Antiferromagnetic ordering of Cu ions in $NdBa_2Cu_3O_{6.1}$

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Neutron-scattering experiments performed on single crystals $NdBa_2Cu_3O_{6.1}$ reveal antiferromagnetic order for $T < T_N = 385 \pm 2$ K in which the structure is characterized by the magnetic wave vector $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$; this had previously been observed only at low temperature in single crystals of $YBa_2Cu_3O_{6+x}$ [the Y(1:2:3) compound]. The magnetic intensities are accounted for by Cu^{2+} spins coupled antiferromagnetically in the CuO_2 planes as in the yttrium compounds $YBa_2Cu_3O_{6+x}$ ($x < 0.5$). However, unlike the Y(1:2:3) compound case, the oxygen-deficient planes in the Nd(1:2:3) compound exhibit small staggered magnetization ϵS which induces the spin ordering $-S-\epsilon S-S+S+\epsilon S+S$, along the tetragonal axis. The average staggered magnetization evaluated at room temperature is about $0.40\mu_B$ in the CuO_2 planes while in the oxygen deficient (Cu-chain) layers it is about $0.04\mu_B$. The exchange coupling between the Cu atoms in the oxygen deficient layer containing Cu chains and its nearest-neighbor CuO_2 layers (Cu planes) is thus ferromagnetic; this may be readily understood by consideration of the relevant Cu^{2+} orbitals.

Magnetic pairing mechanisms are among the most prominent of the various interactions proposed to act as progenitors of the superconductivity in the new high-T_c superconductors.[1,2,3] These proposals have stimulated many interesting magnetic neutron-scattering experiments in these materials. First, the nonsuperconducting material $La_2CuO_{4-\delta}$ has been reported[4] to undergo an antiferromagnetic transition at high temperature, with Cu^{2+} moments ordered in the CuO_2 planes. The fact that such planes are also present in the family of $RBa_2Cu_3O_{6+x}$ [the R(1:2:3) compound], where R is almost any rare earth, has motivated further research for magnetic ordering in these systems. The magnetic long-range order in $YBa_2Cu_3O_{6+x}$ was first detected by Nishida *et al.*[5] using μ^+ spin-relaxation techniques. The antiferromagnetic structure was then clearly identified by Tranquada *et al.*[6] using neutron diffraction on pressed-powder sample uniaxially preoriented in a magnetic field. For the case of $x \approx 0.15$, Traquada *et al.*[6] have shown that the Cu^{2+} spins are coupled antiferromagnetically in the CuO_2 planes and along the tetragonal axis, assuming no moments in the oxygen deficient Cu-chain layers. The best agreement between their data and calculated magnetic structure factors was obtained for spin direction in the tetragonal planes. Similar conclusions have been reported by Li *et al.*[7] in the case of the $NdBa_2Cu_3O_{6+x}$ single crystal with unknown oxygen content.

