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MAGNETIC PHASE TRANSITIONS AND STRUCTURAL DISTORTION IN Nd_2CuO_4

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Neutron and X-ray diffraction have been used to study the magnetic and structural properties of single crystal Nd_2CuO_4. Long range magnetic order of the Cu moments develops at $T_N = 245$ K, with a noncollinear antiferromagnetic arrangement of spins. Additional abrupt transitions are observed at 75 K and 30 K, in which a spin reorientation takes place. Bragg peaks associated with the crystal structure are found at the same positions as the magnetic Bragg peaks, and indicate that a distortion of the basic tetragonal structure has occurred above 300 K.

The magnetic properties of the oxide superconductors are of particular interest because of the intimate relationship between the magnetic and superconducting properties, which raises the possibility that the copper magnetism may play an important role in the Cooper pairing. The structures of the La_2CuO_4 and $YBa_2Cu_3O_7$ classes of materials consist of strongly bound planes of CuO_2 ions, which results in highly anisotropic magnetic and superconducting properties [1]. Recently, a new class of superconductors has been discovered [2], typified by the parent material Nd_2CuO_4. Similar Cu–O planes occur in this system, but without the apical O ions which give the approximate octahedral O coordination in the other layered systems [3]. Hall effect data on the new system indicate [2] that the carriers are electrons rather than holes, and if indeed these new materials are electron superconductors [4–6], their existence places important constraints on any theory which is successful in describing the overall behavior of these systems. It is interesting in this regard to establish the nature of the magnetic ordering in the parent material. In the present work we report neutron and X-ray scattering experiments, in which we find a relatively simple but noncollinear magnetic spin arrangement. We also find evidence for a small structural distortion, which breaks the tetragonal symmetry of the Nd_2CuO_4.

The neutron experiments were carried out at the research reactor at the National Institute of Standards and Technology (formerly the National Bureau of Standards). Unpolarized diffraction data were taken with a wavelength of 2.359 Å and a pyrolytic graphite monochromator and filter, at the BT-2 triple-axis spectrometer. Polarized neutron measurements were taken at approximately the same wavelength, with a Heusler alloy monochromator and a multilayer polarizing analyzer. The polarization analysis measurements were essential in establishing that the spin structures are noncollinear. X-ray diffraction measurements were taken with a sealed copper ($\lambda = 1.54$ Å) tube diffractometer, and were used to measure the temperature dependence of the structural peaks. The sample used in these measurements was a thin plate-like single crystal weighing 20 mg, and was grown from a PbO based flux [7]. The basic crystal structure [3] is tetragonal I4/mmm (T′-phase), with lattice parameters at 78 K of $a = 3.939$ Å

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and $c = 12.137$ Å, and is similar to the La_2CuO_4 (T-phase) in that there are Cu–O planes of atoms, but there are no apical O atoms. We will see, however, that there is a small distortion of the structure away from tetragonal symmetry.

The magnetic behavior of this system turns out to be rather complicated; we have in fact already found five magnetic transitions. We therefore first summarize the overall behavior we have observed, before proceeding to the detailed experimental observations. The initial ordering of the Cu spins occurs at a Néel temperature of 245 K, in good agreement with the results of muon precession experiments [8]. The spin configuration is described by a simple antiferromagnetic arrangement of spins in each Cu plane, but with the spin direction in adjacent planes rotated by $\pi/2$. At 75 K, an abrupt reorientation of the spins takes place in which the sense of rotation changes to $-\pi/2$, instead of $+\pi/2$, in adjacent layers along the tetragonal axis. At 30 K a second spin rotation takes place in which the spin directions return to their original directions. At lower temperatures (1.5 K), the Nd ions also order antiferromagnetically, in good agreement with specific heat data [9], and we find a fifth transition of a continuous nature at 0.15 K. Since we are primarily interested in the Cu ordering here, the details of the low temperature transitions associated with the Nd will be presented elsewhere [10]. Finally, above the Néel temperature there are still weak Bragg peaks which are observed at the same positions as the magnetic peaks, and are associated with a small distortion of the lattice away from the basic tetragonal crystal structure.

