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Antiferromagnetism in $YBa_2Cu_3O_{6+x}$

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Neutron diffraction has been used to study antiferromagnetic ordering in $YBa_2Cu_3O_{6+x}$ as a function of x. Evidence for such ordering has been observed only in the tetragonal, nonsuperconducting phase ($x \lesssim 0.4$). The magnetic origin of the superlattice reflections has been confirmed with polarized beam measurements. A single antiferromagnetic structure was observed throughout the ordered phase, with a maximum Néel temperature of ~500 K and average ordered moment of $(0.66 \pm 0.07)\mu_B$ per magnetic Cu atom at $x \approx 0$. Magnetic susceptibility measurements suggest that two-dimensional correlations are strong, as in La_2CuO_{4-y}, and may survive into the orthorhombic phase.

I. INTRODUCTION

The initial discovery[1] of high-temperature superconductivity in alkaline-earth-doped lanthanum cuprate and the subsequent discovery[2] of the 90-K superconductor $YBa_2Cu_3O_7$ has stimulated a great deal of speculation[3] on possible new mechanisms for electron pairing in these systems. Anderson[4] was the first to emphasize the importance of antiferromagnetic interactions and their possible relevance to superconductivity in the cuprate perovskites. Several schemes for electron (and hole) pairing involving antiferromagnetic correlations and spin fluctuations have now been proposed.[4–6]

The observation[7–10] of three-dimensional (3D), long-range antiferromagnetic order in insulating La_2CuO_{4-y} was the first direct experimental evidence for superexchange interactions in the layered copper oxides. That a Néel state exists is no great surprise as the antiferromagnetic ordering of the simplest cupric oxide, CuO, has been known for quite some time.[11] However, by analogy with other layered antiferromagnetic systems,[12] one might expect the magnetic behavior of La_2CuO_{4-y} to be dominated by interactions within the CuO_2 planes, which are separated by layers of La_2O_2. Indeed, neutron scattering measurements on single crystals have shown[13] that the intraplanar exchange coupling is quite large (on the order of 1000 K), and that above the Néel temperature spin correlations within the planes are consistent with calculations based on an isotropic, spin-$\frac{1}{2}$, 2D Heisenberg model.[14]

The long-range order in La_2CuO_{4-y} is easily destroyed by the addition of oxygen or by substitution of small amounts of Ca, Sr, or Ba for La. X-ray-absorption,[15] electron-energy-loss,[16] and photoelectron[17] spectroscopic studies have shown that with doping there is essentially no change in the electronic configuration of the copper ions, which is essentially $3d^9$ (2+ valence), while holes appear in the $2p$ levels of oxygen. That work suggests that the Cu magnetic moment should survive into the metallic phase. Single-crystal neutron scattering studies[13] have shown that while the addition of holes by doping causes, for a given temperature, a reduction in the in-plane antiferromagnetic correlation length, the 2D correlations are still present in weakly doped systems. Thus, antiferromagnetic correlations may be significant in the superconducting phase.

With the expectation that antiferromagnetic correlations should be common to all layered cuprate perovskites, we began a search for antiferromagnetic order in the insulating phase of $YBa_2Cu_3O_{6+x}$ using neutron diffraction. Other studies[18,19] have shown that the oxygen content in this system can be varied from $x = 0$ to 1, with superconductivity occurring exclusively in the orthorhombic phase ($x \gtrsim 0.4$). At lower oxygen contents the structure is tetragonal, the material is nominally insulating, and antiferromagnetism might be anticipated; however, as the nominal valence of the Cu atoms varies with the oxygen content, the most likely composition with which to begin the search was not immediately obvious. Magnetic susceptibility measurements[18] gave no clear indication of a three-dimensional transition.

The first evidence for magnetic order came from muon-spin-rotation (μ^+SR) measurements on samples with x near 0.[20] Subsequent room-temperature diffraction measurements on $x = 0$ and 0.15 samples revealed a single weak superlattice reflection which we had difficulty indexing, partially because of our prejudice against ordering at such a relatively high temperature. Measurements on a uniaxially oriented powder of $x = 0.15$ material eventually led to a proper indexing, from which the magnetic structure was quickly deduced.

We recently published a short report[21] on the antiferromagnetic structure in $YBa_2Cu_3O_{6+x}$ with $x \approx 0$. Two other groups have since corroborated the structure.[22,23] In this paper a more complete study of magnetic ordering as a function of oxygen concentration is presented. Measurements with a polarized neutron beam and polarization analysis have been used to confirm the magnetic origin of the superlattice reflections. A single antiferromagnetic structure, the same as previously presented, is observed throughout the insulating tetragonal phase. In this structure, copper atoms within the two CuO_2 layers couple antiferromagnetically, as do the layers to one another; however, Cu atoms in the oxygen-deficient layer do not order. The spin direction is found to be perpendicular to the c axis. The Néel temperature T_N has a maximum of ~ 500 K at $x \sim 0$ and decreases toward zero at the tetragonal-orthorhombic boundary ($x \approx 0.4$). The averaged ordered magnetic moment also has a maximum at $x \sim 0$ with a value of $0.66\mu_B$, and it decreases with decreasing T_N. While no evidence of ordering has been observed in the superconducting orthorhombic phase, magnetic susceptibility measurements indicate that the magnetic behavior is dominantly two dimensional (2D) for samples with small x, and that the changeover to Pauli-like behavior, which is found at $x \approx 1$, is smooth and gradual.