Recently, Kadowaki *et al.*[8] observed in the

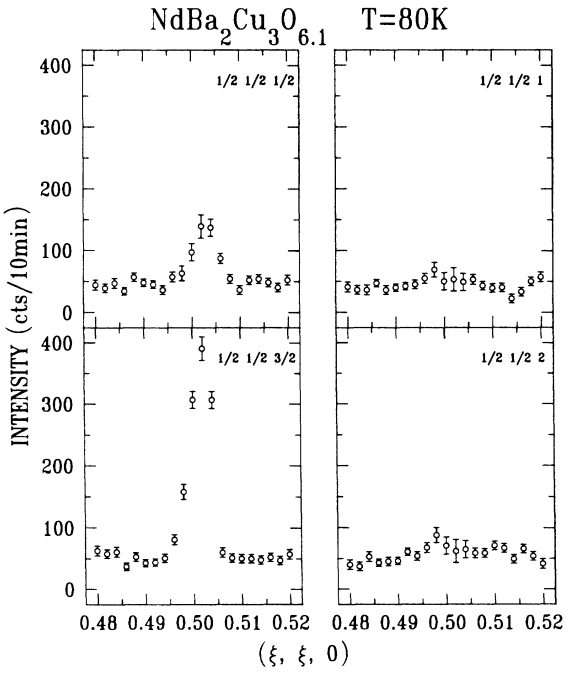

FIG. 1. Neutron scans at 80 K, through the magnetic reflections $(\frac{1}{2}\ \frac{1}{2}\ l)$ with half integer l, compared to the scans made, with the same statistic, through $(\frac{1}{2}\ \frac{1}{2}\ l)$ reflections with integer l.

$YBa_2Cu_3O_{6.35}$ single crystal, well below the Néel temperature, a second transition to a new magnetic structure characterized by both $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, 1)$ wave vectors. The competition between the two types of ordering was then attributed to frustrated spins due to the presence of Cu^{2+} moments in the oxygen deficient layers. In this paper we report on a new magnetic ordering in a single crystal of $NdBa_2Cu_3O_{6.1}$. The structure is uniquely characterized by the magnetic wave vector $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The $(\frac{1}{2}, \frac{1}{2}, 1)$ ordering type is only barely detected as fluctuations.

The single crystals were obtained using proper amounts of $BaCO_3$, Nd_2O_3, and CuO mixed and heated up to 1300°C in a Pt crucible. The mixture was slowly cooled at the rate of 0.5°C/min down to 800°C and then quenched. Single crystals were grown on the inside wall of the solid mixture of oxides. The single crystal used in this neutron experiment was annealed in Ar-gas atmosphere for 100 h at 800°C. It is a tetragonal single crystal $1.2\times1.2\times0.2$ mm^3 in volume with the lattice parameters $a=3.882$ Å and $c=11.689$ Å; these were measured at room temperature using neutrons with well calibrated energy. The oxygen content of approximately 6.1 which is known from electron-probe microanalysis, seems compatible with the measured Néel temperature T_N implied by the (T_N,x) phase diagram of Transquada *et al.*,[9] determined for yttrium compounds. The neutron scattering measurements were carried out at the Brookhaven high-flux-beam reactor on the H9 triple-axis spectrometer, using 5-meV neutrons and a Be filter to suppress shorter wavelength contamination. The pyrolitic graphite (PG) (002) reflection was used for the double monochromator and analyzer. The collimations were set to 60′-40′-60′-40′-80′. A second set of measurements was taken on the H7 triple-axis spectrometer using neutrons with energy 14.7 meV; this allowed us to collect a larger number of Bragg reflections for structural calibrations. Two PG filters as well as a PG(002) monochromator and analyzer were employed with 20′-40′-40′-80′ collimations. All of the scans in this work were performed in the (110),(001) horizontal scattering plane so that reflections with Miller indices (hhl) could be accessed.

In Fig. 1 we show at 80 K two sets of scans through the $(\frac{1}{2}\,\frac{1}{2}\,l)$ magnetic reflections for both integer and half integer l. The data clearly indicate the presence of strong $(\frac{1}{2}, \frac{1}{2}, l)$ with l half integer while the intensity at the scattering vectors $(\frac{1}{2}, \frac{1}{2}, l)$ with l integer, is barely above the background; the integer-l scattering was carefully monitored over a wide temperature range. Although there may be $(\frac{1}{2}, \frac{1}{2}, l$ integer) fluctuations we find no evidence for a genuine long-range-ordered component from 80 to 385 K. This result is somewhat surprising since Li *et al.*[7] have found the exact opposite result. Specifically, they have systematically searched for half integer-l peaks in similar single crystals of $NdBa_2Cu_3O_{6+x}$ but instead have observed $(\frac{1}{2},\frac{1}{2},1)$-type ordering only. We will discuss these differences at the end of this paper.

