RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 37, NUMBER 13 1 MAY 1988

Successive magnetic phase transitions in tetragonal $YBa_2Cu_3O_{6+x}$

H. Kadowaki,* M. Nishi, Y. Yamada, H. Takeya, and H. Takei
The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

S. M. Shapiro and G. Shirane
Brookhaven National Laboratory, Upton, New York 11973-5000
(Received 25 January 1988)

Neutron diffraction experiments on a nonsuperconductivity tetragonal single crystal of $YBa_2Cu_3O_{6+x}$ (with $x\sim0.35$) reveal a second magnetic phase transition associated with appearance of superlattice peaks at $(\frac{1}{2}\frac{1}{2}l)(l$ = half-integer) at about 40 K, which is well below the Néel temperature 405 ± 5 K. This transition is associated with the ordering of the Cu^{2+} moments on the oxygen-deficient layers. The observed magnetic intensities at 9 K are consistent with ground-state spin configurations of a model which takes account of frustration.

Since the discovery of high-T_c superconductors,[1] considerable effort has been devoted to elucidating the mechanism of the pairing interactions.[2] Magnetic origins of the interaction are considered to be important.[3] The magnetic scattering experiments[4] on semiconducting $La_2CuO_{4-\delta}$ showed that it can be considered as an $S=\frac{1}{2}$ quasi-two-dimensional antiferromagnet on a square lattice with a large coupling constant on the order of 10^3 K. The other class of high-T_c superconductors, $YBa_2Cu_3O_{6+x}$, was expected to have similar magnetic properties, because the valence[5] of Cu in the CuO_2 layers is expected to remain 2+. Detection of the magnetic ordering remained elusive until the muon-spin-relaxation (μSR) measurement of Nishida *et al.*[6] showed that long-range order was present. The magnetic structure of $YBa_2Cu_3O_{6+x}$ ($x=0$ and 0.15) was very recently established by Tranquada *et al.*[7] using powder neutron diffraction. They showed that the Cu atoms on the oxygen-deficient layers (*B* layer in Fig. 1) have no magnetic moment. The other two layers are coupled antiferromagnetically. The resultant diffraction pattern from this structure gives a series of $(\frac{1}{2}\frac{1}{2}l)$ (l=integer) superlattice peaks. In this Rapid Communication we report the first neutron scattering study of antiferromagnetism on a nonsuperconducting single crystal of $YBa_2Cu_3O_{6+x}$. The new result is that a second magnetic phase transition occurs well below the Néel temperature resulting from the ordering of Cu atoms on the *B* layers. The important consequence of this is that the spins on the next-nearest-neighboring *A* and *C* layers have parallel components.

Single crystals of $YBa_2Cu_3O_{6+x}$ were grown by a CuO flux method.[8] The sample ($5\times10\times1.5$ mm^3) contains many thin single crystals of $YBa_2Cu_3O_{6+x}$ among sintered powders of Y-Ba-Cu-O and CuO. The oxygen content is not uniform. The sample contains a tetragonal crystal and an orthorhombic crystal whose axes are aligned to within 0.3 degree. Thus, the crystal has a triplet structure: one tetragonal phase with *c*-lattice parameter $c=11.785(4)$ Å and a twinned orthorhombic phase with $c=11.679(4)$ Å at room temperature. From the known variation of *c* with oxygen content[9] *x*, we find that $x\simeq0.35$ for the tetragonal crystal and $x\simeq0.99$ for the orthorhombic crystal. The volume of both are comparable ($3\times7\times0.1$ mm^3). From the positions of the magnetic peaks we can establish that the magnetic scattering is associated with the tetragonal crystal.

The neutron scattering measurements were performed on the H4M triple axis spectrometer at the Brookhaven High Flux Beam Reactor. Pyrolytic graphite (002) reflection was used for the monochromator and the

