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Magnetic ordering of Nd in $(Nd,Ce)_2CuO_4$

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Neutron-diffraction techniques have been used to study the magnetic ordering of the Nd ions in semiconducting Nd_2CuO_4 and superconducting $Nd_{1.85}Ce_{0.15}CuO_4$. For the Ce-doped system a sharp transition to long-range antiferromagnetic order occurs at $T_N \approx 1.2$ K, with a simple magnetic unit cell which is double the chemical unit cell along the *a* and *b* directions. The same magnetic structure is observed in the parent system Nd_2CuO_4, in which the Cu spins are also ordered magnetically, but strong coupling between the Nd and Cu sublattices is indicated.

The microscopic magnetic properties of superconductors have been of interest for many years, first for "magnetic superconductor" systems,[1] then in heavy-fermion materials,[2] and most recently in the oxide superconductors.[3] In magnetic superconductors such as RMo_6S_8 and RRh_4B_4 (R represents heavy rare-earth element), the R ions are physically isolated in the crystal structure from the superconducting electrons. This feature leads to a major role for the dipole-dipole interaction as reflected in the very low magnetic ordering temperatures. The magnetic and superconducting order parameters are coupled via the electromagnetic interaction. The heavy-fermion systems, on the other hand, do not have an "isolation" of the magnetic and superconducting subsystems, and in fact the magnetic fluctuations are likely responsible for the superconducting pairing.[2] The oxide superconductors provide the interesting situation of having both heavy rare earths which are often isolated in the lattice and order at low temperatures, and strongly coupled Cu spins which reside in the Cu-O superconducting planes.

We have been investigating the magnetic properties of the recently discovered Nd_2CuO_4 class of electron superconductors,[4-6] which of course possess both rare-earth and Cu-spin subsystems. In the insulating phase the Cu spins order at relatively high temperatures (~245 K),[7-9] with strong spin correlations within the Cu-O layers.[8] At low temperatures the Nd ions have also been observed to order magnetically.[7,10] We have carried out neutron scattering experiments to characterize the nature of this ordering, and have found a simple antiferromagnetic arrangement of spins. For the superconducting material a sharp Néel transition is observed, but in the parent insulating compound the transition appears "smeared" due to substantial coupling with the ordered Cu sublattice. Hence the rare-earth and Cu sublattices cannot be isolated electronically. In the superconducting system, where the Cu spins are disordered, it may be particularly interesting to determine the effect of the Nd ordering on the superconducting properties such as the critical fields, since this could provide an important clue to the origin of the superconducting pairing depending on whether the magnetic ordering hinders or enhances the superconductivity.

The neutron experiments were carried out at the research reactor at the National Institute of Standards and Technology. 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. Single-phase polycrystalline samples of Nd_2Cu-

O_4 and $Nd_{1.85}Ce_{0.15}CuO_4$ were prepared by the usual solid-state reaction technique,[11] and were characterized by x-ray diffraction, susceptibility, and magnetization measurements. For the $Nd_{1.85}Ce_{0.15}CuO_4$ sample, the magnetization data indicated a superconducting transition temperature (onset) of ~25 K. Neutron measurements were also made on a 20-mg single crystal of Nd_2CuO_4, which was grown from a PbO-based flux.[12] This is the same crystal that has been used in our earlier studies of the Cu ordering and structural phase transition.[7] The basic crystal structure[6] for these materials is tetragonal $I4/mmm$ (T' phase), with lattice parameters at 78 K of $a = 3.94$ Å and $c = 12.14$ Å.

Figure 1 shows two magnetic diffraction peaks for the Nd_2CuO_4 powder sample, obtained by subtracting diffraction data taken at low temperatures from the data taken well above the Nd ordering temperature. Data from powder samples provide a good survey technique for determining the overall magnetic structure, assuming that the magnetic peaks are strong enough to be observed. Over the range of scattering angles from 2° to 62°, we observed four magnetic peaks, and they can all be indexed as $(h/2, k/2, l)$ based on the chemical unit cell, with h and k odd integers. The half-integral values for the first two Miller indices signify that the magnetic unit cell is double the chemical unit cell in the (pseudo)tetragonal a and b directions, while in the c direction they are the same size. The propagation vector which describes this structure is the $(\frac{1}{2}\,\frac{1}{2}\,0)$. The magnetic spin configuration is shown in the inset, and corresponds to a simple antiferromagnetic arrangement of Nd moments. The intensity data can then be used to determine the spin direction, which in this case is [110], i.e., parallel to the propagation direction. This same indexing for the magnetic peaks is found to be valid for all three samples, and hence we conclude that the magnetic structure for the Nd is independent of the Ce concentration.

