Field-induced staggered magnetic order in $La_2NiO_{4.133}$

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At low temperature the holes doped into the NiO_2 planes of $La_2NiO_{4.133}$ by the excess oxygen collect in diagonal stripes that separate narrow antiferromagnetic domains. The magnetic order drops abruptly to zero at $T_m = 110.5$ K, but charge order remains with a period of $\frac{3}{2}a$. We show that application of a magnetic field in the regime $T > T_m$ induces staggered magnetic order of period $3a$ due to the net magnetic moment of the high-temperature bond-centered stripes, together with the odd number of Ni spins across an antiferromagnetic domain. [S0163-1829(97)50314-6]

It is now experimentally established that holes doped into the NiO_2 planes of La_2NiO_4 tend to order in a periodic structure consisting of parallel charge stripes.[1–3] The segregation of the holes into charge stripes leaves intervening regions that are essentially undoped. The magnetic moments of the Ni ions in these regions are correlated antiferromagnetically.[4,5] Neighboring antiferromagnetic domains, separated by a charge stripe, have an antiphase relationship; that is, the phase of the magnetic order shifts by π on crossing a charged domain wall.[2,3] Evidence for related stripe correlations has been found in hole-doped La_2CuO_4,[6–8] and there are indications that dynamical stripe correlations have a connection with the superconductivity found in the layered cuprates.[9]

The problem of stripe order in a doped two-dimensional antiferromagnet has received considerable attention from theorists.[10–19] One feature of theoretical interest concerns the alignment of the charge stripes with the lattice. In particular, one would like to know whether the domain walls are centered on rows of metal atoms (site-centered stripes) or on rows of oxygens (bond-centered stripes). This alignment is difficult to determine in a standard scattering experiment because of the loss of the phase information carried by the scattered beam. In the present paper, we determine the stripe alignment in a crystal of $La_2NiO_{4+\delta}$ through an unusual effect, in which a staggered magnetization is induced in a paramagnetic phase by the application of a uniform magnetic field. This effect can be understood as a ferrimagnetic response associated with the ferromagnetic nature of bond-centered stripes in the high-temperature charge-ordered phase.

The particular crystal of $La_2NiO_{4+\delta}$ studied has an oxygen excess of $\delta = \frac{2}{15} = 0.133$, and a detailed characterization of the charge and spin order will be presented elsewhere.[20] The oxygen interstitial order is the same as that in samples with a nominal $\delta = 0.125$ studied previously,[2] but we believe that $\delta = \frac{2}{15}$ corresponds to the optimal interstitial concentration for this particular phase. The magnetic Bragg peaks measured on the present crystal are sharper than those observed in our own previous work, allowing better sensitivity to intrinsic properties.

To provide a context for understanding our results, it is first necessary to review some details concerning the previously determined order.[2,20] We consider a unit cell of size $\sqrt{2}a_t \times \sqrt{2}a_t \times c$ relative to the tetragonal unit cell of the K_2NiF_4 structure. Antiferromagnetic order within a NiO_2 plane would then be characterized by the modulation wave vector $\mathbf{Q}_{AF} = (1,0,0)$, where the components are in units of $(2\pi/a, 2\pi/a, 2\pi/c)$. The charge order is characterized by the wave vector $(2\epsilon,0,0)$,[21] with the average distance between domain walls in real space equal to $a/2\epsilon$; the magnetic modulation is $(\epsilon,0,0)$ with respect to $\mathbf{Q}_{AF}$. (Note that, relative to the simple square lattice of a NiO_2 plane, the stripes run diagonally.) For $\delta = \frac{2}{15}$, charge order occurs at $T \lesssim 220$ K with $\epsilon = \frac{1}{3}$, while magnetic order appears abruptly at $T_m = 110.5$ K with a concomitant jump in ϵ to 0.295. The modulation parameter ϵ continues to decrease as the temperature is lowered below T_m.