In Fig. 2 we show the temperature evolution of the $(\frac{1}{2}, \frac{1}{2}, \frac{3}{2})$ magnetic reflection. As T is increased up to $T_N\approx385$ K, the intensity vanishes continuously. The

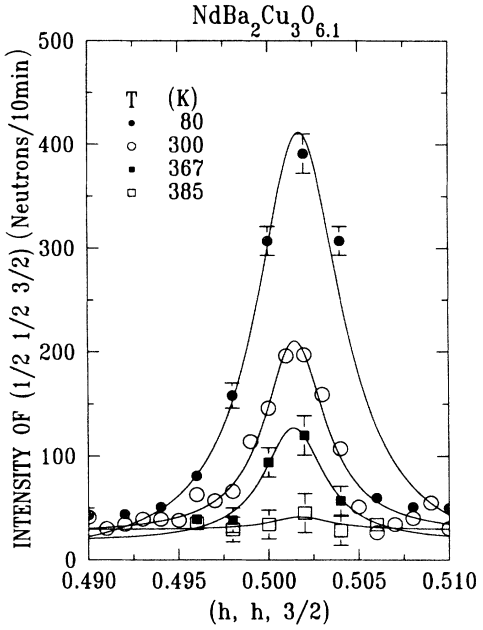

FIG. 2. Temperature dependence of the magnetic $(\frac{1}{2}, \frac{1}{2}, \frac{3}{2})$ peak. The solid lines are Lorentzian fits of the peak profile.

variation of the integrated intensity, proportional to the square of the average staggered magnetization, is shown in Fig. 3. The continuous line is a fitted power-law curve $I\sim(T_N-T)^{2\beta}$ with $\beta\approx0.30\pm0.05$; this should be viewed as a parametrization of the data and not the determination of the order-parameter critical exponent.

In Table I we list the integrated intensities of the measured $(H/2, H/2, L/2)$ peaks with H and L being odd integers. These intensities were collected at room temperature using a $\theta-2\theta$ scan mode. The evolution of these measured magnetic intensities with the L component of the scattering vector is clearly compatible with spins lying in the tetragonal planes. As for the Y(123) com-

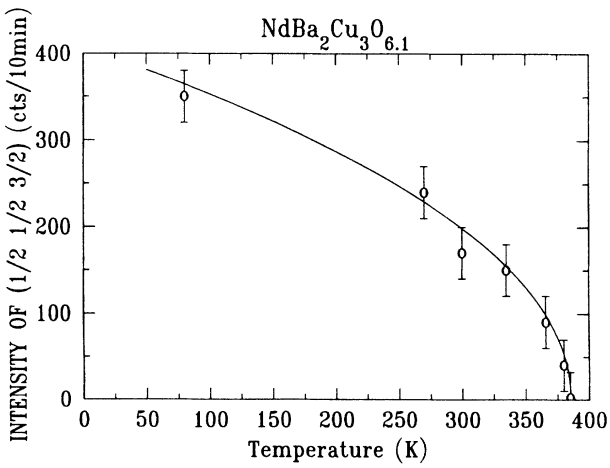

FIG. 3. Temperature variation of the integrated intensity of the $(\frac{1}{2}, \frac{1}{2}, \frac{3}{2})$ peak, proportional to the square of the magnetization. The solid line is a fit to a power-law curve $\sim(T_N-T)^{2\beta}$ with $T_N=385$ K and $\beta=0.30\pm0.05$.

TABLE I. Integrated intensity of magnetic reflections ($H/2$, $H/2$, $L/2$) observed (I_o) and calculated (I_c) for single crystal of $NdBa_2Cu_3O_{6.1}$ assuming collinear spins lying in the tetragonal planes with $\epsilon=0.10$ and $\epsilon=0$.

