

## Neutron-Diffraction Determination of Antiferromagnetic Structure of Cu Ions in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ with $x = 0.0$ and $0.15$

J. M. Tranquada, D. E. Cox, W. Kunmann, H. Moudden,<sup>(a)</sup> G. Shirane, M. Suenaga, and P. Zolliker  
*Brookhaven National Laboratory, Upton, New York 11973*

and

D. Vaknin,<sup>(b)</sup> S. K. Sinha, M. S. Alvarez, A. J. Jacobson, and D. C. Johnston<sup>(c)</sup>  
*Corporate Research Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801*  
 (Received 23 November 1987)

Neutron-diffraction experiments on ceramic powders of  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  (nonsuperconducting, with  $x = 0.0$  and  $0.15$ ) have confirmed the existence of long-range, three-dimensional, antiferromagnetic order of the Cu spins. The structure determination was aided by the use of uniaxially oriented powders. The ordering wave vector within a  $\text{CuO}_2$  plane is  $(\frac{1}{2} \frac{1}{2})$  and the planes are coupled antiferromagnetically along the  $c$  axis. The Néel temperature is  $400 \pm 10$  K for the  $x = 0.15 \pm 0.05$  sample and  $\geq 500$  K for  $x = 0.0$ .

PACS numbers: 74.70.Vy, 75.25.+z

Since their discovery,<sup>1</sup> a great deal of effort has been expended in an attempt to understand the electronic and magnetic structures of the superconducting copper oxides. X-ray absorption measurements<sup>2</sup> indicated that in  $\text{La}_{2-x}(\text{Ba},\text{Sr})_x\text{CuO}_{4-y}$  the Cu ions have localized  $d$  electrons in a  $3d^9$  configuration, essentially identical to that in other  $\text{Cu}^{2+}$  compounds such as the antiferromagnetic insulator  $\text{CuO}$ .<sup>3</sup> This view was at least partially confirmed by the discovery<sup>4</sup> of antiferromagnetism in  $\text{La}_2\text{CuO}_4$  and is in agreement with some theoretical expectations.<sup>5</sup> It has since been established<sup>6</sup> that the dominant magnetic correlations in  $\text{La}_2\text{CuO}_4$ , existing to very high temperature, occur within the  $\text{CuO}_2$  planes. The Néel temperature  $T_N$ , which varies from 0 to 300 K (depending on the oxygen content<sup>7</sup>), does not properly reflect the large in-plane exchange interaction, but is actually determined by both the (large) in-plane exchange and the much weaker interplanar coupling. The system  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  contains almost identical  $\text{CuO}_2$  layers,<sup>8,9</sup> and following the realization that the compound is stable (at least at room temperature) for  $0 \leq x \leq 1$ , it became clear to us that antiferromagnetic order of the Cu ions should also occur in this material for small  $x$ .

The unit cell of tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  consists essentially of three oxygen-defect perovskite cubes stacked along the  $c$  axis, so that  $c \approx 3a$ . For  $x = 0$ , there are two planes of Cu atoms in which each pair of coppers is bridged by an oxygen, as in the  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$  compounds, and a third layer of Cu containing no coplanar oxygen atoms, as shown schematically in Fig. 1. As  $x$  increases above zero, the extra O atoms go into the third layer.<sup>8,9</sup>

From a simple electron-counting analysis, one would expect  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  to be an antiferromagnetic insulator for  $x \leq 0.5$ . Indeed, experimental studies<sup>9,10</sup> show

that  $x = 0.5$  is approximately the point above which superconductivity appears. The simple analysis also suggests that for  $x = 0.5$  all of the Cu should have a valence of  $2+$ , while for  $x \leq 0.5$  some  $\text{Cu}^{2+}$  might be reduced to