The magnetic peaks can all be indexed as $(h/2, k/2, l)$, with h, k odd integers, which is the same indexing as found for La_2CuO_4 [11,12] and related compounds [13]. Some diffraction data for the $(\frac{1}{2}\ \frac{1}{2}\ 3)$ Bragg peak are shown in fig. 1. The half-integral values for the first two Miller's indices signify that the unit cell is doubled in size in the

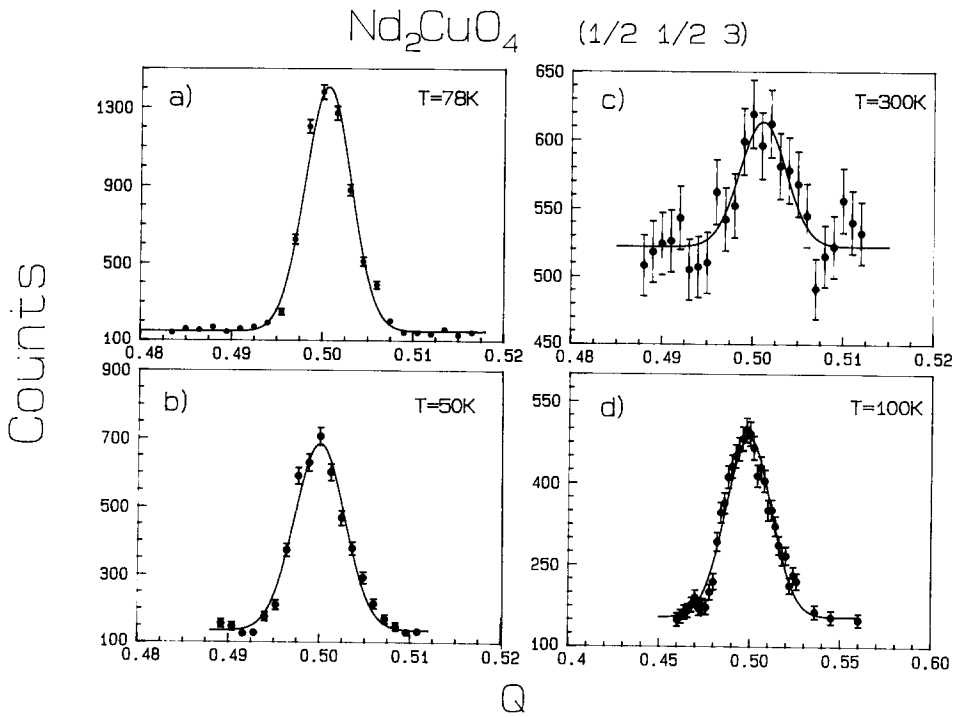

Fig. 1. Magnetic and structural peaks observed at the $(\frac{1}{2}\ \frac{1}{2}\ 3)$ reciprocal lattice position. a) Peak observed with neutrons at 78 K, where it is predominantly magnetic. b) $T = 50$ K, below the spin reorientation transition. c) $T = 300$ K, above the Néel temperature of 245 K. d) Same peak, observed with X-rays. In the X-ray experiments the intensity of this peak was independent of temperature over the range of 100 K to 300 K.

(pseudo)tetragonal a and b directions, while in the c direction the unit cell above and below T_N is the same size. The propagation vector which describes this structure is the $(\frac{1}{2}\ \frac{1}{2}\ 0)$. The simplest spin configuration would be the collinear [14] structure found for La_2CuO_4, with the spin direction along the [1 1 0] since the $(\frac{1}{2}\ \frac{1}{2}\ 0)$ peak is found to have negligible intensity. However, peaks with l even are observed to have quite different intensities compared to those with l odd, which would require the unlikely situation that domain populations to be correspondingly unbalanced.