The paper is arranged as follows. The sample preparation and experimental procedure are described first, after which the spin structure is analyzed from measurements on the $x = 0.15$ sample. Polarized-beam measurements, confirming the magnetic origin of the superlattice peaks, are presented next. The oxygen dependence of T_N and the average ordered magnetic moment are then discussed, followed by an analysis of magnetic susceptibility measurements. The paper concludes with a discussion of the results.

TABLE I. Oxygen content and lattice parameters of $YBa_2Cu_3O_{6+x}$ samples studied with neutron diffraction. The values of x were determined by thermogravimetric analysis or weight loss as discussed in the text. Lattice parameters are taken from x-ray diffraction measurements at room temperature. All samples are essentially single phase, except as indicated. Values in parentheses are estimated standard deviations.

x	Volume fraction	a (Å)	b (Å)	c (Å)
−0.06		3.8576(1)		11.8298(5)
−0.01		3.8586(1)		11.8318(4)
0.15		3.8597(4)		11.8173(12)
0.31[a]		3.8598(4)		11.790(2)
0.34		3.865(2)		11.794(3)
0.40		3.8608(4)		11.793(2)
0.42	71%	3.8604(3)		11.775(1)
	29%	3.8327(9)	3.8839(9)	11.779(4)
0.54	56%	3.874(1)		11.744(7)
	44%	3.828(1)	3.890(1)	11.720(5)
0.64		3.862(9)	3.8811(10)	11.740(3)
0.99		3.8242(2)	3.8869(3)	11.680(1)

[a] Contained 3% orthorhombic phase.

II. EXPERIMENTAL PROCEDURE

The $YBa_2Cu_3O_{6+x}$ samples studied in this work were prepared by two different methods. In both cases the starting material was orthorhombic, superconducting $YBa_2Cu_3O_7$, which had been produced by the (relatively standard) solid-state reaction technique.[18,24] The first Brookhaven National Laboratory sample, $x = 0.15$, was obtained by heat treating a sintered pellet of $x = 1$ material at 940 K in nitrogen for one day, followed by furnace cooling. The $x = 0.34$ sample was prepared by heating a pellet to 1070 K in air for a day and then quenching it in liquid nitrogen. (This sample was initially orthorhombic, but transformed to tetragonal after being heated to 550 K in helium.) The oxygen content was determined from each sample's weight loss and confirmed by profile refinement of neutron-diffraction data.[24]

Samples of $x = 0.40$ and $x \approx 0.0$ were prepared at Exxon Research and Engineering Co. (Annandale, NJ) by reducing powdered $x = 0.96$ material in helium at 830 and 1110 K, respectively, for 48 h. Other oxygen concentrations were obtained by mixing appropriate amounts of $x = 0$ and $x = 1$ and annealing the mixtures in sealed silica tubes at 920–940 K for 16 h, followed by furnace cooling. The oxygen content of the Exxon samples was determined by thermogravimetric analysis in hydrogen. The two most oxygen-deficient samples were found to have compositions corresponding to $x = -0.06$ and $x = -0.01$. The compositions and lattice parameters (determined by x-ray diffraction) for all of the samples studied are listed in Table I. X-ray powder-diffraction patterns revealed that most of the samples were entirely tetragonal or orthorhombic; however, the dominantly tetragonal $x = 0.31$ and $x = 0.42$ samples contained small amounts of superconducting phases (presumably orthorhombic), as revealed by magnetic susceptibility measurements.

The unpolarized neutron scattering measurements were performed on triple-axis spectrometers H4M, H4S, H7, and H9A at the High Flux Beam Reactor, Brookhaven National Laboratory. The (002) reflections of pyrolytic graphite crystals were used for the monochromator and analyzer. 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 an incident energy of 14.7 meV and pyrolytic graphite filters. Measurements using polarized neutrons with polarization analysis of the diffracted beam were performed on triple-axis spectrometer H8 with vertically-magnetized Heusler (111) transmission crystals as monochromator and analyzer. The incident neutron energy was 14.7 meV.

Each sample was mounted in an aluminum cylinder which was sealed inside an aluminum can filled with He exchange gas. The sample can was then mounted on the cold finger of a Displex refrigerator. For measurements above room temperature, the sample cylinder was clamped in a furnace which was filled with a stagnant He atmosphere in order to avoid oxygen uptake at high temperatures. The $x = -0.06$ sample (denoted as $x = 0.0$ in Ref. 21) was inadvertently heated in air, resulting in some modification of the sample at high temperature.

III. SPIN STRUCTURE

The $YBa_2Cu_3O_{6+x}$ system has a layered perovskitelike structure.[25] The arrangement of copper atoms and bridging oxygens for the $x = 0$ composition are shown schematically in Fig. 1. The *A* and *C* planes are infinite sheets made up of CuO_2 units, while the oxygen content of the *B* layer increases as *x* increases from zero to one.[18,26] Starting with empty oxygen sites in the *B* plane at $x=0$, oxygen atoms randomly fill sites between the copper atoms along the *a* axes, so that the tetragonal symmetry is maintained up to $x\approx 0.4$. Beyond that point the oxygens tend to order into chains parallel to a unique axis, labeled *b*, resulting in an orthorhombic phase. At $x=1$, all of the bridging sites parallel to the *b* axis are full.