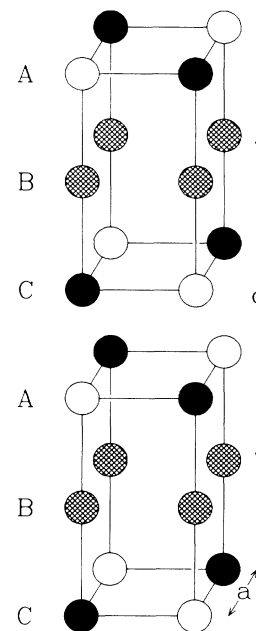


FIG. 1. Proposed magnetic spin structure for  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  with  $x$  near zero. Only copper atoms are shown for clarity; cross-hatched circles represent nonmagnetic  $\text{Cu}^{1+}$  ions, while filled and open circles indicate antiparallel spins at  $\text{Cu}^{2+}$  sites. Solid lines connect pairs of sites bridged by oxygen atoms. Two full chemical unit cells are shown stacked vertically; the magnetic unit cell has the same height as the chemical one, but it has double the area in the basal plane.

$\text{Cu}^{1+}$ . Some x-ray spectroscopic evidence<sup>11</sup> does indicate that  $\text{Cu}^{1+}$  is present in samples corresponding to small  $x$ . Structurally, one would expect the  $\text{Cu}^{1+}$  ions to be localized in the layer with little coplanar O, where the copper atoms are twofold coordinated by O along the  $c$  axis with the short interatomic spacing of 1.81 Å.

Our initial search for antiferromagnetism in samples with  $x=0.3, 0.4,$  and  $0.5$  was unsuccessful. (The  $x \approx 0.5$  sample was found to be orthorhombic and superconducting.) No anomalies have been observed<sup>9</sup> in the magnetic susceptibility which might have indicated appropriate oxygen concentrations or temperatures at which to look. However, subsequent muon-spin-rotation measurements<sup>12</sup> demonstrated that steady-state, local magnetic fields indicative of antiferromagnetic ordering occur near room temperature for  $x \lesssim 0.2$ . The neutron-diffraction studies were continued on ceramic samples of  $x=0.15$  and  $x=0.0$ . In both samples a very weak peak was observed at  $Q=1.268 \text{ \AA}^{-1}$  at room temperature. A proper interpretation of this feature was inhibited by our prejudice against the likelihood of antiferromagnetism at room temperature in these compounds. However, measurements on an  $x=0.15$  pressed-powder sample, which had been uniaxially oriented in a magnetic field (following Farrel *et al.*<sup>13</sup>), led to the proper indexing of the peak as  $(\frac{1}{2} \frac{1}{2} 1)$ .

Before continuing the discussion, the experimental procedures will be briefly discussed. The neutron-scattering measurements were performed on several triple-axis spectrometers at the high-flux beam reactor at Brookhaven National Laboratory. The (002) reflections of the pyrolytic-graphite monochromator and analyzer crystals were used. Much of the work to be discussed was performed with 5.0-meV neutrons, where a Be filter was used to reduce higher-order contamination. Some measurements were also made with  $E=14.7$  meV and pyrolytic-graphite filters.

The low-oxygen-content samples were prepared from  $\text{YBa}_2\text{Cu}_3\text{O}_7$  material which had been produced by the solid-state reaction technique.<sup>9,14</sup> The  $x=0.15 \pm 0.05$  sample was made at Brookhaven by our annealing the  $x=1$  material at 970 K in  $\text{N}_2$  for a day and then furnace cooling it. The oxygen content was characterized by weight loss and by profile refinement of neutron-diffraction data.<sup>14</sup> The few impurity peaks observed in the diffraction pattern had intensities of less than 0.7% of the strongest peak of the majority phase. The  $x=0$  sample was prepared at Exxon by the heating of  $x=1$  material in a He atmosphere at 1120 K for 8 h. Thermogravimetric analysis yielded  $x=-0.01$  for the final product.