At 10 K we find $\epsilon = \frac{5}{18} = 0.278$.[20] This is close to the value 0.266 $(= 2\delta)$ that one would expect to find if there were exactly one hole per site along a charge stripe, as suggested by the calculations of Zaanen and Littlewood.[11] The fact that ϵ increases with temperature indicates that the density of stripes becomes greater as the magnetic order parameter is reduced. [Note that, with a fixed hole concentration, the hole density (per Ni site) within a stripe, given by $2\delta/\epsilon$, must correspondingly decrease.] In principle, the change in density could be accommodated with a single type of stripe (either site or bond centered). For example, near 100 K where ϵ locks into a value of $\frac{2}{7}$, the observed wave vector could be explained by alternating stripe spacings of $\frac{3}{2}a$ and $2a$. In terms of the magnetic order, the positions of the domain walls would be far from the nodes of a sinusoidal modulation with the same wave vector, and hence one would expect significant magnetic harmonics at 3ϵ and 5ϵ. On the other hand, if the stripes alternate between site- and bond-centered positions, then they have a uniform spacing of $\frac{7}{4}a$, resulting in much weaker harmonics. Quantitative analysis of experimentally observed harmonic intensities supports the latter model. Hence, it appears that there is a mixture of site- and bond-centered stripes whose respective densities change with

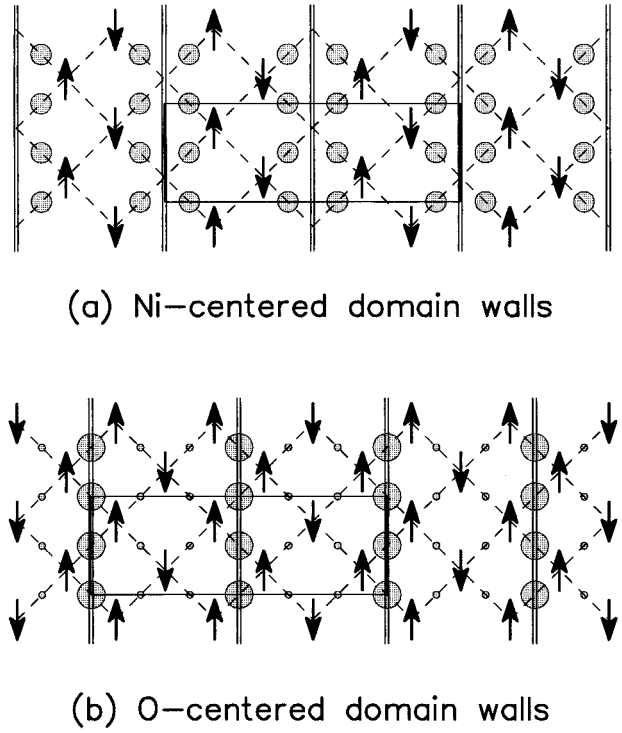

FIG. 1. Stripe models for $\epsilon=\frac{1}{3}$. Arrows indicate correlated Ni magnetic moments; shaded circles indicate locations of holes (on oxygen). Dashed lines trace the bonding paths of the square lattice, while solid lines outline a unit cell. Double lines indicate positions of domain walls. (a) Ni-centered (i.e., site-centered) domain walls. All Ni moments (between domain walls) are equivalent. (b) O-centered (i.e., bond-centered) domain walls. Moments near domain walls and in the center of domains, respectively, are not equivalent.

temperature; however, we do not know experimentally which type dominates at low temperature.

Now let us consider the situation when $\epsilon=\frac{1}{3}$. In this state the charge is still ordered, but the Ni spins are only dynamically correlated. The wave vector is such that the stripes must all be either site centered or bond centered; these two possibilities are illustrated in Fig. 1. In the figure we have also indicated the spin arrangements one might find if a ''snapshot'' were taken. For case (a), the antiferromagnetic domains are just 2 spins wide, and each spin has an antiparallel partner. In case (b), the domains are 3 spins wide, and an uncompensated moment may appear. The magnetic moments on sites adjacent to a charge stripe are likely to be reduced in magnitude compared to those in the middle of a domain, but perfect compensation would be a suprising coincidence. Furthermore, every domain contains two up spins for each down spin, so that this spin configuration should exhibit a ferrimagnetic response. Note that in both cases (a) and (b) the phase of the antiferromagnetic order shifts by π on crossing a domain wall; however, for a bond-centered stripe the adjacent spins are ferromagnetically aligned, whereas for a site-centered stripe adjacent spins are antiparallel.

