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Observation of noncollinear magnetic structure for the Cu spins in Nd_2CuO_4-type systems

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Field-dependent neutron-diffraction measurements have been taken on Nd_2CuO_4 and Sm_2CuO_4 in order to distinguish between the proposed collinear and noncollinear spin structures for the Cu ions. For magnetic fields applied along the (110) direction, both systems exhibit Bragg intensities that are continuous and reversible with H. For Nd_2CuO_4 we have also taken data for fields applied within an angle α of the (100) direction, and we have found that the intensities of the magnetic reflections increase or decrease depending on the sign of α. Both of these observations are only consistent with the noncollinear spin model.

In the parent insulating compounds of the high-T_c electron superconductors, such as Nd_2CuO_4, Sm_2CuO_4, and Pr_2CuO_4, the Cu spins occupy a body-centered-tetragonal lattice, and order antiferromagnetically at ~ 280 K.[1] The nature of the magnetic interactions which determine the magnetic structure in these materials is of fundamental importance. In the ordered state nearest-neighbor spins in the a-b (basal) plane are antiparallel, as found in all the other cuprate oxide systems. However, due to the tetragonal crystal symmetry there are two possible orientations of the spins in adjacent planes, and these two possibilities give identical neutron Bragg intensities in the case of zero applied field. One structure is where the spins in adjacent layers are collinear, that is, all the spins point either parallel or antiparallel to a single direction [the (110) in this case], and the other structure is noncollinear where the spins in adjacent layers are orthogonal.[1-5] We have been carrying out diffraction experiments as a function of the magnitude and direction of the applied magnetic field in order to establish which structure is correct. We have concentrated our measurements on the Nd_2CuO_4 system, and have found that the data are only consistent with the noncollinear model. Less extensive measurements on Sm_2CuO_4 show identical behavior to that of Nd_2CuO_4, and thus we believe it is likely that the noncollinear structure is the correct one for this entire class of materials.

The neutron experiments were carried out on the BT-2 and BT-9 triple axis spectrometers at the Research Reactor at the National Institute of Standards and Technology. Unpolarized diffraction data were taken on single crystals of Nd_2CuO_4 and Sm_2CuO_4 using a pyrolytic graphite monochromator and filter. For measurements with the field applied perpendicular to the scattering plane (vertical field), we employed a split-coil superconducting magnet that has a maximum field of 7 T. Crystals were mounted in the (h,h,l) scattering plane and the field was applied in the (110)-type direction. A second set of measurements was taken on the Nd_2CuO_4 crystal with the field applied within the scattering plane (horizontal field). For these measurements, an electromagnet with a field capability of 0.65 T was used. The field was applied in the vicinity of (100) direction, with the crystal mounted in the $(h,k,2k)$ scattering plane.

We begin by briefly reviewing the zero-field behavior of the Nd_2CuO_4 system of particular interest here. The Cu spins order below $T_{N1}=276$ K, which we denote phase I. With further decrease of temperature there are two spin reorientation transitions at $T_{N2}=75$ K (into phase II) and again at $T_{N3}=30$ K (phase III).[1-3] At T_{N2} all the Cu spins rotate by 90° about the c axis, and they rotate back to their original direction at T_{N3}. Below T_{N3} there is a substantial induced staggered moment on the Nd moments, which become ordered at low T (~ 1 K). All the observed antiferromagnetic peaks in these systems can be indexed as $(h/2,k/2,l)$ based on the tetragonal chemical unit cell. Here h and k are odd integers, which signifies that nearest-neighbor spins in the a-b plane are antiparallel. Along the c axis, there are two Cu ions in the unit cell, at the origin and at the body-centered position, and the magnetic and chemical unit cells are identical in this direction. Thus l can be any integer. It is the relative orientation of the spins in adjacent layers that has remained an unresolved question, and the two possible structures are shown in Figs. 1(a) and 1(b). We will confine our discussion to phases I and II where the Nd and Cu sublattices can be treated as essentially independent, and we will see that both phases correspond to the noncollinear Cu magnetic structure. We remark that recently it has been concluded on the basis of magnetization measurements that the low-T ordered magnetic structure for the Nd moments is also noncollinear,[6] and a full description of the neutron measurements for both of these noncollinear structures, and their mutual interaction, will be reported elsewhere.[7] Finally, we remark that in some earlier work[3] strong thermal hysteresis effects were observed in the temperature dependence of the magnetic intensities. However, our measurements do not in-