The spin structure in the antiferromagnetic phase was determined from superlattice reflections observed in the $x=0.15$ sample.[21] Figure 2 shows some of the antiferromagnetic and weak nuclear Bragg peaks measured at 9 K with an incident energy of 5.0 meV. The low energy, together with fairly tight collimation,[27] were required to separate the $(\frac{1}{2}\,\frac{1}{2}\,2)$ from the (003) and the $(\frac{1}{2}\,\frac{1}{2}\,3)$ from the (102). The indexing of the $(\frac{1}{2}\,\frac{1}{2}\,l)$ peaks was facilitated by measurements on an oriented powder as discussed previously.

The derivation of the spin structure from the measured peaks, once the indexing is known, is fairly straightforward. The only superlattice peaks observed correspond to $(\frac{1}{2}\,\frac{1}{2}\,l)$ reflections, where *l* is an integer. Assuming that the magnetic moments are localized at the Cu sites, the fact that *h* and *k* are half-integers implies that within a CuO_2 layer nearest-neighbor Cu atoms have antiparallel spins, just as in the CuO_2 planes of La_2CuO_{4-y}.[9] The resulting magnetic unit cell has twice the volume of the chemical one.

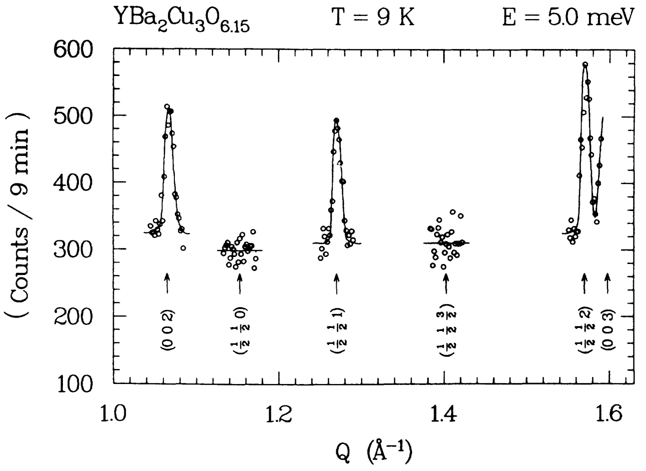

FIG. 2. Neutron-diffraction scans of several magnetic and weak nuclear peaks measured on $YBa_2Cu_3O_{6.15}$ at 9 K. The lines are guides to the eye.

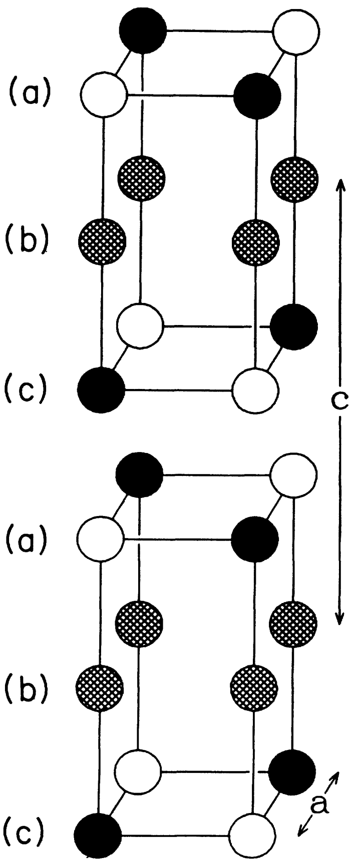

FIG. 1. Proposed magnetic spin structure for $YBa_2Cu_3O_{6+x}$ with *x* near zero. Only copper atoms are shown for clarity; cross-hatched circles represent nonmagnetic Cu^{1+} ions, while solid and open circles indicate antiparallel spins at Cu^{2+} sites. Solid lines connect pairs of sites bridged 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.

The remaining problem is then to determine the stacking phase of the three layers along the *c* axis. Assuming a collinear spin structure, the magnetic structure factor, normalized to the chemical unit cell, is

$$F^{M}_{hkl}=i\sin(\pi h)\sin(\pi k)(p_A e^{i2\pi zl}+p_B+p_C e^{-i2\pi zl})\ , \tag{1}$$

where p_A, p_B, and p_C, are the amplitude factors for the *A*, *B*, and *C* antiferromagnetic layers, as denoted in Fig. 1, and *z* is the fraction of a unit-cell length *c* by which the *A* and *C* layers are displaced from *B*. Each amplitude factor p_i is given by

$$p_i=\pm\gamma_0 M_i f(Q)\sin\eta, \tag{2}$$

where $\gamma_0=0.269\times10^{-12}$ cm/μ_B, M_i is the average ordered magnetic moment (in Bohr magnetons, μ_B) for a Cu atom in the *i*th layer, $f(Q)$ is the magnetic form factor for a Cu atom, and η is the angle between the scattering vector **Q** and the direction of the magnetic moment.

From the symmetry of the lattice, we expect that $M_A=M_C$. To constrain the relative magnitudes of M_A and M_B it is helpful to consider independent information. X-ray absorption measurements[28] at the Cu *K* edge in $YBa_2Cu_3O_{6+x}$ indicate the presence of Cu^{1+} as well as Cu^{2+} ions for small *x*. Similar measurements on uniaxially oriented powder samples demonstrate that the Cu^{1+} is located in the *B* layer.[29] In a purely ionic model one would expect one-third of the Cu ions to be 1+ at $x=0$, with the fraction of Cu^{1+} decreasing linearly to zero as *x* goes to $\frac{1}{2}$. For the $x=0.15$ sample in question, 70% of

TABLE II. Integrated intensities of magnetic reflections observed and calculated using two simple models of the spin orientation for $YBa_2Cu_3O_{6.15}$. Measurements were made at $T=9$ K.