Magnetization measurements by Yamada *et al.*[5] provided the first indication of a ferrimagnetic response in the paramagnetic phase. They found a sharp peak in the magnetization at the magnetic ordering temperature when the magnetic field is applied parallel to the NiO_2 planes. (An example of such a measurement on a piece of our crystal is shown in Fig. 2.) They also showed that the peak disappears when the field is applied along the c axis, perpendicular to the planes. (We have checked that there is no significant dependence of the magnetization on the direction of the field within the plane, so the spins are apparently XY-like.) The peak was attributed to the response of Ni spins with spiral correlations within the planes, by analogy with the response associated with out-of-plane spin canting that occurs in La_2CuO_4 (Ref. 22) and La_2NiO_4 (Ref. 23); however, we have shown elsewhere[2] that, in the magnetically ordered phase, the spins are essentially collinear and oriented parallel to the stripes, which is inconsistent with spiral order.

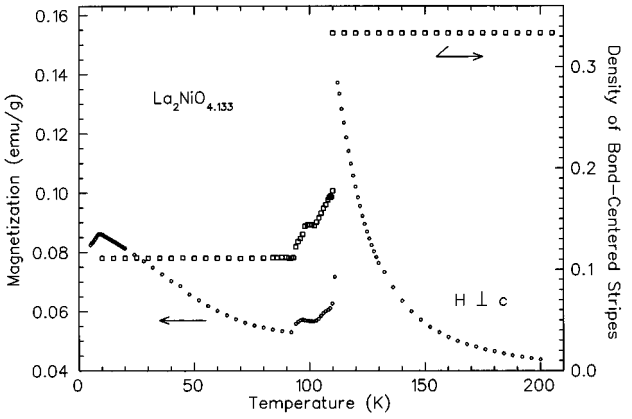

FIG. 2. Bulk magnetization measured (on warming, after zero-field cooling) with an applied field of 1 T aligned parallel to the NiO_2 planes (circles), and density of bond-centered stripes (squares), which is equal to $4\epsilon-1$, where values of ϵ are taken from Ref. 20.

In terms of the stripe model, the peak in the magnetization for $T=T_m^+$ appears to be evidence for bond-centered ferromagnetic domain walls. If this picture is correct, then it should be possible to induce a staggered magnetization by applying a uniform magnetic field. To test this model, we performed a neutron-diffraction experiment on a piece of the same crystal of $La_2NiO_{4.133}$ that we have characterized in detail elsewhere.[20] The crystal was mounted in a flow cryostat that was placed in a vertical-field superconducting magnet. The [010] axis of the crystal was aligned parallel ($<1°$ error) to the magnetic field, both of which were perpendicular to the scattering plane. Elastic scattering measurements were performed using 5 meV neutrons at the H9A triple-axis spectrometer, located at the High Flux Beam Reactor, Brookhaven National Laboratory. Most of the scans were performed along $\mathbf{Q}=(h,0,1)$, through magnetic peaks at $h=1-\epsilon$.

Representative scans are shown in Fig. 3. In the scans of Fig. 3(a), measured at $T=111$ K ($>T_m$), there is no magnetic peak in zero field,[24] but a clear peak at $h=\frac{2}{3}$ ($\epsilon=\frac{1}{3}$) appears in a field of 6 T. The staggered magnetization (proportional to the square root of the intensity) varies linearly with the applied field. On cooling just below T_m [Fig. 3(b)], a zero-field peak appears at $h=0.705$ ($\epsilon=0.295$). As the field is raised from zero, the $h=0.705$ peak decreases in