To resolve this discrepancy, we employed the technique of polarized beam Bragg scattering with polarization analysis [15]. In the high temperature phase ($75\ K < T < 245\ K$) we found that the ratios of the spin-flip scattering intensities for the even-integral peaks were quite large (~ 6), while the odd-integral peaks we measured had ratios near unity. These results directly conflict with the assumption that the spins lie along the [110], and in fact reveal that the magnetic structure must be noncollinear. These data then led us to the spin structure proposed in fig. 2. Note that the spins within each Cu–O layer are antiferromagnetically coupled, with the spin direction in one layer in the [1 0 0] direction, and in the next layer it is in the [0 1 0] direction. The basic propagation vector for the structure is still $(\frac{1}{2}\ \frac{1}{2}\ 0)$. This

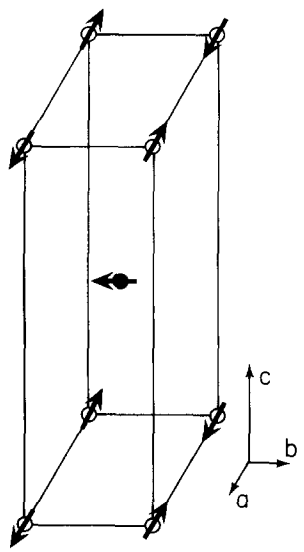

Fig. 2. Magnetic spin configuration of the Cu spins in Nd_2CuO_4.

structure explains the difference between the l-odd and l-even intensities, yields a negligible intensity for the $(\frac{1}{2}\ \frac{1}{2}\ 0)$ peak and overall provides a good description of our experimental data. At 78 K (fig. 1a) essentially the full Cu moment has ordered, and we obtain a saturated moment of $0.4\mu_B$.

The temperature dependence of several reflections is shown in fig. 3. All the $(\frac{1}{2}\ \frac{1}{2}\ l)$ type reflections increase in intensity with decreasing temperature, and reveal a Néel temperature $T_N = 245$ K. This temperature dependence for the intensity with decreasing temperature is quite typical of a magnetic order parameter. The data in fig. 3 also show that at 75 K the intensity of the odd-integral peaks suddenly drops, while the even-integral peaks increase abruptly in intensity. We interpret this as a spin reorientation transition, in which the sense of the spin configuration changes from $+\pi/2$ to $-\pi/2$. This then reverses the strong and weak intensities for even and odd l, respectively, as found experimentally, and reverses the character of the spin-flip ratios observed in the polarized beam data. Note that at 50 K the peaks are still sharp (fig. 1b), only the peak heights have changed. A similar type of transition has been observed recently for La_2CoO_4 [13], but the structure is different in that case.

At 30 K another abrupt spin reorientation takes place, where the spins rotate back to the original spin sense as indicated by the negligible intensity for $T < 30$ K of the $(\frac{1}{2}\ \frac{1}{2}\ 0)$ peak (fig. 3c). Below 30 K the intensities continue to evolve in a rather complicated way. The $(\frac{1}{2}\ \frac{1}{2}\ 3)$ peak in particular grows in intensity at lower temperatures (fig. 3d), and this growth is related in part to the Nd ordering at low temperatures. We remark that the intensity changes shown in fig. 3d, although large compared to the Cu ordering, are relatively weak compared to the intensity related to the Nd ordering: the $(\frac{1}{2}\ \frac{1}{2}\ 3)$ peak grows by another order of magnitude below the Néel temperature (1.5 K) for the Nd order [10].

We now turn to the evidence that there is a distortion in this material from the tetragonal crystal structure. Direct evidence for a distortion is presented in fig. 1c,d [16]. Above the Néel temperature we find that there are small remnant peaks as observed with neutrons, such as at the $(\frac{1}{2}\ \frac{1}{2}\ 3)$ position as shown in fig. 1c. For comparison, the intensity of this peak is 0.011% of the (0 0 4) fundamental