(khl)	Q (Å^{-1})	$I_{\rm obs}$	$I_{\rm calc}$ $\mathbf{M}\perp\mathbf{c}$	$I_{\rm calc}$ $\mathbf{M}\parallel\mathbf{c}$
$(\frac{1}{2}\,\frac{1}{2}\,0)$	1.152	0 ± 100	0	0
$(\frac{1}{2}\,\frac{1}{2}\,1)$	1.268	1300 ± 70	1329	1811
$(\frac{1}{2}\,\frac{1}{2}\,2)$	1.566	1760 ± 110	1724	1241
$(\frac{1}{2}\,\frac{1}{2}\,3)$	1.964	210 ± 80	245	97
$(\frac{1}{2}\,\frac{1}{2}\,4)$	2.414	90 ± 110	79	21

the Cu atoms in the B layer should be 1+. We therefore conclude that $M_B \ll M_A$.

Assuming for the time being that $p_B \approx 0$, the A and C layers can couple either ferromagnetically or antiferromagnetically, yielding a factor of $\cos(2\pi z l)$ or $\sin(2\pi z l)$, respectively, in Eq. (1). The lack of a $(\frac{1}{2}\,\frac{1}{2}\,0)$ peak clearly indicates that the latter ordering is the correct one. [Note that the spin direction, when averaged over equivalent reflections, cannot cause the $(\frac{1}{2}\,\frac{1}{2}\,0)$ intensity to be zero.] A finite-ordered moment in the B layer would tend to frustrate the antiferromagnetic next-nearest-neighbor A-C coupling, leading to the conclusion that $p_B=0$.

The final problem is to determine the spin direction. As the symmetry of the lattice is tetragonal, the most that one can determine from powder-diffraction measurements is the angle between the magnetic moment and the c axis. It seems likely that the spins either lie in the plane or are perpendicular to it, and hence we will limit our analysis to these two choices. Table II shows a comparison of magnetic Bragg intensities observed (Fig. 2) and calculated for the two models. The agreement is clearly much better with the calculations which have the spin in the plane. Using a linear interpolation of the magnetic form factor measured[30] for Cu^{2+} in ferromagnetic K_2CuF_4, the average ordered moment is found to be $(0.50\pm0.05)\mu_B$ assuming that only the Cu atoms in the A and C planes contribute to the Bragg scattering.

IV. POLARIZED-BEAM MEASUREMENTS

It was assumed in the preceding section that the observed temperature-dependent superlattice reflections are magnetic in origin. To verify this hypothesis, measurements were made with polarized neutrons and polarization analysis. The technique is described in detail elsewhere.[31] Briefly, the spectrometer is set up so as to measure the cross section for spin-flip (magnetic) scattering. Measurements are made with a magnetic field applied to the sample, with the field first parallel (horizontal) and then perpendicular (vertical) to the scattering vector. By taking the difference between the horizontal field (HF) and vertical field (VF) intensities, one obtains a signal proportional to one-half of the magnetic cross section, with the background and residual nuclear scattering contributions in each channel canceling. Figure 3 shows $I(\mathrm{HF})-I(\mathrm{VF})$ measured for the $(\frac{1}{2}\,\frac{1}{2}\,1)$ reflection. The peak is clearly present, and a comparison with non-spin-flip measurements of nuclear peaks indicates that the relative intensity of the $(\frac{1}{2}\,\frac{1}{2}\,1)$ is consistent with that observed in the unpolarized measurements. We conclude that our interpretation of the $(\frac{1}{2}\,\frac{1}{2}\,l)$ reflections as indicating antiferromagnetic order of the Cu spins is correct.

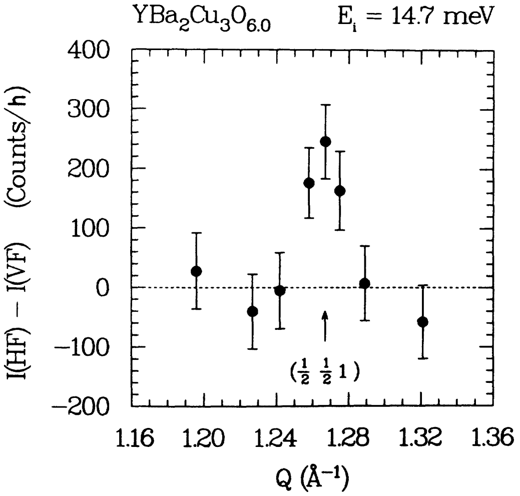

FIG. 3. Polarized-beam results plotted as the difference between horizontal and vertical field configurations (discussed in text) for the $(\frac{1}{2}\,\frac{1}{2}\,1)$ reflection showing that it is indeed magnetic in origin.

Because of a high background level, it was difficult to observe any magnetic peaks for the $x=0.34$ sample with unpolarized neutrons. However, polarized-beam measurements indicated a finite $(\frac{1}{2}\,\frac{1}{2}\,1)$ peak up to room temperature. (We did not check the sample at higher temperatures.) Polarization measurements were also made on several weak, unidentified peaks observed in the $x=0.64$ sample. None of these was found to be magnetic.

