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Long-range antiferromagnetic order of the Cu in oxygen-deficient $R\mathrm{Ba_2Cu_3O_{6+x}}$

W-H. Li and J. W. Lynn
Department of Physics, University of Maryland, College Park, Maryland 20742
and National Bureau of Standards, Gaithersburg, Maryland 20899

H. A. Mook and B. C. Sales
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

Z. Fisk
Los Alamos National Laboratory, MS-K764, Los Alamos, New Mexico 87545

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We have employed polarized and unpolarized neutron-diffraction techniques on both powders and single crystals to establish the nature of the magnetic order of the Cu ions in oxygen-deficient (nonsuperconducting) $R\mathrm{Ba_2Cu_3O_{6+x}}$ (R=Y,Nd). Magnetic Bragg peaks of the type $(h/2,k/2,l)$ are observed that yield a magnetic structure in which the Cu spins are coupled antiferromagnetically both in the Cu-O planes as well as along the tetragonal c axis, with the spin direction in the tetragonal plane. The Néel temperature is very sensitive to the oxygen content, with $T_{N(x\sim 0)} \approx 500$ K, while the spin configuration is independent of x.

The relation between magnetism and superconductivity has attracted considerable interest for many years. In the ternary magnetic superconductors such as $\mathrm{ErRh_4B_4}$ and $\mathrm{HoMo_6S_8}$, the magnetic and superconducting electrons reside on separate sublattices, and hence there is only a weak electromagnetic coupling between these two cooperative phenomena which nevertheless gives rise to some interesting competitive behavior at very low temperatures.[1] An analogous situation exists for the present oxide superconductors, where the heavy rare-earth moments also order at very low temperatures.[2-5] However, a much more interesting and direct competition has been observed in the $\mathrm{La_2CuO_{4-x}}$ system, where the oxygen-deficient (nonsuperconducting) materials are found to order antiferromagnetically at quite high temperatures,[6-9] and with magnetic fluctuation energies which are much larger than kT_N.[8] Similar behavior might be expected for the oxygen-deficient $R\mathrm{Ba_2Cu_3O_{6+x}}$ (R=rare earth),[10] and initial powder neutron data indicate magnetic ordering of the Cu spins.[11] This correlation between the magnetic and superconducting properties is interesting not only from the magnetic-superconductor point of view, but also because it may hold the key to the origin of the superconductivity in these oxides.[12-15] Here we report our neutron scattering results on $\mathrm{YBa_2Cu_3O_{6+x}}$ powders and $\mathrm{NdBa_2Cu_3O_{6+x}}$ single crystals (for $x < \frac{1}{2}$). We observe long-range antiferromagnetic order of the Cu spins, with transition temperatures as high as 500 K.

The neutron measurements were carried out at the National Bureau of Standards Research Reactor, and consisted of three separate types of experiments. Initially unpolarized powder diffraction measurements were made with an incident energy of 13.5 meV and a pyrolytic graphite PG(002) monochromator at the BT-9 triple-axis spectrometer to characterize the sample and search for possible additional Bragg peaks which might reveal a phase transformation. Polarized neutron measurements were then taken to establish that the phase transition which was found was magnetic in origin. These data were obtained at the BT-2 triple-axis polarized beam spectrometer with a Heusler alloy monochromator, also with an incident energy of 13.5 meV. A supermirror was employed to determine the polarization of the scattered beam. Finally, measurements were taken on a small single crystal utilizing an incident energy of 14.8 meV, along with a PG(002) analyzer to improve the signal-to-noise ratio. Angular collimations before and after the monochromator and analyzer (when used) were 40′ (full width at half maximum) in all cases, and a PG filter was employed to suppress higher-order wavelengths.

Powder diffraction patterns over a wide angular range were taken with unpolarized neutrons at several temperatures at and below room temperature to characterize the system. The sample of $\mathrm{YBa_2Cu_3O_{6+x}}$ weighed ~9 g and was prepared by the usual solid-state reaction technique discussed in the literature. This fully oxygenated sample was then warmed in flowing helium gas at the rate of 10 °C/min up to 855 °C, and then rapidly cooled to room temperature. Thermogravimetric analysis revealed an average oxygen concentration of 6.13 ± 0.05. The sample was subsequently sealed in a cylindrical sample holder with an atmosphere of helium gas for the neutron measurements. The basic diffraction pattern was consistent with tetragonal symmetry[16] with room-temperature lattice parameters of $a = 3.894(4)$ Å and $c = 11.784(2)$ Å. However, several additional weak Bragg peaks were also observed, and an example of one such peak is shown in Fig. 1(a). The counting time was ~4 min/point. For comparison, the intensity of this peak is about 0.79% of the (001) nuclear peak at this temperature. The intensity is also quite sensitive to T, and hence it is likely to originate from either a structural distortion which increases the size of the unit cell or an antiferromagnetic transition. Although we do not have detailed measurements at tem-