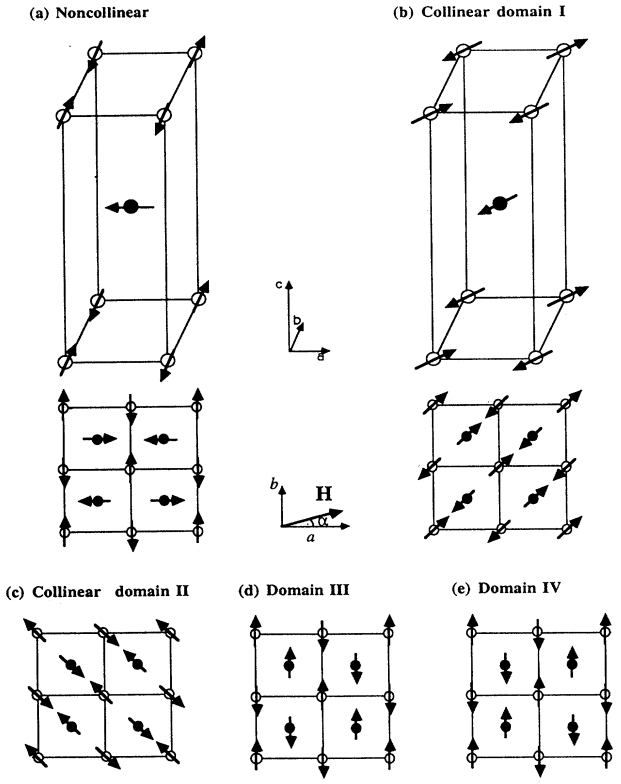

FIG. 1. Proposed noncollinear (a) and collinear (b) zero-field spin structures for the Cu spins in Nd_2CuO_4. For both structures the spins within the tetragonal layer are antiparallel, but for the noncollinear structure spins in adjacent layers are orthogonal. In addition, the zero-field Bragg intensities dictate that for the collinear structure the spins must point along the (110) direction, while in the noncollinear model the spins must point along the a or b axes. The second zero-field domain for the collinear structure is shown in (c), while the high-field domains are shown in (d) and (e). In the projected domains the spins at $z=0$ are denoted by open circles, and the spins at the body-centered positions are denoted by solid circles.

dicate such strong thermal hysteresis effects, and we believe those early observations can be attributed to the rather substantial equilibration times we have found for this system.

The qualitative behavior for these two structures in an applied magnetic field can be understood by noting that the energetics is dominated by the huge in-plane exchange interaction, while the magnetic anisotropy is quite modest. Thus laboratory-size fields will not be able to significantly affect the antiparallel configuration of the spins within the a-b plane, but can only rotate the spin direction. In this case of large ratio of exchange to anisotropy the spins will then want to rotate perpendicular to the applied field. Moreover, the bilinear exchange interaction between planes cancels exactly; indeed, it is this cancellation that renders this class of materials as prototypical two-dimensional magnets.[8] Thus to a first approximation the layers behave independently, and (weak) higher-order interactions must be invoked to stabilize the collinear or noncollinear structure that is actually realized. The qualitative behavior in a field is then clear—the spins will tend to rotate perpendicular to the field, and thus the behavior of the system for fields applied along the (110) and (100) directions will be very different for the two models.

We first measured the field dependence of the magnetic Bragg peaks for Nd_2CuO_4 and Sm_2CuO_4 at a series of temperatures for (vertical) fields applied along the (110)-type crystallographic direction [denoted $(1\bar{1}0)$ for this experimental configuration]. This is the usual experimental configuration for neutrons, utilizing a superconducting magnet with 360° access of the sample in the scattering plane. The $(\frac{1}{2},\frac{1}{2},1)$ magnetic Bragg-peak intensity for Nd_2CuO_4 at 125 K is shown in Fig. 2. We remark that both field-cooled and zero-field-cooled (from 300 K) data show identical behavior. The principal result is that the data are reversible within experimental uncertainties; identical results have been obtained for Sm_2CuO_4. For the collinear model there are two nontrivial zero-field domains as shown in Figs. 1(b) and 1(c). If we let $\alpha=45°$ in this figure, then the spins in domain II are already perpendicular to the field, and thus we do not expect much effect, while for domain I we would expect these spins to rotate to become domain II. This could certainly explain the decrease in intensity with increasing field shown in Fig. 2. However, once domain II is established, there is no reason for it to rotate back to domain I as the field is lowered, and in fact this should be a method for preparing a single-domain sample. Thus we would expect strong irreversibility effects if the collinear model were correct, in contrast to experiment. For the noncollinear model [Fig. 1(a)], on the other hand, the field is initially applied at an angle of 45° to the spins. We would then expect the spins to gradually rotate toward a configuration perpendicular to the field as H increases, but then with decreasing field the spins would rotate (continuously) back to the noncollinear configuration, in agreement with our observations. Hence these data strongly suggest that the noncollinear structure is the correct one for this ma-