The $(\frac{1}{2}\,\frac{1}{2}\,3)$ Bragg peak turns out to have the strongest magnetic intensity, and the temperature dependence of this peak for the two polycrystalline samples is shown in Fig. 2. Recall that the magnetic Bragg intensity is proportional to the square of the sublattice magnetization. For the superconducting sample a well-defined transition at 1.2 K is observed, which is in good agreement with the specific-heat data.[10] Note that there is a small amount of rounding of the intensity in the vicinity of the Néel temperature, which is typical for second-order transitions and likely originates from critical scattering.

The lower portion of the figure shows the temperature dependence of the same reflection for the Nd_2CuO_4 powder sample. In this case it is difficult to determine the Néel temperature with accuracy since the scattering appears to be "smeared" over several degrees, although the data are certainly consistent with the T_N of ~1.5 K determined from specific-heat measurements on the pure system.[10] Such a smeared order parameter might be caused by sample inhomogeneities and a consequent distribution of Néel temperatures, but this interpretation is inconsistent with the sharp transition for the superconducting sample, and with the behavior observed for the single-crystal sample as we now discuss.

We have taken extensive data on the single crystal of Nd_2CuO_4. In this case the signal-to-noise ratio is much better than for the powders, and we have been able to measure the magnetic intensities as a function of temperature for a large number of reflections. Representative data for the $(\frac{1}{2}\,\frac{1}{2}\,3)$ peak are shown in Fig. 3. To understand these data it is essential to recall that the Cu spins have already ordered at 245 K in this sample, and that the Cu magnetic Bragg peaks occur at the same positions as

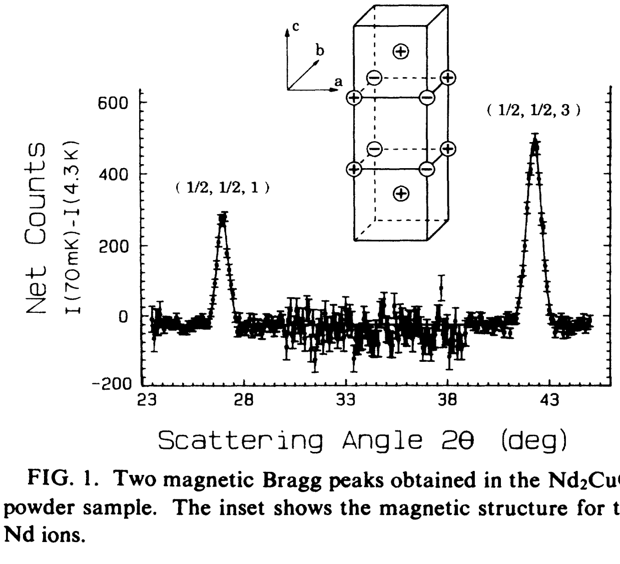

FIG. 1. Two magnetic Bragg peaks obtained in the Nd_2CuO_4 powder sample. The inset shows the magnetic structure for the Nd ions.

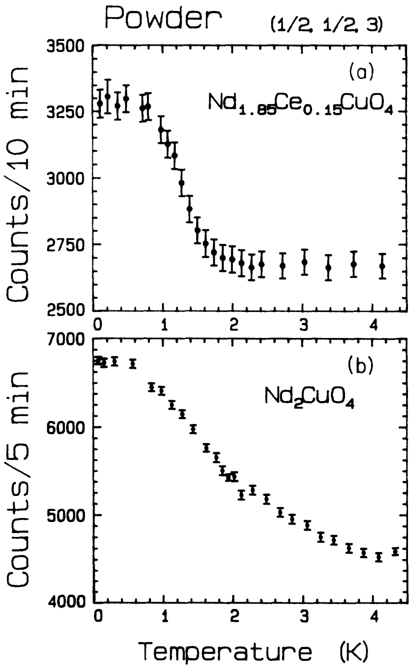

FIG. 2. Magnetic intensity for the $(\frac{1}{2}\,\frac{1}{2}\,3)$ Bragg peak. The top portion of the figure shows the data obtained on the $Nd_{1.85}Ce_{0.15}CuO_4$ sample, where a well-defined Néel temperature of ~1.2 K is found. The lower portion of the figure shows the data for the Nd_2CuO_4 sample, where the intensity is seen to be spread over a large range of temperature.