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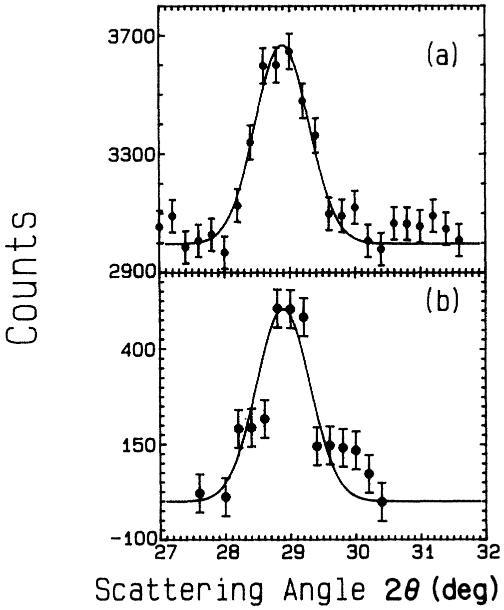

FIG. 1. ($\frac{1}{2}\frac{1}{2}1$) peak observed in a powder sample of $YBa_2Cu_3O_{6.13}$. (a) Unpolarized beam result for $T=330$ K. (b) Polarized beam result (at $T=200$ K), showing that the scattering is magnetic in origin. The solid curves are a least-squares fit to a Gaussian (resolution) function.

peratures above 330 K (due to the experimental restrictions), the temperature dependence of the magnetic scattering intensity indicates a transition temperature for this sample of approximately 500 K.

To determine if this peak is magnetic in origin we employed polarized neutron techniques. For antiferromagnets it is essential to not only polarize the incident beam, but to also analyze the polarization, and hence this type of measurement requires a triple-axis instrument. The technique to isolate the magnetic response has been discussed at length in the literature.[17] Briefly, the principle is that when a magnetic field **H** is applied parallel to the scattering vector **Q**, all the magnetic scattering is associated with a reversal of the neutron spin (spin-flip scattering), while for **H**⊥**Q**, half the magnetic scattering is spin-flip and half is non-spin-flip. The nuclear (spin incoherent) scattering, on the other hand, is independent of the orientation of **H** and **Q**. Hence the magnetic scattering can be uniquely determined by measuring the spin-flip cross section with **H**∥**Q**,**H**⊥**Q**, and then subtracting. The results of such a polarized beam measurement are shown in Fig. 1(b), and clearly show that this peak originates from magnetic Bragg scattering. As a check of the technique, we noted that the spin-flip scattering intensity with **H**⊥**Q** was half the intensity with **H**∥**Q**, and the intensity relative to the nuclear (001) peak was just the intensity expected based on the unpolarized diffraction data. In addition, the polarization subtraction technique yielded zero net intensity for the nuclear (001) peak, as expected if there is no ferromagnetic component.

The antiferromagnetic structure which can be deduced from these data is rather simple. There are three Cu-O layers in the unit cell. If we assume that the spins are coupled antiferrromagnetically within the tetragonal layer, then we expect to have the first two of Miller's indices (hkl) half integral. The second layer along the c axis has no oxygen (at $x=0$) in the plane, and we assume that there is no moment on the Cu. To match the d spacings for the observed peaks, the third layer must then be coupled antiferromagnetically to the first, so that we have a $(+-)$ arrangement of spins along all three crystallographic directions. The magnetic unit cell is then doubled in both directions in the tetragonal plane, while it is the same as the chemical unit cell along the c axis.