Approximately 2 g of the  $x=0.15$  sample was ground to a fine powder, passed through a 400-mesh sieve, and placed in a cup made of aluminum foil. The sample cup was vibrated in an 8-T magnetic field at room temperature in order to align the  $c$  axes of the particles parallel to the magnetic field.<sup>13</sup> After removal from the field, the

sample was pressed to form a pellet. A rocking-curve measurement of the (001) nuclear peak indicated an intensity enhancement of 10 for the peak-to-minimum ratio and a full width at half maximum of  $\approx 50^\circ$ . Treating the oriented sample like a single crystal, we performed scans along various directions in reciprocal space in which it seemed likely that magnetic peaks might be found. These scans led to the identification of the  $(\frac{1}{2} \frac{1}{2} 1)$  peak, which caused us to search for other  $(\frac{1}{2} \frac{1}{2} l)$  reflections, and allowed us to solve the antiferromagnetic structure.

The observation of a peak, assumed to be magnetic, with  $h=k=\frac{1}{2}$  implies that within a Cu layer nearest-neighbor atoms have antiparallel spins, just as in the  $\text{CuO}_2$  layers of lanthanum cuprate. This, together with integer values for the third index  $l$ , implies the antiferromagnetic structure shown in Fig. 1. It simply remains to deduce with which phase the three layers stack along the  $c$  axis. In terms of the notation of Fig. 1, and assuming a collinear spin structure, we have for the magnetic structure factor

$$F_{hkl}^M = i \sin(\pi h) \sin(\pi k) (p_A e^{i2\pi z l} + p_B + p_C e^{-i2\pi z l}),$$

where  $p_A, p_B,$  and  $p_C$  are the amplitude factors for the  $A, B,$  and  $C$  antiferromagnetic layers, and  $z$  is the fraction of a unit-cell length  $c$  by which the  $A$  and  $C$  layers are displaced from  $B$ . (Diffraction studies have shown<sup>8,9</sup> that  $z=0.36$ .) As discussed previously, we expect that the  $\text{Cu}^{1+}$  ions should be located in the  $B$  layer. In that case,  $p_B \approx 0$ , and the other two layers are coupled either antiferromagnetically (denoted as  $+0-$ ) or ferromagnetically ( $+0+$ ). We have also considered the case in which all three layers have the same average sublattice magnetization, in which case the most reasonable possible sequences are  $+++$  and  $-+-$ . The magnetic structure factors for these four possible layer orderings are listed in Table I. The different cases can be distinguished experimentally by the relative intensities of  $(\frac{1}{2} \frac{1}{2} l)$  reflections with  $l=0-4$ .

Figure 2 shows measurements of several  $(\frac{1}{2} \frac{1}{2} l)$  reflections at room temperature in a large ( $\approx 9$  g), unoriented, sintered pellet of  $x=0.15$  material. Peaks are clearly observed for  $l=1$  and 2, but no peak is found

TABLE I. Magnetic structure factors for several different models (discussed in the text) of antiferromagnetic ordering in  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ .

$(hkl)$	$ F_{hkl}^M ^2$			
	$+0-$	$+0+$	$+++$	$-+-$
$(\frac{1}{2} \frac{1}{2} 0)$	0.0	4.0	9.0	1.0
$(\frac{1}{2} \frac{1}{2} 1)$	2.4	1.6	0.1	5.2
$(\frac{1}{2} \frac{1}{2} 2)$	3.9	0.1	0.4	1.9
$(\frac{1}{2} \frac{1}{2} 3)$	0.9	3.1	7.6	0.6
$(\frac{1}{2} \frac{1}{2} 4)$	0.5	3.5	0.7	8.2