V. TEMPERATURE AND OXYGEN DEPENDENCE

For all of the tetragonal-phase ceramic samples studied, the $(\frac{1}{2}\,\frac{1}{2}\,1)$ peak was observed at low temperatures. No evidence for any half-integer l peaks was observed, although in several cases the position of the $(\frac{1}{2}\,\frac{1}{2}\,\frac{3}{2})$ reflection (the first strong peak which would be expected if the unit cell were doubled along the c axis) was obscured by impurity peaks (probably from $BaCuO_2$). The Néel temperatures of the various samples were determined by monitoring the peak intensity of the $(\frac{1}{2}\,\frac{1}{2}\,1)$ reflection as a function of temperature. For the $x=0.31$ sample the $(\frac{1}{2}\,\frac{1}{2}\,1)$ was strongly contaminated by the (321) reflection of $BaCuO_2$, and so the temperature dependence of the $(\frac{1}{2}\,\frac{1}{2}\,2)$ was studied. The temperature dependence of the $(\frac{1}{2}\,\frac{1}{2}\,1)$ measured for the $x=0.15$ sample is shown in Fig. 4. Because of the weak intensity of the magnetic scattering and the resultant large uncertainties in the measurements, it is not possible to draw any conclusions concerning the nature of the transition.

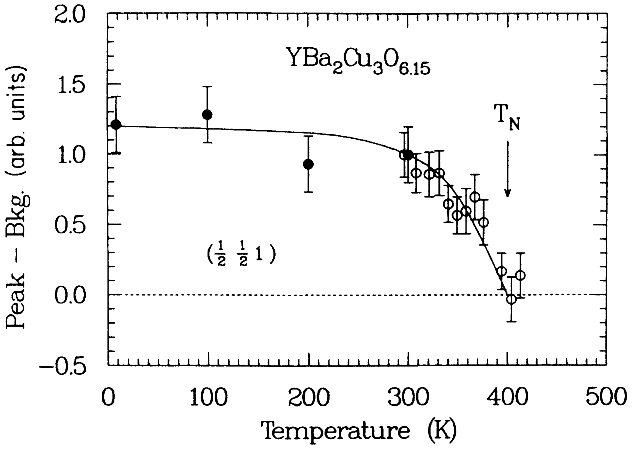

FIG. 4. Difference between peak and background intensities for the $(\frac{1}{2}\,\frac{1}{2}\,1)$ magnetic reflection in $YBa_2Cu_3O_{6.15}$ as a function of temperature. Solid circles: measurements at 14.7 meV with sample in Displex refrigerator; open circles: measured at 5.0 meV in furnace. Intensity units are arbitrary and the two sets of data have been normalized at 300 K. Counting time was a minimum of 7 min/point.

The Néel temperature as a function of oxygen concentration is shown in Fig. 5. At small x, T_N is significantly greater than the maximum of ~ 300 K observed[8,9] in oxygen-deficient La_2CuO_{4-y}. As x increases, T_N changes slowly until the tetragonal-to-orthorhombic transition is approached, at which point it quickly falls to zero. There appears to be no region of overlap between the antiferromagnetically-ordered and the superconducting phases. The results presented here appear to be in reasonable agreement with those obtained in a recent muon-spin-rotation and relaxation study.[32]

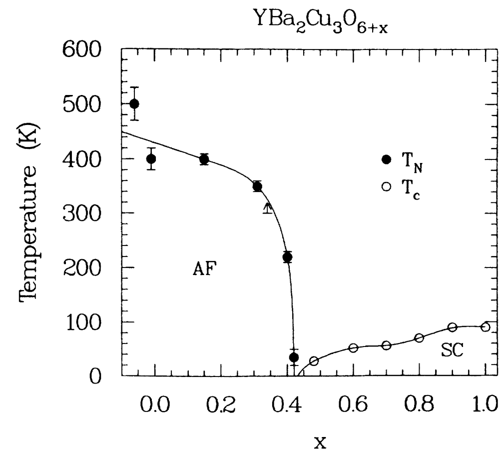

FIG. 5. Phase diagram for $YBa_2Cu_3O_{6+x}$ showing Néel temperatures determined by neutron diffraction; AF denotes antiferromagnetic, SC denotes superconducting. Representative values of the superconducting transition temperature T_c have been taken from Ref. 18. Solid lines are guides to the eye.

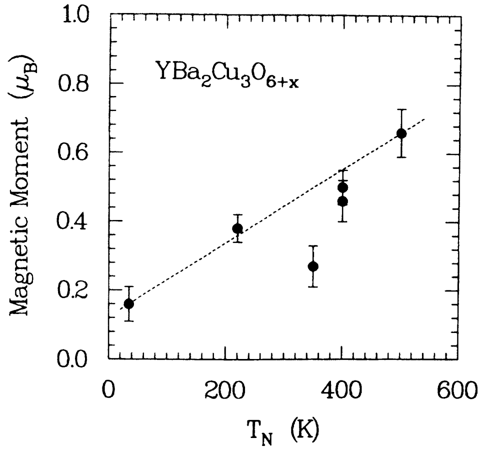

FIG. 6. Average ordered magnetic moment per ordered copper atom determined by neutron diffraction, plotted as a function of Néel temperature. The line is a guide to the eye.