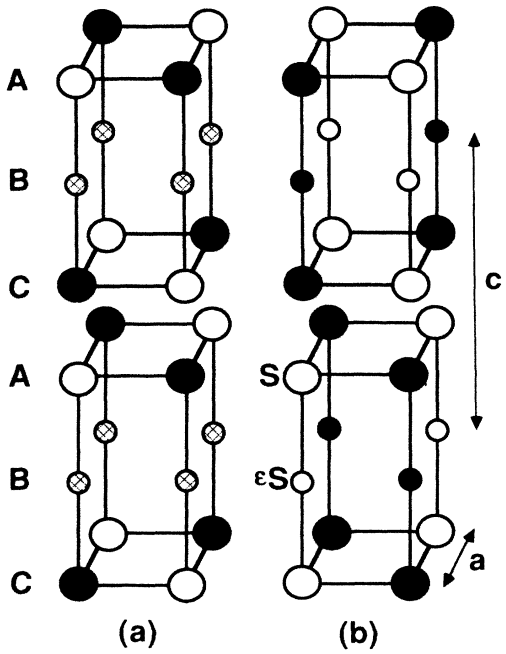

FIG. 1. (a) Magnetic structure corresponding to $(\frac{1}{2}\frac{1}{2}l)(l$=integer) reflections. Open and closed circles at Cu sites in CuO_2 planes stand for up and down spins. Cross-hatched small circles represent no ordering in oxygen-deficient planes. Solid lines connect pairs of sites bridged by fully occupied oxygen atoms. Previous powder measurement (Ref. 7) shows this structure with spins in the *c* plane ($T_{N2}<T<T_{N1}$). (b) Magnetic structure which gives $Q=(\frac{1}{2}\frac{1}{2}l)(l$=half-integer) reflections. Small circles are ordered moments in oxygen-deficient planes.

analyzer. Higher-order neutrons were removed by the pyrolytic graphite filter. The neutron energy was fixed at 14.7 meV, and the collimation 40′−40′−40′−80′ was employed. The sample was mounted in either a Displex refrigerator or in an air furnace, with the $(1\bar{1}0)$ axis vertical so as to measure the (hhl) zone.

Several scans along $Q=(\frac{1}{2}\ \frac{1}{2}\ \zeta)$ measured at 9, 80, and 470 are shown in Fig. 2. Peaks observed at $(\frac{1}{2}\ \frac{1}{2}\ l)(l=1,2,3,\ldots)$ correspond to the spin structure [Fig. 1(a)] previously determined by the powder measurements.[7] Temperature dependence of the $(\frac{1}{2}\ \frac{1}{2}\ 1)$ peak intensity is shown in Fig. 3. From this figure, it is seen that the intensity disappears at the Néel temperature $T_{N1}=405\pm5$ K. After heating in air to 470 K, no hysteresis is observed when cooling back to room temperature which indicates that the oxygen content did not change during heating.

The new features observed in Fig. 2 are magnetic peaks at $(\frac{1}{2}\ \frac{1}{2}\ l)(l=\frac{1}{2},\frac{3}{2},\frac{5}{2},\ldots)$. The temperature dependence of the $(\frac{1}{2}\ \frac{1}{2}\ \frac{3}{2})$ peak intensity is also shown in Fig. 3. One can easily see that a second phase transition occurs at $T_{N2}\simeq40$ K below which the intensity begins to increase. Associated with this increase is a decrease of $(\frac{1}{2}\ \frac{1}{2}\ 1)$ intensity at nearly the same temperature. No hysteresis is observed between heating and cooling which means that the transition is second order or first order with a broad transition temperature presumably because of nonuniform oxygen content or degree of disorder of oxygen. The transition at T_{N1} appears sharper than T_{N2}, which suggest that the lower transition may be more susceptible to such nonuniformity. However, this transition is not a peculiar property of only this crystal. Another crystal from the same batch also shows similar behavior at nearly the same temperature.

The observation of peaks at $(\frac{1}{2}\ \frac{1}{2}\ l)$ implies that the magnetic structure in the c plane is the simple up-down structure as shown in Fig. 1. Thus, the stacking sequence of six spins in the magnetic unit cell (in Fig. 1) remains to be determined. We utilize the fact that the two classes of the Fourier components ($l=$ integer and half-integer) can be treated separately. The $l=$ integer component has a structure of a period c with three adjustable spins (A,B,C). The $l=$ half-integer component has a structure which has a period $2c$ and satisfies the relation $\mathbf{S}_r=-\mathbf{S}_{r+c}$ and also has three adjustable spins (A,B,C). We assume collinear structures with the same magnitude of spins on the CuO_2 layers (A,C) for the both structures. For the $l=$ integer component, there exists an extinction rule that $l=0$ is missing, which implies that the summation of the three spins (A,B,C) is zero and consequently the B layers have zero moment. Therefore, the structure is that shown in Fig. 1(a), which is in agreement with Ref. 7. For the $l=$ half-integer component, a moment develops on the oxygen-deficient B layers and therefore the two spins on the next-nearest neighboring A and C layers must be parallel. Thus, the structure is that shown in Fig. 1(b) with an adjustable parameter ϵ, the ratio of the magnitude of spins of B to A layers.