To determine the value of the moment we need a detailed comparison of the magnetic and nuclear intensities. The nuclear intensity is given by[18,19]

$$I_N = C\frac{|F_N|^2 M_{hkl}}{\sin(\theta)\sin(2\theta)}\ , \tag{1}$$

where M_{hkl} is the multiplicity of the reflection, C is an instrumental constant, and 2θ is the scattering angle for the reciprocal-lattice vector $\boldsymbol{\tau}$. The nuclear structure factor is defined by

$$F_N = \sum_{j=1}^{N} b_j e^{-W_j} e^{i\boldsymbol{\tau}\cdot\mathbf{r}_j}\ , \tag{2}$$

where b_j is the coherent nuclear scattering amplitude for the jth atom at position $\mathbf{r}_j$, W_j is the Debye-Waller factor for the atom, and the sum extends over all atoms in the unit cell. The magnetic intensity is given by a similar expression:

$$I_M = C\left(\frac{\gamma e^2}{2mc^2}\right)^2 \langle\mu_z\rangle^2 f^2(\boldsymbol{\tau})\langle 1-(\hat{\boldsymbol{\tau}}\cdot\hat{M})^2\rangle \times \frac{M_{hkl}}{\sin(\theta)\sin(2\theta)}|F_M|^2\ , \tag{3}$$

where the constant in parentheses is -0.27×10^{-12} cm, $f(\boldsymbol{\tau})$ is the magnetic form factor, $\langle\mu_z\rangle$ is the thermal average of the aligned magnetic moment of the Cu, $\hat{\boldsymbol{\tau}}$ and $\hat{M}$ are unit vectors in the direction of $\boldsymbol{\tau}$ and the spin direction, respectively, and the orientation factor $\langle 1-(\hat{\boldsymbol{\tau}}\cdot\hat{M})^2\rangle$ must be calculated for all possible domains. The magnetic structure factor F_M is the same as for Eq. (2), but with $b_j=1$ and only the Cu ions included in the sum, and one must take into account the difference in the volume sizes for the chemical and magnetic unit cells. The low-temperature ordered moment we obtain from these data is then $\langle\mu_z\rangle=(0.64\pm0.06)\mu_B$.

With a basic model for the spin configuration, we have taken additional measurements on a small single crystal of $NdBa_2Cu_3O_{6+x}$. The sample was grown by slow cooling a flux of BaO, CuO, and PbO from 1220 °C. A high-quality crystal was separated from the boule and was in the shape of a square plate weighing 9.5 mg. The crystallographic axes coincided with plate axes, with the c axis perpendicular to the largest face. The single crystal was also mounted in an aluminum holder which contained an atmosphere of helium for thermal conduction purposes. The room-temperature lattice parameters were determined to be $a=3.895(6)$ Å and $c=11.704(4)$ Å. Most of the diffraction measurements were taken in the (110)-

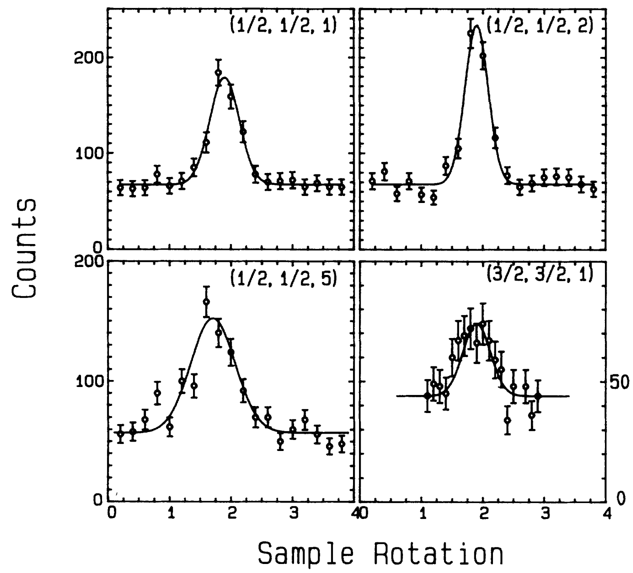

FIG. 2. Several antiferromagnetic peaks obtained on a single crystal of $NdBa_2Cu_3O_{6+x}$. The data were obtained by rotating the sample through the Bragg peak, and are normalized to a counting time of ~10 min/point. The solid curves are a least-squares fit to a Gaussian.