We have also evaluated the average ordered magnetic moment for the antiferromagnetic samples; the results are plotted in Fig. 6 as a function of T_N. Except for the value corresponding to the $x = 0.31$ sample, which is known to be mixed phase, the moments show a roughly linear variation with the Néel temperature. The range of moments and their variation with T_N are quite comparable to those observed[9] in La_2CuO_{4-y}. Possible reasons for the variation will be considered in the Discussion section.

VI. MAGNETIC SUSCEPTIBILITY

Before antiferromagnetic ordering was demonstrated by μ^+SR (Ref. 20) and neutron-diffraction[21] experiments, dc magnetic susceptibility had been measured as a function of temperature.[18] No features indicative of a three-dimensional phase transition were identified in the susceptibility data. It is of interest to reconsider the susceptibility measurements in light of the present diffraction results.

In order to isolate the features intrinsic to $YBa_2Cu_3O_{6+x}$ it is important to first correct for contributions from impurity phases. One common impurity, $BaCuO_2$, is known to be paramagnetic from both susceptibility[33,34] and electron-paramagnetic-resonance[34] (EPR) measurements. In fact, $BaCuO_2$ impurities are believed to be entirely responsible for the low-temperature EPR spectra typically measured on $RBa_2Cu_3O_{6+x}$ (R denotes rare earth) samples. The susceptibility measurements[18] on samples of $YBa_2Cu_3O_{6+x}$ all appear to contain a paramagnetic contribution which tends to dominate at low temperature. To extract the intrinsic signal, a Curie-like contribution $(=C_g/T)$ was fit to the data and subtracted.[35] The corrected susceptibility, $\chi^{\text{corr}} = \chi_g - (C_g/T)$, is shown in Fig. 7(a), with the coefficients C_g plotted in Fig. 7(b). The fitted Curie coefficients are consistent with a maximum of 1.7% of isolated paramagnetic Cu^{2+} impurities, equivalent to 5% of the Cu in the B layers. The sharp drops in χ^{corr} below 100 K for the nonsuperconducting samples probably result from trace (ppm) amounts of superconductivity.

First consider the corrected susceptibility for the nonsuperconducting samples shown on an expanded scale in Fig. 8. Each curve is dominated by a broad maximum at

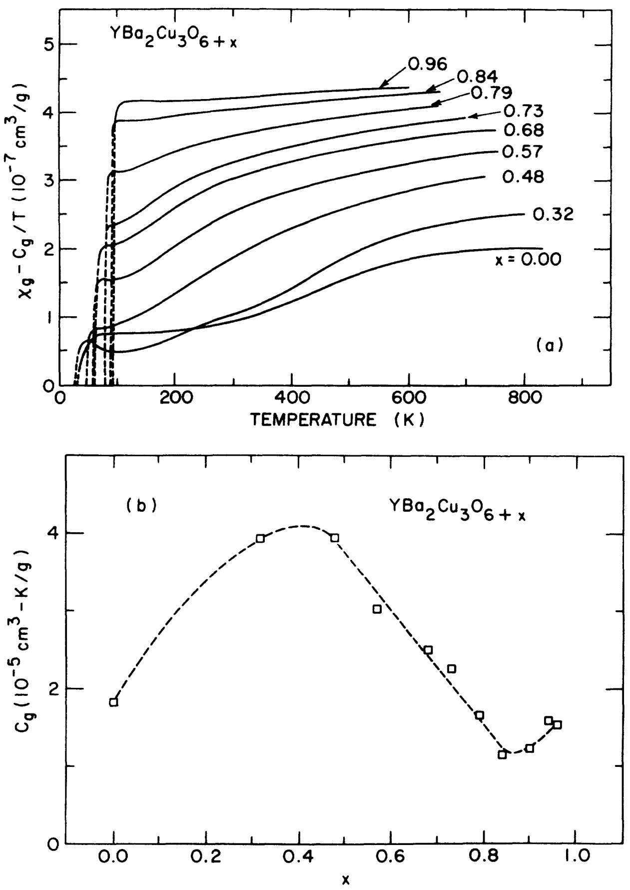

FIG. 7. (a) Magnetic susceptibility, corrected for a Curie-like contribution, plotted vs temperature for a range of oxygen concentrations in $YBa_2Cu_3O_{6+x}$. (b) Curie coefficient C_g for the correction applied in (a) as a function of x.

$\gtrsim 800$ K, and χ is found to decrease with decreasing temperature.[36] This behavior is quite similar to that observed in other layered antiferromagnetic compounds, a large group of which share the K_2NiF_4 structure.[12] Such broad maxima are believed to be explainable in terms of the paramagnetic properties of a 2D Heisenberg model. From calculations based on high-temperature series-expansion techniques, Lines[37] found that the position of χ_{max} should occur at a temperature comparable to the intraplanar exchange parameter J. In the present case, $T(\chi_{max})$ is quite similar to the value of J estimated from the spin-wave dispersion measured in La_2CuO_{4-y} by neutron scattering.[13]

Looking at more-detailed features, one may notice that each of the curves in Fig. 8 has a weak bump or kink (indicated by arrows) at a temperature close to the corresponding Néel temperature measured by diffraction. The small change in slope at T_N is consistent with the susceptibility observed in the region of the 3D ordering temperature in other quasi-2D antiferromagnetic compounds.[12] (In contrast, the strong peaks observed[7,8] at T_N in La_2CuO_{4-y} are rather anomalous.) Ironically, these cusps were noticed previously, but not mentioned,[18] because they were so small and so different from the behavior in $\chi(T)$ seen in La_2CuO_{4-y} near T_N.