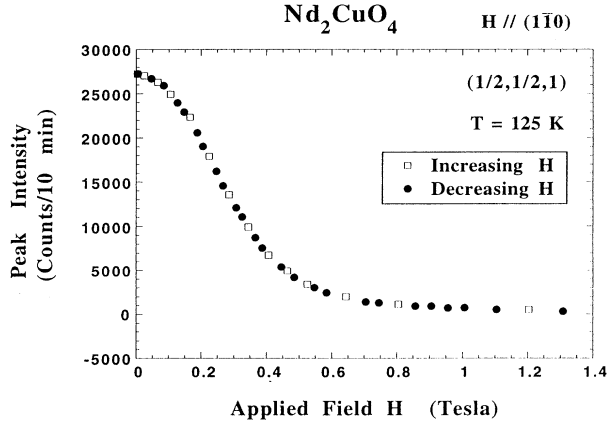

FIG. 2. The $(\frac{1}{2},\frac{1}{2},1)$ magnetic peak intensity as a function of field applied along the $(1\bar{1}0)$ direction in phase I (125 K). The data are reversible on increasing and decreasing field, strongly indicating that the noncollinear spin structure is correct for the Cu spins in this class of materials.

terial. Similar field-dependent behavior has recently been observed by Petigrand *et al.*[9]

Even though these vertical-field measurements strongly suggest that the noncollinear structure is correct, a direct experimental measurement which can distinguish between these two models is highly desirable. Such a method can be realized by taking (additional) measurements with the field applied at a series of angles α from the (100) direction. These measurements required utilizing a horizontal field electromagnet, which geometrically is much more restrictive for these scattering experiments than the vertical field case, and the maximum field capability is also much lower. However, it can provide an unambiguous distinction between these two models. Data were typically collected for $\alpha = \pm 4°$. The angle α had to be set manually, and we estimate an accuracy of $\pm\frac{1}{2}°$.

First consider the behavior of the collinear spin model in this field geometry. The Cu spins in both domains would now make an angle of $45° \pm \alpha$ to the field, and they would then want to rotate approximately perpendicular to the (100) direction as the field is increased. Domain I of the collinear structure would change into domain III [Fig. 1(d)] at high field, and domain II would become domain IV. As the spins rotate the intensities of the magnetic Bragg peaks would be expected to change, in a field range similar to the behavior observed in Fig. 2. The rate of change should not be very sensitive to the magnitude of α, and should certainly not depend qualitatively on the sign of α. Some typical data for the $(\frac{3}{2}, \frac{1}{2}, 1)$ and $(\frac{3}{2}, -\frac{1}{2}, -1)$ magnetic peaks at 80 K (phase I) and 50 K (phase II) are shown in Fig. 3. These two peaks would originate from the two different domains of the collinear model [Figs. 1(b) and 1(c)]. Consider first the behavior of the $(\frac{3}{2}, \frac{1}{2}, 1)$ peak in phase I [Fig. 3(a)]. For $\alpha > 0$ it decreases in intensity, while for $\alpha < 0$ it increases. This is clearly inconsistent with the collinear model, as the field would make an angle of 49° in one case, and 41° in the other. The $(\frac{3}{2}, -\frac{1}{2}, -1)$ peak [Fig. 3(b)], on the other hand, behaves in the opposite manner to the $(\frac{3}{2}, \frac{1}{2}, 1)$ peak, whereas the collinear model would predict that they vary in the same way. These data are qualitatively inconsistent with the collinear spin model, but are in good agreement with the behavior expected for the noncollinear model as we now discuss.