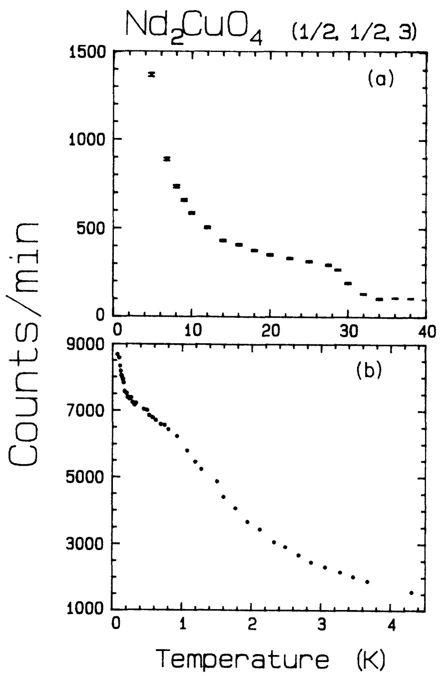

FIG. 3. The temperature dependence of the $(\frac{1}{2}\,\frac{1}{2}\,3)$ Bragg peak observed for a single crystal of Nd_2CuO_4. The top shows the data at and below the Cu sublattice spin-reorientation transition at 30 K. The bottom shows the temperature dependence at low temperatures, where the Nd moments order spontaneously.

for the Nd peaks. Hence the intensities of these peaks represent a coherent addition of the Cu and Nd order parameters. At high temperatures where only the Cu spins are ordered the intensity is, of course, directly related to the Cu order parameter, while at low T the Nd contribution dominates since the Nd moment becomes much larger than Cu and there are twice as many Nd as Cu. At 75 K an abrupt spin reorientation of the Cu spins occurs, in which the Cu spins rotate from the [110] direction parallel to the propagation vector $(\frac{1}{2}\,\frac{1}{2}\,0)$ to the $[1\bar{1}0]$ direction perpendicular.[13] Another spin reorientation occurs at 30 K in which the Cu spins rotate back parallel.[7,8] The data in the top portion of the figure indicate this second spin reorientation, and then a continuous increase in the intensity of the $(\frac{1}{2}\,\frac{1}{2}\,3)$ peak below 30 K. Since the ordered Cu moments are essentially saturated at these low temperatures, we believe that the intensity change below 30 K is due to the polarization of the Nd sublattice. In the bottom portion of the figure the data for the $(\frac{1}{2}\,\frac{1}{2}\,3)$ peak in the low-temperature regime is shown. We see that the intensity slowly increases with decreasing T, until the temperature becomes comparable with the Nd ordering temperature of ~ 1.5 K. Then the Bragg intensities rapidly increase as the Nd spontaneously order. We also note that at very low temperatures (0.15 K) another transition is evident. The nature of this transition is not yet clear, and additional details are given elsewhere.[7]

The temperature dependence shown in Fig. 3 is similar to other two-sublattice magnetic systems, such as $R\mathrm{Fe}_2$,[14] where the coupling between the R ions is weak. In the present case the Cu sublattice is antiferromagnetically aligned, and nearest-neighbor interactions at the Nd site cancel by symmetry. Next-nearest-neighbor and third-neighbor interactions,[15] however, do not cancel, but instead produce a staggered field which polarizes the Nd sublattice antiferromagnetically, and this polarization field has the same symmetry as when the Nd ions order. Hence a net sublattice magnetization of the Nd is induced at elevated temperatures. The Nd-Cu interaction may also be the cause of the second spin reorientation observed at 30 K, where the Cu spins rotate back parallel to the propagation direction, and thus the Nd and Cu spin systems are collinear. In the related Pr_2CuO_4 system, where the Pr appears not to carry a moment, no spin reorientation transitions are observed.[9]

In the Ce-doped superconducting material the Cu-spin system is not magnetically ordered, and hence we do not see any effect on the Nd sublattice. However, when the Nd sublattice orders at low temperatures, we might expect an induced polarization on the Cu sublattice. If the Cooper pairing is mediated by magnetic interactions, for example, then the induced magnetic order of the Cu spins might quench the superconducting state. We believe it would be particularly interesting to measure the superconducting properties, such as the critical fields, to determine whether such a polarization is occurring, and whether it enhances or hinders the superconducting pairing.

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