H	L	Q (Å^{-1})	I_o	I_c ($\epsilon=0.1$)	I_c ($\epsilon=0$)
1	1	1.18	56(21)	54	45
1	3	1.40	186(22)	190	240
1	5	1.77	91(21)	98	87
1	7	2.20	6(12)	5	1
1	13	3.68	0(18)	1	1
3	1	3.44	4(18)	7	6
3	3	3.53	53(18)	26	29
3	5	3.69	28(18)	16	14
3	7	3.92	0(20)	1	0
3	9	4.20	23(24)	17	22
$\sum \lvert I_c-I_o \rvert / \sum I_o=$				0.14	0.26

pounds we expect for structural reasons, the Cu^+ ions to be mostly located in the oxygen deficient B planes (Cu chain) which should thence have a small staggered magnetization relative to that of CuO_2 (A,C) planes (see Fig. 4). If we assume collinear spins with the same magnitude $\langle S \rangle$ on the CuO_2 layers with antiferromagnetic nearest-neighbor ordering of A and C planes, we can readily write the magnetic structure factor as

$$F_M \sim \langle S \rangle [\epsilon + 2\cos(2\pi/u)] ,$$

where l is half integer and ϵ is the fractional staggered magnetization lying in the oxygen deficient planes; here u is the z coordinate of the CuO_2 plane in units of c. We have used ϵ and $\langle S \rangle$ as adjustable parameters to fit the observed magnetic intensities of ten reflections listed in Table I. Making use of the magnetic form factor $f(\mathbf{Q})$ of the Cu^{2+} ions determined experimentally in La_2CuO_4 by Freltoft *et al.*,[10] we obtained the best fit of our data for the positive value of $\epsilon=0.10\pm0.02$ and the ordered moment on the CuO_2 planes of the order of $\langle S \rangle=0.40\pm0.02$. For these values the calculated intensities are reported in the table as

$$I_c \sim f(\mathbf{Q})^2 \lvert F_M \rvert^2 \langle 1-(\hat{\mathbf{Q}}\cdot\hat{\mathbf{S}})^2 \rangle / \sin(2\theta) ,$$

where $\hat{\mathbf{Q}}$ and $\hat{\mathbf{S}}$ are the unit vectors in the direction of the scattering vector $\mathbf{Q}$ and the spin S, respectively; $1/\sin(2\theta)$ is the angular (Lorentz) factor for single crystals. In this fit u was fixed equal to the value 0.355 ± 0.002 which we determined on the same sample from structural refinement of 20 independent nuclear reflections. The agreement in general is quite good given the small number of adjustable parameters and the uncertainties in $f(\mathbf{Q})$. Figure 4 shows the resulting magnetic structure; the positive polarity of ϵ, central for the sequence of alternating $3+$ spins and $3-$spins, was carefully established by performing various fits starting from many different initial values. This sequence is clearly more energetically favored than the sequence $+-+-+-$ which one would obtain with exclusively antiferromagnetic interplanar interactions.

The magnetic structures observed in Y(123) and

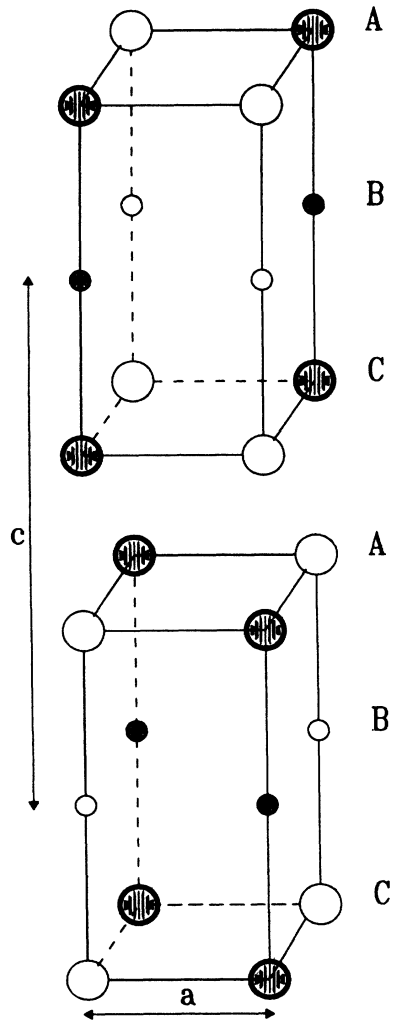

FIG. 4. The magnetic spin structure for $NdBa_2Cu_3O_{6.1}$. Two chemical unit cells are shown with white and black circles representing the Cu atoms only. Along the c axis, the sequence three white circles next to three black circles corresponds to a sequence of $3+$ spins and $3-$spins. The oxygen deficient layer (B) has smaller moment represented by smaller circle. In the tetragonal plane the spins are ordered antiferromagnetically in both a and b directions.