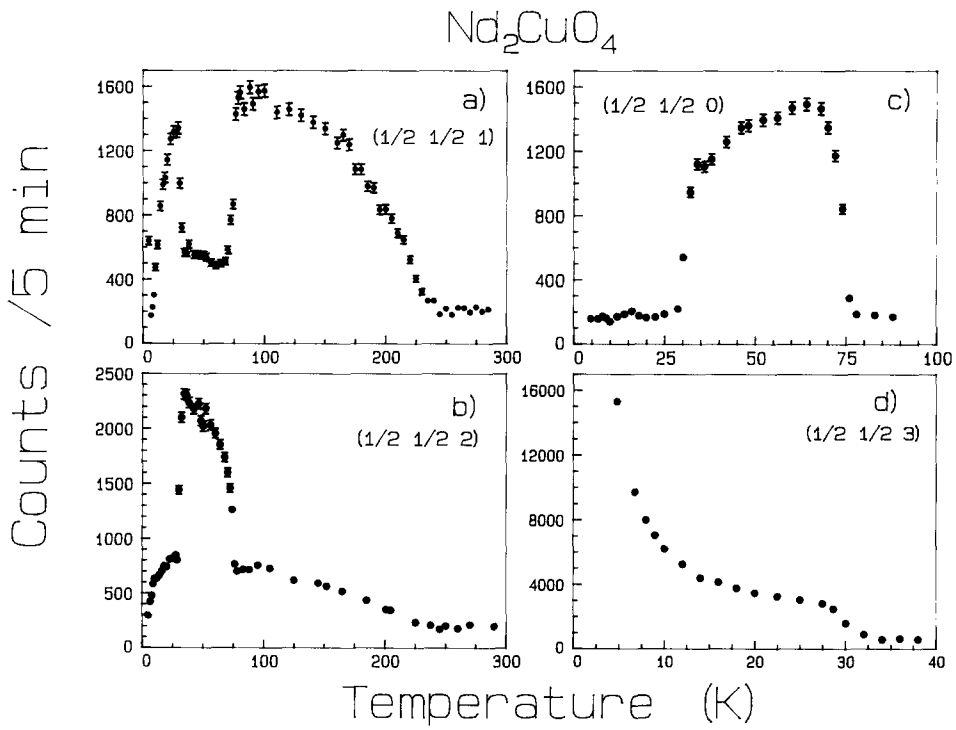

Fig. 3. The intensity of several peaks as a function of temperature. Below the Néel temperature 245 K the intensities of all the peaks increase with decreasing T. At 75 K there is a sudden spin reorientation, in which the even-integral peaks $[(h/2, k/2, 2n)]$ increase in intensity while the odd-integral peaks $[(h/2, k/2, 2n+1)]$ decrease in intensity. At 30 K a second spin reorientation occurs, as clearly seen in ($\frac{1}{2}$ $\frac{1}{2}$ 0) peak (c). Below 30 K, the ($\frac{1}{2}$ $\frac{1}{2}$ 3) grows continuously with temperature, and becomes by far the peak with the strongest intensity. At low temperature (1.5 K) the Nd moments order, and the ($\frac{1}{2}$ $\frac{1}{2}$ 3) is the strongest peak in that ordering, with an intensity which is an additional order of magnitude higher than shown in d).

Bragg reflection. The ($\frac{1}{2}$ $\frac{1}{2}$ 3) peak is also observed with X-rays as shown in fig. 1d, and hence these small extra peaks cannot be magnetic in origin. The X-ray intensities were found to be essentially independent of temperature over the range 100 K to 300 K, and hence we conclude that the structural and magnetic peaks behave independently over this temperature range. Note that since these structural and magnetic peaks occur at the same reciprocal lattice positions, then the distortion can also be represented by fig. 2, where the arrows represent atomic displacements rather than spin directions. The relatively moderate intensity for the ($\frac{1}{2}$ $\frac{1}{2}$ 3) peak (0.7% of the (2 2 0) fundamental peak) suggests that the distortion involves the Nd and/or Cu ions, as the O ions are difficult to see with X-rays. Clearly these preliminary data are only indicative of a distortion, and a complete crystallographic refinement will need to be carried out before the details of the distortion can be elucidated.

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[16] The neutron data in parts a, b, and c of fig. 1 are counts per five minutes, but the data in part c were taken under somewhat different instrumental conditions. The X-ray data are counts per minute.