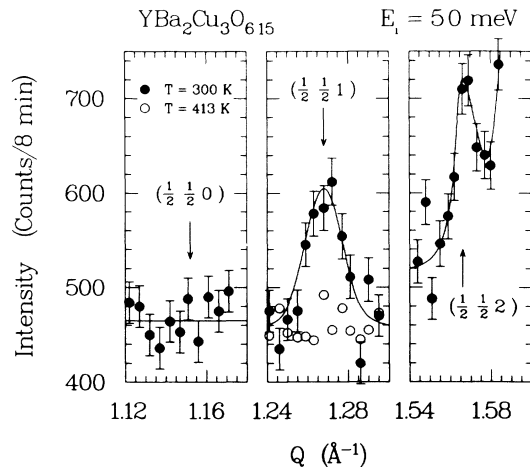


FIG. 2. Neutron-diffraction scans of the  $(\frac{1}{2} \frac{1}{2} l)$  magnetic peaks measured for the unoriented sintered pellet of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.15}$ . Solid lines are guides to the eye. The reciprocal-lattice parameters for this sample at room temperature were measured to be  $a^* = 1.629 \text{ \AA}^{-1}$  and  $c^* = 0.530 \text{ \AA}^{-1}$ .

at  $l=0$ , nor at  $l=4$  (not shown). Measurements on the uniaxially oriented sample showed the  $l=3$  reflection to be missing also. We find by inspection that, of the models considered in Table I, the only stacking sequence consistent with the data is  $+0-$ . Assuming the ordering to be  $+0-$ , we next consider the orientation of the magnetic moment  $\mathbf{M}$  of a Cu spin with respect to the lattice. Table II compares the integrated intensities of the same peaks (obtained at higher resolution) with scaled intensities calculated for two simple models,  $\mathbf{M} \parallel \mathbf{c}$  and  $\mathbf{M} \perp \mathbf{c}$ . The intensity ratio of the  $(\frac{1}{2} \frac{1}{2} 1)$  peak to the  $(\frac{1}{2} \frac{1}{2} 2)$  is consistent with the spins lying in the  $\text{CuO}_2$  planes, as they do in  $\text{La}_2\text{CuO}_{4-y}$ ; however, unlike the latter case, there is no unique direction within the plane.

The intensity of the  $(\frac{1}{2} \frac{1}{2} 1)$  peak is 0.5% of the (001). Making use of the magnetic form factor measured<sup>15</sup> for  $\text{Cu}^{2+}$  in  $\text{K}_2\text{CuF}_4$ , we obtain an ordered magnetic moment of  $(0.48 \pm 0.08) \mu_B$  per Cu atom at room temperature (assuming that only  $\frac{2}{3}$  of the copper atoms order magnetically). This value falls within the range of  $(0.2$  to  $0.6) \mu_B$  observed<sup>16</sup> as a function of oxygen content in  $\text{La}_2\text{CuO}_{4-y}$ .

The temperature dependence of the  $(\frac{1}{2} \frac{1}{2} 1)$  peak was studied by our heating the  $x=0.15$  sintered pellet in a stagnant He atmosphere. As shown in Fig. 3, the peak intensity gradually decreases to the background level at high temperature, and we conclude that  $T_N = 400 \pm 10$  K. Temperature-dependent measurements of the  $(\frac{1}{2} \frac{1}{2} 1)$  reflection made on the  $x=0$  sample indicated that antiferromagnetic ordering survives in that material to at least 500 K.<sup>17</sup>

To verify that the observed scattering is indeed magnetic, we have performed two tests. In the first, a search was made for the  $(\frac{1}{2} \frac{1}{2} 1)$  and  $(\frac{1}{2} \frac{1}{2} 2)$  reflections in the

TABLE II. Integrated intensities of magnetic reflections observed and calculated with use of two simple models of the spin orientation for  $\text{YBa}_2\text{Cu}_3\text{O}_{6.15}$ .