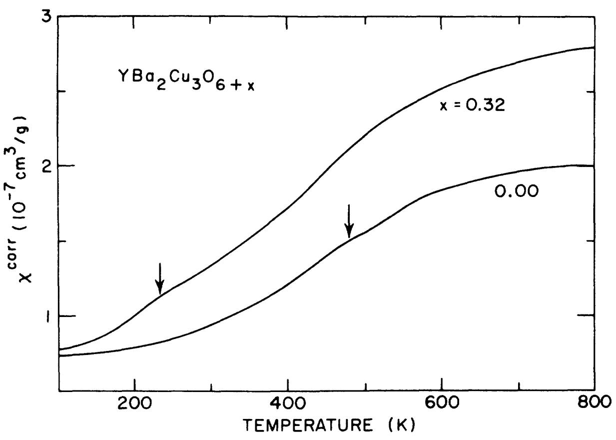

FIG. 8. Corrected magnetic susceptibility data for antiferromagnetic samples plotted on an expanded scale. The arrows indicate bumps which correspond to the Néel temperature. For clarity the curve for $x = 0.32$ has been shifted upward by $0.3\times10^{-7}\ cm^3/g$.

Returning to Fig. 7(a), one can see that the susceptibility measured for samples with high oxygen contents is more temperature independent and Pauli-like. As the oxygen concentration is varied, χ varies smoothly between the 2D-antiferromagnetic and Pauli-like extremes. No distinct change in behavior is observed in χ for $T > 100$ K) near the orthorhombic-tetragonal phase boundary. [For a quantitative assessment of this evolution in $\chi(T)$ with oxygen content, see Ref. 38.] It appears that the effective strength of antiferromagnetic interactions decreases gradually and continuously with increasing oxygen content, in contrast to the distinct disappearance of long-range order and the onset of superconductivity. Similar conclusions have been reached in recent inelastic light-scattering studies of spin-pair excitations.[39]

VII. DISCUSSION

Planes of CuO_2 units are the common structural element shared by $YBa_2Cu_3O_{6+x}$ and La_2CuO_{4-y}. It is now well established that the strongest magnetic interactions in the latter system occur within the planes. Recent theoretical analyses[14] have explained quantitatively the temperature dependence of the antiferromagnetic correlations within the CuO_2 planes above T_N. When the 2D correlations become sufficiently long range, 3D ordering follows because of weak but finite interplanar coupling. One reason that the interplanar interaction is weak is due to the body-centered stacking of CuO_2 planes in La_2CuO_{4-y}. The magnetic coupling between a given Cu atom and its four Cu neighbors 7.1 Å away in a nearest-neighbor plane would cancel exactly, resulting in no net coupling, if not for the orthorhombic distortion of the nearly-tetragonal lattice. The Cu spins lie within the planes along the c axis, which is a special direction due to the orthorhombic distortion.

In $YBa_2Cu_3O_{6+x}$, the Cu spins exhibit the same $\sqrt{2}\times\sqrt{2}$ ordering within the CuO_2 planes; the spin direction is within the plane, but the tetragonal symmetry does not allow one to determine the in-plane orientation. Coupling between planes, however, is significantly different from that in La_2CuO_{4-y}. Along the c axis, Cu atoms in neighboring A and C planes are separated by only 3.3 Å, significantly less than the in-plane Cu-Cu distance. Since these atoms are not bridged by oxygens, the magnetic interactions will be mostly dipolar. Copper atoms in next-nearest-neighbor A and C planes can interact via superexchange through the intervening B layer. In layered systems the Néel temperature is generally assumed to be determined by the relation $kT_N \sim J_\perp^{\text{eff}}\xi_{2D}^2$, where $\xi_{2D}(T)$ is the magnetic correlation length within a layer and $J_\perp^{\text{eff}}$ is the effective coupling between planes. In La_2CuO_{4-y}, ξ_{2D} has been measured as a function of temperature in a crystal with $T_N = 195$ K; the resulting effective between-plane exchange is found to be ~ 0.002 meV. Assuming that the 2D correlations are quantitatively the same in $YBa_2Cu_3O_{6+x}$, a T_N of 400 K would require roughly a hundredfold increase in $J_\perp^{\text{eff}}$, consistent with expectations for the interlayer dipolar and superexchange couplings.

The B layers are another unique feature of $YBa_2Cu_3O_{6+x}$. As discussed previously, we expect this plane to be filled by Cu^{1+} at $x=0$. However, as the amount of Cu^{2+} in the plane increases with x, one might expect the interaction of these moments with the A and C planes to result in either a suppression of T_N due to frustration of the A-C next-nearest-neighbor ordering or a new structure with doubling of the unit cell along the c axis. Because of the small fraction of filled oxygen bridge sites within a B layer, the greatest impact of Cu^{2+} in the plane should be on superexchange coupling with the A and C layers. Somewhat surprisingly, Fig. 5 shows that T_N decreases relatively little up to $x \approx 0.4$ where 80% of the B-plane Cu should be nominally 2+. Furthermore, we have observed no evidence of c-axis doubling in our ceramic samples at any temperature (although it is not absolutely ruled out in the large-x samples). Two other groups have also reported the antiferromagnetic structure shown in Fig. 1 for small-x powders[22,23] and for a $NdBa_2Cu_3O_{6+x}$ single crystal.[22] However, in a study of an $YBa_2Cu_3O_{6+x}$ single crystal with $x \sim 0.35$ and $T_N = 405$ K, Kadowaki *et al.*[40] have observed $(\frac{1}{2}\,\frac{1}{2}\,\frac{l}{2})$ peaks which first appear at ~ 40 K and which grow in intensity as the temperature decreases. The new structure results from ferromagnetic coupling along the c axis of Cu^{2+} ions in nearest-neighbor A-B-C layers;[40,41] the antiferromagnetic coupling between nearest-neighbor A and C layers remains the same. The appearance of such a second phase at low temperature has also been found by Lu and Patton[42] in Monte Carlo simulations for both Ising and x-y models. The calculations indicate that (1) the second type of ordering should not occur until a sufficient fraction of Cu^{2+} ions is present in the B layers, (2) the appearance of the second phase should occur at $T < T_N$, and (3) the two types of ordering may coexist over a large temperature range. Further experimental work will be required to determine the phase boundary for the second type of ordering.