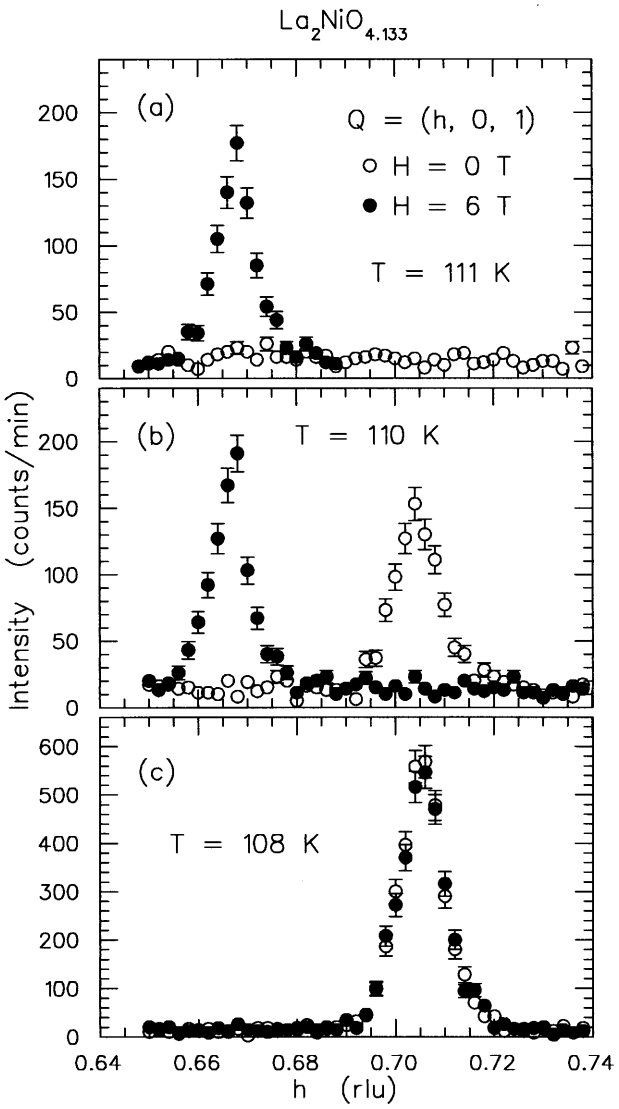

FIG. 3. Elastic scans along $\mathbf{Q}=(h,0,1)$ in zero field (open circles) and in a magnetic field of 6 T (filled circles). Scans were measured at temperatures of 111 K (a), 110 K (b), and 108 K (c).

intensity while the $h=\frac{2}{3}$ peak grows. Rather than a smooth shift of the peak, there is a coexistence of the two wave vectors. When the applied field reaches 6 T, all of the intensity is in the $h=\frac{2}{3}$ peak. By the time that the sample has been cooled to 108 K, the 6-T field has essentially no effect on the magnetic order [Fig. 3(c)]. Note that the width of the $h=\frac{2}{3}$ peak is resolution limited, both along h and in the transverse direction, along l (not shown). The h widths of the incommensurate peaks are slightly broader, indicating a small amount of disorder in the stripe spacing.

Figure 4 shows the temperature dependence of the magnetic peak intensity. In zero field the magnetic peak intensity grows rapidly below the first-order transition at 110.5 K. In a 6-T field the $\epsilon=\frac{1}{3}$ peak is observable over a wide temperature range $\gtrsim$110 K. The inset shows the logarithm of the normalized peak intensity versus temperature at 6 T. Since the intensity is proportional to the square of the staggered magnetization, M, the linear variation (denoted by the fitted line) indicates that