$(hkl)$	$Q$ ( $\text{\AA}^{-1}$ )	$I_{\text{obs}}$	$I_{\text{calc}}$ $\mathbf{M} \perp \mathbf{c}$	$I_{\text{calc}}$ $\mathbf{M} \parallel \mathbf{c}$
$(\frac{1}{2} \frac{1}{2} 0)$	1.152	$< 75$	0	0
$(\frac{1}{2} \frac{1}{2} 1)$	1.268	$430 \pm 60$	440	616
$(\frac{1}{2} \frac{1}{2} 2)$	1.566	$590 \pm 45$	571	422
$(\frac{1}{2} \frac{1}{2} 3)$	1.964	$< 240$	81	33
$(\frac{1}{2} \frac{1}{2} 4)$	2.414	$< 75$	26	7

$x=0.15$  sample using powder x-ray diffraction. No signal was observed at the level of 0.01% of the strongest peak, which in the case of x rays is the (103). Secondly, preliminary measurements of the  $(\frac{1}{2} \frac{1}{2} 1)$  reflection in the  $x=0$  sample were made with use of polarized neutrons and polarization analysis.<sup>18</sup> The purely magnetic signal obtained in the spin-flip channel at the center of the peak is  $110 \pm 24$  counts/h, falling to  $10 \pm 35$  counts/h at points  $0.06 \text{ \AA}^{-1}$  to either side of the center.

We have argued that the magnetic model shown in Fig. 1 is the most likely structure for  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  with  $x$  near 0. Consider what happens as  $x$  approaches 0.5. As oxygen enters the  $B$  plane, neighboring copper atoms will be converted from  $1+$  to  $2+$ , increasing the number of magnetic atoms in that plane. Moments in the  $B$  plane would likely cause some frustration of the  $A$ - $C$  ordering, resulting in a reduction of  $T_N$  and possibly leading to a new structure. Experiments are continuing on samples with  $x \approx 0.3$ - $0.4$  to study such effects. In any case, we expect that, in analogy with  $\text{La}_2\text{CuO}_{4-y}$ ,<sup>6</sup> two-

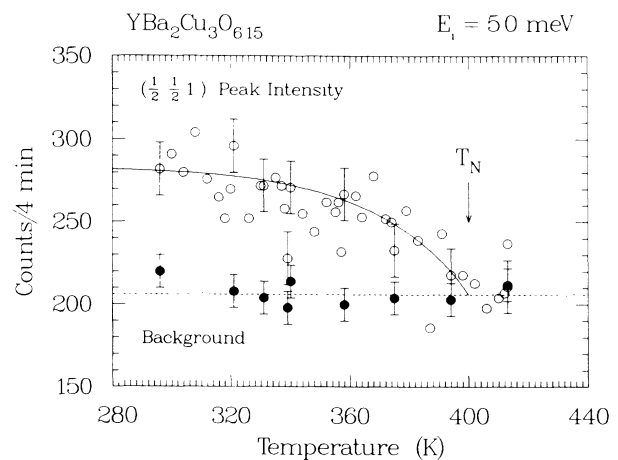


FIG. 3. Peak intensity (open circles) of the  $(\frac{1}{2} \frac{1}{2} 1)$  magnetic reflection as a function of temperature in  $\text{YBa}_2\text{Cu}_3\text{O}_{6.15}$ . Filled circles indicate background measurements. The solid and dashed lines are guides to the eye.

dimensional correlations within the  $\text{CuO}_2$  planes are quite strong. The study of such properties will require large single crystals.

There have already been numerous speculations on the relationship between antiferromagnetic correlations and superconductivity in copper-oxide ceramics. It is gratifying that the  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  system is now confirmed to have very similar magnetic behavior to  $\text{La}_2\text{CuO}_{4-y}$ . Further work will be required to determine the precise relationship between magnetic interactions and superconductivity in these materials.

We are pleased to acknowledge helpful discussions with J. D. Axe, R. J. Birgeneau, V. J. Emery, A. R. Moodenbaugh, M. Strongin, and Y. J. Uemura. Work at Brookhaven National Laboratory is supported by the Division of Materials Science, U.S. Department of Energy, under Contract No. De-AC02-76CH00016.

---

<sup>(a)</sup>Permanent address: Centre National de la Recherche Scientifique, Université de Paris-Sud, Orsay, France.

<sup>(b)</sup>Also at the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, PA 19104.

<sup>(c)</sup>Present address: Physics Department, Iowa State University, Ames, IA 50010.