Nd(123) may be readily understood. The two basic sequences are given by

		A	B	C	A	B	C
Type 1	$(\frac{1}{2},\frac{1}{2},1)$	1	ϵ	-1	1	ϵ	-1
Type 2	$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	1	ϵ	1	-1	$-\epsilon$	-1

In both cases the nearest-neighbor Cu^{2+} spins in the Cu planes, that is C and A, are antiparallel; we label the direct CuO_2 plane-CuO_2 plane interplanar exchange J^{pp}_{NN}. There is then, in addition, a next nearest-neighbor interplanar (A-C) coupling J^{pp}_{NNN} and a nearest-neighbor interplanar coupling between the Cu^{2+} chains and Cu^{2+} planes (AB,BC) which we label J^{cp}_{NN}. In mean field theory one has

$$E_{(\frac{1}{2},\frac{1}{2},1)} \sim -J^{pp}_{NN} - J^{pp}_{NNN}$$

and

$$E_{(\frac{1}{2},\frac{1}{2},\frac{1}{2})} \sim -J^{pp}_{NN} - J^{pp}_{NNN} + 2\epsilon J^{cp}_{NN} \ .$$

We expect on general grounds $|J^{pp}_{NN}| \gg |J^{pp}_{NNN}|$, $|\epsilon J^{cp}_{NN}|$, consistent with the two observed structures. Consequently the competition between the two types of ordering and other eventual magnetic structures is mainly governed by J^{pp}_{NNN} and ϵJ^{cp}_{NN}. Accordingly it is easy to see that there exists an $\epsilon_0 = -J^{pp}_{NNN}/J^{cp}_{NN}$ such that for $\epsilon > \epsilon_0, E_{(\frac{1}{2}\frac{1}{2}\frac{1}{2})} < E_{(\frac{1}{2}\frac{1}{2}1)}$ and thus the magnetic ordering of type 2 is expected to be the ground-state configuration. This is the case for the single crystal of $NdBa_2Cu_3O_{6.1}$ we studied and for which we measured $\epsilon = 0.10 \pm 0.02$ so that $|J^{pp}_{NNN}| < |0.10 J^{cp}_{NN}|$. The fact that Li *et al.*[7] reported the other type of ordering in a similar single crystal with an unspecified oxygen content (x) would suggest that ϵ is probably strongly dependent on (x) and possibly also on subtle oxygen ordering or lattice imperfections.

The fact that J^{cp}_{NN} is ferromagnetic may be readily understood by considering the relevant Cu orbitals. Specifically, the Cu^{2+} chain hole spin will occupy a $3d(z^2-y^2)$ orbital which will then be admixed through the intervening oxygen with the filled $3d(2z^2-x^2-y^2)$ orbital of the Cu^{2+} atoms in the plane. The latter is orthogonal to the unoccupied Cu^{2+} $3d(x^2-y^2)$ orbital. Hence by Hund's rules, this Cu^{2+}-Cu^{2+} exchange J^{cp}_{NN} must be ferromagnetic. The sign of J^{pp}_{NNN} which rests on long range coupling cannot be readily deduced.

In conclusion, by showing the existence of a different type of magnetic ordering in $NdBa_2Cu_2O_{6.1}$ we have shown that the oxygen deficient layer can have a magnetic moment, and that its presence is essential in determining the three dimensional magnetic structure. Further studies are needed to draw a complete phase diagram.

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