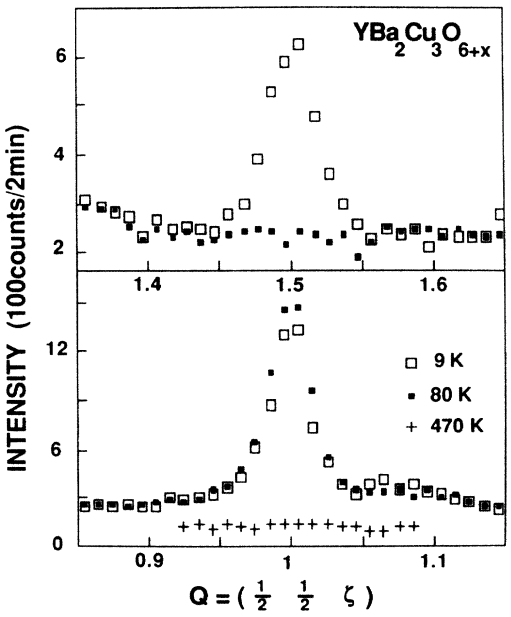

FIG. 2. Scans along $Q=(\frac{1}{2}\ \frac{1}{2}\ \zeta)$ at $T_{N2}>T=9.0$ K, $T_{N2}<T=80$ K $<T_{N1}$, and $T_{N1}<T=470$ K.

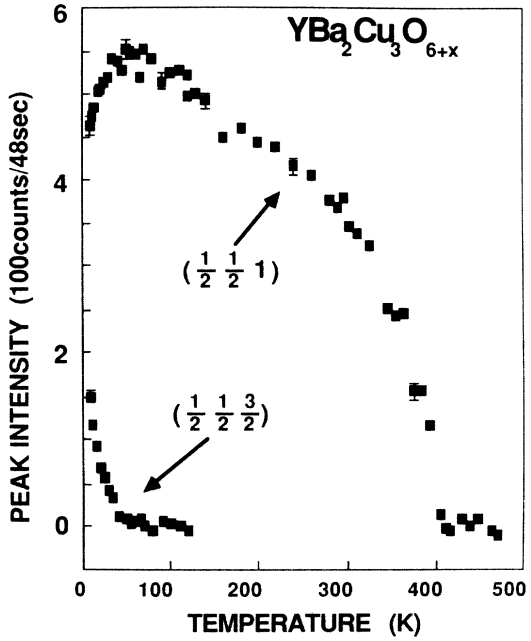

FIG. 3. Peak intensities of $(\frac{1}{2}\ \frac{1}{2}\ 1)$ and $(\frac{1}{2}\ \frac{1}{2}\ \frac{3}{2})$ magnetic reflections as a function of temperature. Background (~90 counts/48 sec) is subtracted.

In order to determine the structures, we have measured integrated intensities of Bragg reflections using the $\theta-2\theta$ mode at 9 K. The observed and calculated intensities of integral l which are not contaminated by powder lines are listed in Table I. In the calculation, we assume $g=2$ (g factor), $z=0.36$ (the positional parameter[10] of the Cu sites of the A and B layers), and use values of the form factor $f(Q)$ calculated in Ref. 11. The result that the spin direction is in the c plane confirms the powder measurement[7] as shown in Fig. 4(a). The ordered moment is es-

TABLE I. Integrated intensity multiplied by sin $2\theta_B$ of magnetic reflections at 9 K.

(hkl)	I_{obs}	$I_{calc}S\perp c$	$I_{calc}S\parallel c$
$(\frac{1}{2}\ \frac{1}{2}\ 1)$	16.1 ± 0.5	16.0	20.3
$(\frac{1}{2}\ \frac{1}{2}\ 3)$	7.2 ± 0.7	7.4	2.7
$(\frac{3}{2}\ \frac{3}{2}\ 2)$	9 ± 1	10	15
$(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$	1.2 ± 0.2	1.2	1.6
$(\frac{1}{2}\ \frac{1}{2}\ \frac{3}{2})$	6.2 ± 0.3	6.2	6.5
$(\frac{1}{2}\ \frac{1}{2}\ \frac{5}{2})$	5.3 ± 0.4	5.3	2.4
$(\frac{1}{2}\ \frac{1}{2}\ \frac{7}{2})$	0 ± 0.5	0.01	0.01

timated to be $0.45\ \pm0.07\mu_B$ at 9 K.

