concentration for comparison purposes, based on the data of Johnston et al. (Ref. 2).