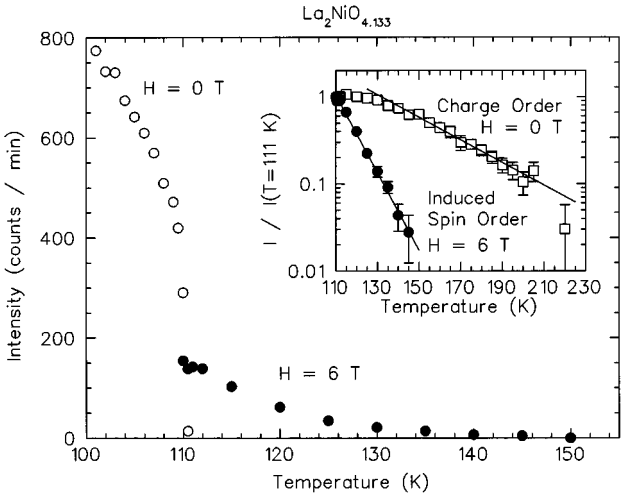

FIG. 4. Temperature dependence of the intensity of the magnetic peak at $\mathbf{Q}=(1-\epsilon,0,1)$ measured with $H=0$ (open circles) and $H=6$ T (filled circles). Below $\sim$109 K the magnetic peaks become independent of field. Inset: logarithm of normalized intensity vs temperature for the magnetic peak at $H=6T$ (filled circles), and for the charge-order peak at $(4-2\epsilon,0,1)$ (open squares, from Ref. 20). Lines through points are linear fits, as discussed in the text.

$$M^2 \sim e^{-2T/T_0}, \tag{1}$$

with $T_0=20\pm5$ K. The exponential dependence on temperature is similar to what one would get from a Debye-Waller factor, suggesting that the magnetization is limited by fluctuations of the correlated spins about the stripe-ordered state. (We have not tested for the Q dependence that one would expect for a Debye-Waller factor.) Also shown in the inset is the temperature dependence of a charge-order peak intensity, obtained in a separate measurement in zero field.[20] In the temperature range where the field-induced magnetic peak is observed, the charge-order intensity is fairly constant; however, it is somewhat surprising that, at higher temperatures, the charge-order intensity also decreases exponentially with temperature. The fit shown in the inset of Fig. 4 corresponds to $T_0=67\pm5$ K. This unusual behavior might indicate that the charge correlations are fluctuating about the commensurate lattice potential caused by the ordered interstitial oxygens. For $\epsilon=\frac{1}{3}$, the charge-order wave vector is equal to the second harmonic of one of the two interstitial-order wave vectors.[2]

The observation of field-induced magnetic scattering corresponding to $\epsilon=\frac{1}{3}$ is direct evidence that the high-temperature domain walls are bond centered. For $T<T_m$ the density of stripes decreases, and the stripes become increasingly site centered. The density of bond-centered stripes (per diagonal row of Ni sites) is equal to $4\epsilon-1$, and can be calculated using the results for ϵ from Ref. 20. The bond-centered stripe density is shown by the squares in Fig. 2. A comparison of this density with the magnetization shows that corresponding structures are found in the temperature range 90–110 K. This indicates that there is a bulk response from the ferromagnetic domain walls even in the ordered state. Note that there is no net macroscopic ferrimagnetism in the

ordered state because, with $\epsilon < \frac{1}{3}$, the ferromagnetic domain walls are no longer all in phase with one another. The drop in the magnetization at $T < 10$ K suggests another shift in ϵ below the minimum temperature studied by neutron diffraction.[20]

What are the implications of these results for stripe correlations in the cuprates? One significant difference in the cuprates is that the domain walls are ''vertical'' (or ''horizontal'') instead of diagonal within a square lattice.[8] As a result, the Cu spins next to a domain wall alternate in direction as one moves along the wall. With one hole per site along a wall, all spin correlations would remain antiferromagnetic; however, for doped La_2CuO_4 the hole concentration is $\approx \frac{1}{2}$ hole per site along a charge stripe. For a bond-centered domain wall, it is possible to imagine a configuration that yields a net magnetic moment. It would be interesting to see whether such a configuration can be detected in a real compound.

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[21] We have previously reported that the wave vector for the charge modulation is $(2\epsilon,0,1)$. More recent results show that the charge modulations in the two nearest-neighbor NiO_2 layers are not related by symmetry. Instead, the modulation phases for a pair of layers are related by the basis vectors (0,0,0) and (a,0, c/2).

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[24] Charge-order scattering is also allowed at $(\frac{2}{3},0,1)$. Neutrons detect the presence of charge order via the induced atomic displacements. For small displacements, the scattered intensity varies roughly as Q^2. The reciprocal lattice point $(\frac{2}{3},0,1)$ is at sufficiently small Q that the charge-order contribution is negligible.