The relative insensitivity of the ordering temperature to the value of x in $YBa_2Cu_3O_{6+x}$ is in stark contrast to the behavior observed[8,38] in La_2CuO_{4-y}, where a change in y of 0.03 results in a 300-K swing in T_N. The cause of this difference can also be traced to the B layers. In the lanthanum compound, the addition of oxygen is believed[38,43] to result in valence-band holes, similar to those which occur when Sr is substituted for La. The holes, which are localized on the O atoms,[15-17] tend to frustrate Cu-Cu superexchange interactions,[5,43] thus weakening the net magnetic couplings and reducing T_N. Holes introduced into $YBa_2Cu_3O_{6+x}$ should have a similar effect. A finite number of paired holes are presumably[5] responsible for the superconductivity observed in the orthorhombic phase. In the tetragonal structure, however, a neutral oxygen atom added to a B layer can satisfy its desire for electrons by converting two Cu^{1+} atoms to Cu^{2+}. Holes must be relatively insignificant throughout most of the tetragonal phase; otherwise, T_N could not remain so high over such a broad range of oxygen concentration.

The maximum ordered moment of $0.66\mu_B$ observed for $x = -0.06$ is quite similar to the moment of $0.68\mu_B$ found[11] in CuO and the maximum value of $0.6\mu_B$ obtained[9] in La_2CuO_{4-y}. Assuming a g factor of ~ 2.2, typical for Cu^{2+} ions,[44] and a classical spin of $\frac{1}{2}$, a maximum moment of $1.1\mu_B$ might be expected. The observed value may be lower due to quantum fluctuations and/or covalency effects. The reduction due to quantum fluctuations can be estimated from spin-wave theory.[37] The maximum reduction occurs for a completely isotropic 2D Heisenberg system, in which case a moment of $0.67\mu_B$ would be expected. Interplanar coupling as well as anisotropy will tend to mitigate the zero-point spin deviation; however, as long as these effects are quite weak compared to intraplanar coupling, as we believe they are, the isotropic limit is a reasonable approximation.[37] Thus, it appears that any reduction in the moment due to bonding effects is minimal.

We have found that the average ordered moment decreases with decreasing Néel temperature and increasing oxygen content. Neutron-diffraction measurements have revealed a similar behavior in La_2CuO_{4-y},[9] while μ^+SR studies of the same system show very little variation in local magnetic field with T_N.[10] The μ^+SR technique is a local probe of magnetic order and is sensitive only to magnetic order which is frozen on the time scale of μsec. It appears that in La_2CuO_{4-y} the moment per Cu ion stays relatively constant while the *average* ordered moment observed by diffraction decreases with increasing oxygen content. We expect that the same is true in $YBa_2Cu_3O_{6+x}$. How can one explain this behavior? In La_2CuO_{4-y} it is believed[43] that the presence of holes causes a reduction of the effective magnetic coupling between planes as well as within planes, so that locally some planes may not order three dimensionally or may order in a random fashion, thus reducing the fraction of Cu atoms contributing to the Bragg peaks. While the presence of holes should have a similar effect in $YBa_2Cu_3O_{6+x}$, another possibility involves the increasing numbers of Cu^{2+} ions in B layers which could cause frustration in A-C next-nearest-neighbor coupling. If locally some of the A-B-C trilayers were to couple ferromagnetically rather than as shown in Fig. 1, the Bragg peak intensities would be reduced. The average ordered moment would therefore be reduced, while the local moments would remain unchanged.

Several theories[4-6] of the superconducting mechanism in the cuprate perovskites have invoked antiferromagnetic interactions and spin fluctuations. The present neutron-diffraction results demonstrate that antiferromagnetic interactions are quite strong in $YBa_2Cu_3O_{6+x}$, at least in the tetragonal phase. The susceptibility measurements suggest that, as in La_2CuO_{4-y}, coupling within the CuO_2 planes dominates the magnetic behavior, and that 2D correlations survive into the superconducting orthorhombic phase. (The same conclusion has been reached for the superconducting $La_{2-x}Sr_xCuO_{4-y}$ compounds.[38]) It will be interesting to study paramagnetic scattering from both insulating and superconducting phases of $YBa_2Cu_3O_{6+x}$ when sufficiently large crystals become available. In any case, whether or not antiferromagnetism is directly involved in electron pairing, any comprehensive theory of superconductivity in the layered copper oxides should be able to account for long-range magnetic order in the oxygen-deficient insulating phases and for the characteristic behavior of the susceptibility in the superconducting ones.

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