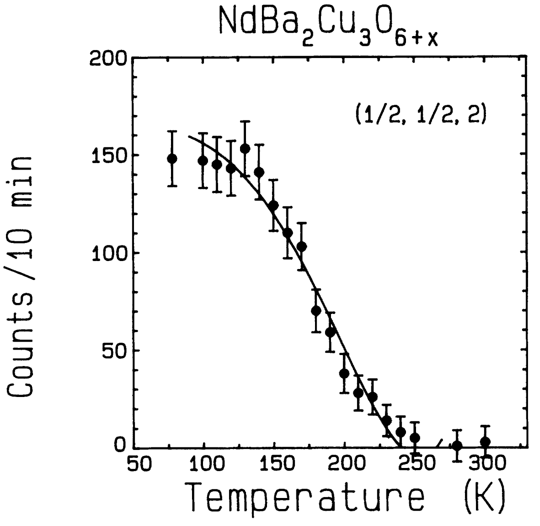

FIG. 3. Temperature dependence of the peak intensity of the $(\frac{1}{2}\,\frac{1}{2}\,2)$ antiferromagnetic peak, which is proportional to the square of the staggered magnetization. The rounding of the transition at $T_N \sim 230$ K is due to either critical fluctuations, or a distribution of T_N's. The solid curve is a guide to the eye.

(001) scattering plane.

Initial measurements at room temperature indicated no peaks of the $(\frac{1}{2}\,\frac{1}{2}\,l)$ type (or other half-integral peaks). Upon cooling to 78 K magnetic peaks appeared, and several are shown in Fig. 2. These data were obtained by rotating the sample through the Bragg peak with the detector set at the Bragg angle, and have been normalized to a counting time of ~10 min/point. Note that the signal is considerably smaller for the single crystal than for the powder data [Fig. 1(a)], but the signal-to-noise ratio is far superior. We also searched for other half-integral peaks which would not be consistent with the assumed structure, such as $(h,h,l/2)$, $(h/2,h/2,l/2)$, etc., but none was found.

The expressions to obtain the integrated intensity from a single crystal are similar to Eqs. (1) and (3) above except for the angular factor,[18] and the observed intensities are given in Table I. A qualitative survey of the intensities shows that the moment direction must lie in the tetragonal plane. Then to make a detailed comparsion with the model calculation we assumed that the moments on the Cu-O planes are equal in magnitude, that the moment on the oxygen-deficient plane is zero, and have used a magnetic form factor appropriate for a 3*d* ion. The overall scale has been set by using the value of the moment obtained from the powder results and then scaling with respect to the (001) nuclear Bragg peak. The agreement between the data and the model is quite good.

TABLE I. Magnetic intensities for the single crystal of $NdBa_2Cu_3O_{6+x}$. The $(\frac{1}{2}\,\frac{1}{2}\,1)$ peak has been defined to have an observed intensity of unity for convenience.

(hkl)	I_{obs}	I_{calc}
$(\frac{1}{2}\,\frac{1}{2}\,0)$	<0.12	0
$(\frac{1}{2}\,\frac{1}{2}\,1)$	1.00 ± 0.12	0.87
$(\frac{1}{2}\,\frac{1}{2}\,2)$	1.45 ± 0.22	1.52
$(\frac{1}{2}\,\frac{1}{2}\,3)$	0.22 ± 0.13	0.27
$(\frac{1}{2}\,\frac{1}{2}\,4)$	0.54 ± 0.30	0.42
$(\frac{1}{2}\,\frac{1}{2}\,5)$	1.40 ± 0.30	1.62
$(\frac{1}{2}\,\frac{1}{2}\,6)$	0.74 ± 0.22	0.94
$(\frac{1}{2}\,\frac{1}{2}\,7)$	<0.15	0.03
$(\frac{3}{2}\,\frac{3}{2}\,0)$	<0.15	0
$(\frac{3}{2}\,\frac{3}{2}\,1)$	0.66 ± 0.32	0.73

The temperature dependence of the $(\frac{1}{2}\,\frac{1}{2}\,2)$ peak intensity of the single-crystal sample is shown in Fig. 3, and reveals a Néel temperature $T_N \approx 230$ K for this particular sample. No hysteresis was observed on the warming and cooling cycles, and the transition appears to be second order. The rounding of the transition is probably due to either critical scattering, or to a small distribution of transition temperatures. The value of T_N indicates that the oxygen content x for this sample is substantially larger than for the powder sample. We should point out that the value of x will affect to some extent the overall scale factor for the data in Table I since the nuclear structure has a dependence on x, but at the present level of precision this is not a significant effect.

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