The structure factor of the structure of Fig. 1(b) is given by $|F_M|^2\propto[2\ \cos(2\pi lz)+\epsilon]^2$ ($l=$ half integer). The observed and the calculated intensities are also listed in Table I. The calculated intensities for the spins located in the c plane are more consistent with the observations. Therefore, we conclude that the spins lie in the c plane [Fig. 4(b)]. The ordered moment at the CuO_2 layers ($g\mu_BS$) is estimated to be $0.22\pm0.07\mu_B$ at 9 K. The estimated parameter ϵ is $\epsilon=0.06\pm0.03$. The parameter ϵ is small and the positive sign yields a slightly better fit to the observed peaks than a negative sign, which cannot be completely ruled out with the present data. The small value of the parameter indicates that the ordered moment of the Cu atoms in the oxygen-deficient layers is much smaller than that of the CuO_2 layers. The important consequence of the ordered moment, however small, is that the spins on the next-nearest-neighboring A and C layers have the parallel components as opposed to the antiparallel moments for the $l=$ integer structure.

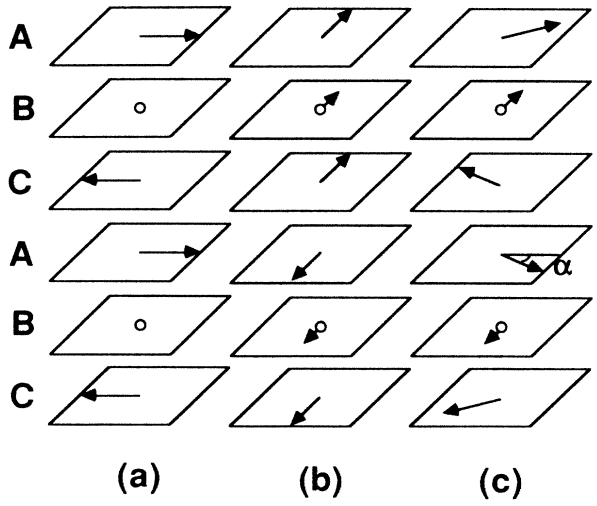

FIG. 4. (a) and (b) represent the stacking along the c axis of the spins of Figs. 1(a) and 1(b) which are confined to the c plane. (c) is the resultant spin structure given by vector summation of (a) and (b). (c) is also ground-state spin configurations of the model described in the text with the canting angle α from an easy axis in the c plane.

Since the magnetic structures corresponding to both $l=$ integer and half-integer are determined, we shall discuss the resultant spin structure. The mutual angle of the both structures [Fig. 4(a) and 4(b)] cannot be obtained from the intensity data. However, if we impose the physically reasonable assumption that the magnitude of the combined spins in the layers A and C are the same, the angle between the structures of Fig. 4(a) and 4(b) must be 90° and the resultant structure is shown in Fig. 4(c). The tilting angle is $\alpha=26\pm7$ deg. The magnitudes of the spins in the A (or C) and the B layers are $0.50\pm0.07\mu_B$ and $0.012\pm0.007\mu_B$ per Cu atom, respectively. If this is the case, the phase transition at T_{N2} is a second-order phase transition characterized by the canting. It should be noted that if nonuniform ordering in the crystal occurs, there are other possibilities. For example, an incoherent mixture of the structures of Figs. 4(a) and 4(b) with the same ordered moment and occupying 85% and 15% of the volume respectively at 9 K, gives the same intensities. In this case the phase transition at T_{N2} is first order.

Let us now discuss the magnetic structure at low temperatures in terms of a simple model calculation which takes account of the frustration brought about by the magnetic moments in the B layers. For simplicity, we assume continuous spins of unit length in the A and C layers and length σ for the B layers. From the known high-temperature structure,[7] the exchange coupling between the next-nearest-neighbor A and C layers, J_2 is antiferromagnetic; the coupling between the nearest-neighbor A and C layers, J_3, is also antiferromagnetic. An additional exchange constant, J_1, is needed to couple the B layers with their nearest A and C layers. J_1 and J_2 give rise to the frustration. We also include a fourfold anisotropy in the easy c plane for the spins in the A and C layers. The minimum energy configuration is the same as that shown in Fig. 4(c), where the canting angle α from the easy axis is an adjustable parameter.