<sup>1</sup>J. G. Bednorz and K. A. Müller, *Z. Phys. B* **64**, 189 (1986); M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang and C. W. Chu, *Phys. Rev. Lett.* **58**, 908 (1987).

<sup>2</sup>J. M. Tranquada, S. M. Heald, A. R. Moodenbaugh, and M. Suenaga, *Phys. Rev. B* **35**, 7187 (1987); J. M. Tranquada, S. M. Heald, and A. R. Moodenbaugh, *Phys. Rev. B* **36**, 5263 (1987).

<sup>3</sup>B. X. Yang, J. M. Tranquada, and G. Shirane, unpublished.

<sup>4</sup>D. Vaknin, S. K. Sinha, D. E. Moncton, D. C. Johnston,

J. M. Newsam, C. R. Safinya, and H. E. King, Jr., *Phys. Rev. Lett.* **58**, 2802 (1987).

<sup>5</sup>V. J. Emery, *Phys. Rev. Lett.* **58**, 2794 (1987).

<sup>6</sup>G. Shirane, Y. Endoh, R. J. Birgeneau, M. A. Kastner, Y. Hidaka, M. Oda, M. Suzuki, and T. Murakami, *Phys. Rev. Lett.* **59**, 1613 (1987).

<sup>7</sup>D. C. Johnston, J. P. Stokes, D. P. Goshorn, and J. T. Lewandowski, *Phys. Rev. B* **36**, 4007 (1987).

<sup>8</sup>A. Renault, G. J. McIntyre, G. Collin, J. P. Pouget, and R. Comès, *J. Phys. (Paris)* **48**, 1407 (1987).

<sup>9</sup>D. C. Johnston, A. J. Jacobson, J. M. Newsam, J. T. Lewandowski, D. P. Goshorn, D. Xie, and W. B. Yelon, in *Chemistry of High-Temperature Superconductors*, edited by D. L. Nelson, M. S. Whittingham, and T. F. George, American Chemical Society Symposium Series Vol. 351 (American Chemical Society, Washington, DC, 1987).

<sup>10</sup>R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak, and D. Weber, *Phys. Rev. B* **36**, 5719 (1987).

<sup>11</sup>H. Oyanagi, H. Ihara, T. Matsubara, T. Matsushita, M. Hirabayashi, M. Tokumoto, K. Murata, N. Terada, K. Senzaki, T. Yao, H. Iwasaki, and Y. Kimura, *Jpn. J. Appl. Phys., Pt. 2*, **26**, L1233 (1987); F. Baudelet, G. Collin, E. Dartyge, A. Fontaine, J. P. Kappler, G. Krill, J. P. Itie, J. Jegoudez, M. Maurer, Ph. Monod, A. Revcolevschi, H. Tolentino, G. Tourillon, and M. Verdaguer, to be published.

<sup>12</sup>N. Nishida *et al.*, *Jpn. J. Appl. Phys., Pt. 2*, **26**, L1856 (1987); J. H. Brewer, private communication.

<sup>13</sup>D. E. Farrell, B. S. Chandrasekhar, M. R. DeGuire, M. M. Fang, V. G. Kogan, J. R. Clem, and D. K. Finnemore, *Phys. Rev. B* **36**, 4025 (1987).

<sup>14</sup>P. Zolliker, D. E. Cox, and A. R. Moodenbaugh, unpublished.

<sup>15</sup>J. Akimitsu and Y. Ito, *J. Phys. Soc. Jpn.* **40**, 1621 (1976).

<sup>16</sup>K. Yamada, E. Kudo, Y. Endoh, Y. Hidaka, M. Oda, M. Suzuki, and T. Murakami, unpublished.

<sup>17</sup>As the sample was inadvertently heated in air, causing some modification of the sample at high temperature, we can only place a lower limit on  $T_N$ .

<sup>18</sup>R. M. Moon, T. Riste, and W. C. Koehler, *Phys. Rev.* **181**, 920 (1969).