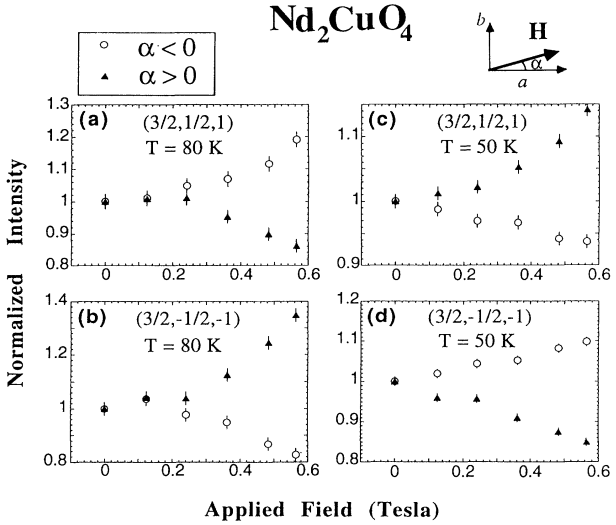

FIG. 3. Normalized intensities of the $(\frac{3}{2}, \frac{1}{2}, 1)$ and $(\frac{3}{2}, -\frac{1}{2}, -1)$ magnetic peaks as a function of field, applied at an angle α from the (100) direction. The magnitude of α is 4° except for $\alpha < 0$ in (b), where it is 10°. The intensities are observed to either increase or decrease depending on the sign of α, which can only be understood on the basis of the noncollinear spin model. Data taken in phase I are shown in (a) and (b), and the zero-field spin configuration is shown in Fig. 1(a). In phase II we note [(c) and (d)] that the qualitative behavior is reversed from that observed in phase I, demonstrating that we still have the noncollinear but with all spins in Fig. 1(a) rotated by 90° (see text).

If the field is applied along the (100) direction then for the noncollinear structure the spins in the $z = 0$ plane [Fig. 1(a)] are already perpendicular to the field and little effect is expected. The spins in the $z = c/2$ plane, on the other hand, are along the field direction, and for $\alpha = 0$ they should undergo an abrupt spin-flop transition and reorient perpendicular to the field. Low-T magnetization measurements as well as antiferromagnetic resonance data[6,10] found this spin-flop transition at ~ 4.4 T, which is above our maximum field of 0.65 T. Thus for $\alpha \equiv 0$ we would then expect little change in the intensity with field, as we in fact observed (not shown). If we now misalign the field by a small angle α, then the "jump" at the critical field becomes rounded, and typically for α of a few degrees the spins rotate in a continuous manner.[11] For $\alpha > 0$ the spins in the $z = c/2$ plane will rotate in the clockwise direction to orient themselves perpendicular to the field, and at sufficiently large fields the spin structure will approach domain IV [Fig. 1(e)], but with spins aligned at an angle $\sim\alpha$ from the (010) axis. This high-field structure gives only the "even" magnetic peaks, which satisfy $h/2 + k/2 + l =$ even integer [e.g., $(\frac{3}{2}, -\frac{1}{2}, -1)$, $(\frac{5}{2}, \frac{1}{2}, 1)$, etc.]. We therefore expect these peaks to increase in intensity at the expense of the others. This is just the behavior that is observed in Figs. 3(a) and 3(b). If we rotate the field so that $\alpha < 0$, on the other hand, domain III will be preferred at high field, and this domain gives only the "odd" magnetic Bragg peaks ($h/2 + k/2 + l =$ odd integer) such as $(\frac{3}{2}, \frac{1}{2}, 1)$ and $(\frac{5}{2}, -\frac{1}{2}, -1)$. Hence for $\alpha < 0$ we expect the role of the two types of peaks to be reversed, as observed. These data conclusively demonstrate that the zero-field magnetic structure realized in phase I is the noncollinear structure shown in Fig. 1(a).

We have studied the field-dependent behavior of these magnetic Bragg peaks in Nd_2CuO_4 at a series of temperatures from 4.5 K and above, that is, in phase I, phase II, and phase III. Data at 50 K (phase II) are shown in Figs. 3(c) and 3(d). The same qualitative dependence on the sign of α is observed, but the role of the "even" and "odd" peaks is reversed. This demonstrates that the magnetic structure is still the noncollinear one, but with all the spins in Fig. 1(a) rotated by 90°. In phase III we find that the magnetic structure for the Cu spins is identi-

cal to phase I, but the quantitative analysis is more complicated because the Cu moments induce a substantial (staggered) moment on the Nd sublattice. In fact we have noted that the effect of an induced moment on the Nd sites is still detectable even in phase I. Our results in phase III lead to the conclusion that the Nd magnetic structure is also noncollinear, in agreement with the conclusions based on low-temperature magnetization and antiferromagnetic resonance measurements.[6,10] Combined with our results on Sm_2CuO_4, our overall conclusion is that the Cu spins form the noncollinear structure in both materials, and thus we believe it is likely that the noncollinear structure is realized in this entire class of materials.

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