We take the model energy which should be minimized with respect to α as

$$\begin{aligned}E&=-J_3+2J_1\sigma\sin\alpha-J_2\cos(2\alpha)-D\cos(4\alpha)\\&=-J_3-J_2+D+2J_1\sigma\sin\alpha\\&\quad+2J_2\sin^2\alpha-8D(\sin^2\alpha-\tfrac{1}{2})^2\ ,\end{aligned}$$

where $D(>0)$ represents the anisotropy parameter. One can see from this equation that the energy is minimum at $-\pi/2<\alpha<\pi/2$ or exactly at $\alpha=\pm\pi/2$, which depends on the parameters $J_1\sigma$, J_2, and D. In the small anisotropy case ($D\ll J_2$), the magnetic structure at $T=0$ is shown in Fig. 4(c) ($-\pi/2\le\alpha\le\pi/2$). It continuously transforms to the structure Fig. 4(a) ($\alpha=0$), when σ approaches zero as T approaches T_{N2}. In the large anisotropy case ($D\gg J_2$), the spin structure at $T=0$ is shown in Fig. 4(b) for negative J_1($\alpha=\pi/2$). The canting angle α discontinuously changes from $\alpha=\pi/2$ to $\alpha\sim0$ with increasing temperature at some value of σ. The proposed two models, the canting model [Fig. 4(c)] and the mixture of structure [Figs. 4(a) and 4(b)], are completely explainable by this simple calculation. Since the temperature dependence of the intensity of $(\frac{1}{2}\ \frac{1}{2}\ \frac{3}{2})$ shows no hysteresis and Cu^{2+} magnetic moments generally have small anisotropies, the

small anisotropy case with the second-order transition seems to be appropriate for T_{N2}.

In conclusion, we have found that the successive phase transitions take place in the tetragonal $YBa_2Cu_3O_{6+x}$ crystal. The newly observed reflections $(\frac{1}{2}\ \frac{1}{2}\ l)$ with half-integral l are consistent with the structure model shown in Fig. 1(b). The finite molecular field at the oxygen-deficient layers clearly shows that the phase transition at T_{N2} is brought about by the frustration due to magnetic moments in this layer; and the simple frustration model accounts for the proposed structures qualitatively. The present work will be useful to understand the whole magnetic properties of tetragonal $YBa_2Cu_3O_{6+x}$, especially the frustration effect.

We would like to thank S. Mitsuda, S. K. Sinha, J. M. Tranquada, and Y. J. Uemura for valuable discussions. This work was carried out as part of the U.S.-Japan Cooperative Neutron Scattering Program. Work at Brookhaven National Laboratory is supported by the Division of Material Sciences, U.S. Department of Energy, under Contract No. DE-AC02-76CH00016.

---

*Present address: Brookhaven National Laboratory, Upton, NY 11973.

[1]J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986); M. K. Wu *et al.*, Phys. Rev. Lett. **58**, 908 (1987).

[2]J. S. Tsai, Y. Kubo, and J. Tabuchi, Phys. Rev. Lett. **58**, 1979 (1987); K. Kitazawa *et al.*, Jpn. J. Appl. Phys. **26**, L751 (1987).

[3]P. W. Anderson, Science **235**, 1196 (1987); P. W. Anderson *et al.*, Phys. Rev. Lett. **58**, 2790 (1987); V. J. Emery, *ibid.* **58**, 2794 (1987); J. E. Hirsch, *ibid.* **59**, 228 (1987).

[4]D. Vaknin *et al.*, Phys. Rev. Lett. **58**, 2802 (1987); S. Mitsuda *et al.*, Phys. Rev. B **36**, 822 (1987); T. Freltoft *et al.*, *ibid.* **36**, 826 (1987); G. Shirane *et al.*, Phys. Rev. Lett. **59**, 1613 (1987).

[5]H. Oyanagi *et al.*, Jpn. J. Appl. Phys. **26**, L1233 (1987); S. Massidda *et al.*, Phys. Lett. A **122**, 198 (1987); **122**, 203 (1987).

[6]N. Nishida *et al.*, Jpn. J. Appl. Phys. **26**, L1856 (1987); J. Phys. Soc. Jpn. **57**, 599 (1988); J. H. Brewer *et al.*, Phys. Rev. Lett. **60**, 1073 (1988).

[7]J. M. Tranquada *et al.*, Phys. Rev. Lett. **60**, 156 (1988).

[8]H. Takei *et al.*, Jpn. J. Appl. Phys. **26**, L1425 (1987); Y. Iye *et al.*, *ibid.* **58**, 1057 (1987).

[9]A. Manthiram *et al.*, J. Am. Chem. Soc. **109**, 6667 (1987); R. J. Cava *et al.*, Phys. Rev. B **36**, 5719 (1987).

[10]F. Izumi *et al.*, Jpn. J. Appl. Phys. **26**, L1193 (1987); **26**, L1214 (1987); W. I. F. David *et al.*, Nature **327**, 310 (1987).

[11]J. Akimitsu and Y. Ito, J. Phys. Soc. Jpn. **40**, 1621 (1976).