Magnetic Correlations in $La_2NiO_{4+\delta}$

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We report neutron-scattering experiments on single crystals of the layered perovskite $La_2NiO_{4+\delta}$. Three-dimensional magnetic order sets in at $T_N = 70$ K for $\delta \cong 0.05$. Strong two-dimensional magnetic correlations exist for T between T_N and the tetragonal-to-orthorhombic transition temperature, $T_s \approx 240$ K. As T is increased through T_s, the 2D correlation length decreases from more than 50 to 10 Å. The excitation spectra for the 3D ordered state are characterized by large effective *in-plane* spin-wave velocities which, like T_N, depend strongly on δ: For $\delta = 0 \pm 0.001$, $c \gtrsim 0.2$ eV-Å, while for $\delta = 0.05$, $c \approx 0.1$ eV-Å.

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$La_2NiO_{4+\delta}$ is a layered perovskite[1] with unusual transport and magnetic properties.[2-6] From one-electron band theory, *stoichiometric* La_2NiO_4 should be metallic.[7] Indeed, for high temperatures ($T \gtrsim 600$ K), the resistivity $\rho(T)$ does generally increase with T.[2,3] Furthermore, infrared spectra[4] for a somewhat nonstoichiometric sample ($La_{1.9}NiO_{3.87}$) are Drude type in the basal planes; no Drude-type features associated with carriers moving perpendicular to the planes could be found. For low temperatures, $\rho(T)$ has been described in terms of simple activated forms with gaps below 80 meV[2] or the Mott variable-range hopping expression,[3] the parameters depending strongly on stoichiometry. The magnetic susceptibility $\chi(T)$ is also a strong function of δ: For $\delta = \pm 0.001$, $\chi(T)$ is temperature independent below 300 K, while for $\delta \approx 0.05$, there is a small cusp in $\chi(T)$ at 160 K.[5]

In the present paper we describe a neutron-scattering study of the magnetic correlations in this material.[8] Our experiments show that where analogous data are available for La_2CuO_4,[9,10] the parent of the original high-T_c superconductors, they are very similar to those for La_2NiO_4. Thus, explanations of the high-T_c phenomenon, especially those involving magnetic interactions, must account for why, in spite of the similarity of the magnetic correlations, no superconducting oxides of nickel have been found to date. We have also discovered several effects which remain to be probed in the cuprates. Most important is the strong influence of the tetragonal-to-orthorhombic transition on the magnetic correlations in the paramagnetic (also called "quantum spin fluid"[10]) state. In other words, we have provided the first demonstration that in the layered transition-metal oxides, the coupling between the electronic (spin) and lattice degrees of freedom is not negligible. Another essential new result is that in addition to the three-dimensional Néel temperature, the *in-plane* magnetic dynamics depends strongly on oxygen stoichiometry. For the more metallic sample ($La_2NiO_{4.05}$) examined, the spin-wave velocity is at least a factor of 2 lower than in $La_2NiO_{4.00}$.

Measurements were performed with polarized and unpolarized triple-axis spectrometers at the high-flux beam reactor of Brookhaven National Laboratory. For inelastic measurements, the final neutron energy E_f was fixed at 13.7 meV, while for quasielastic experiments, no analyzer was used and the incident neutron energy E_i was fixed at 42 meV. Pyrolitic graphite and Heusler (Cu_2MnAl) crystals functioned as monochromators and analyzers, while pyrolitic-graphite filters eliminated higher-order contamination of either incident or scattered beams.

Single-crystal samples were grown by radio-frequency skull melting, as described elsewhere.[11] Subsolidus annealing allowed a variety of oxygen nonstoichiometries δ to be achieved. Standard wet-chemical analysis of similar samples have shown that the La-to-Ni ratio is 2.00 ± 0.01, while density determinations have indicated that oxygen nonstoichiometry arises from interstitials.[12] Two samples, with volumes of order 0.5 cm^3, were studied. The first, an unannealed, as-grown sample with $\delta \approx 0.05$, was mounted on the cold finger of a closed-cycle ^{4}He refrigerator so that the crystal's $(hk0)$ zone coincided with the horizontal scattering plane of the spectrometer. We also examined, but only at room temperature, an annealed crystal ($\delta = 0 \pm 0.001$) with its $(h0l)$ zone in the horizontal plane. In conformity to previous practice[11] for isostructural La_2CuO_4, Bragg points are labeled by orthorhombic notation, where [010] and [100] correspond to the longest (c) and shortest (a) axes, respectively, of the unit cell. Because of orthorhombic twinning, a general momentum transfer Q

$=(Q_x,Q_y,Q_z)$ always represents two points in reciprocal space, $(Q_x/a^*,Q_y/c^*,Q_z/b^*)$ (twin No. 1) and $(Q_z/a^*, Q_y/c^*,Q_x/b^*)$ (twin No. 2); for this paper, we adopt the convention of expression momentum transfers as points in the reciprocal space for twin No. 1. Except for some of our studies of Bragg peaks (to determine, e.g., the lattice parameters), the momentum resolution [0.03 and 0.05 Å^{-1} full-width at half maximum (FWHM) for $E_f=13.7$ meV and $E_i=42$ meV, respectively] of the instrument was generally too poor to resolve the orthorhombic splitting.

Figure 1(a) shows the temperature dependence of the in-plane lattice parameters a and b for $La_2NiO_{4+\delta}$ with $\delta=0.05$. It appears that a tetragonal-to-orthorhombic transition occurs at $T_s\cong 240$ K; the observation of slight hysteresis effect suggests, but does not necessarily prove, that the transition is weakly first order. For comparison, the corresponding transition in $La_2CuO_{4+\delta}$ has generally been reported as second order.[9,13] Further investigations are required to determine how the space group changes at T_s.

Polarized- and unpolarized-neutron studies reveal magnetic Bragg scattering at reciprocal-lattice points $(0kl)$, with k and l both odd, and points $(hk0)$ with h odd and $k\neq 0$ even, results which imply the magnetic structure shown in Fig. 1(b). As for isostructural K_2NiF_4[14] and La_2CuO_4,[9] antiferromagnetically ordered basal planes are stacked so that nearest-neighbor Ni^{2+} ions, separated by distances $\frac{1}{2}(a^2+c^2)^{1/2}<\frac{1}{2}(b^2+c^2)^{1/2}$, are oppositely polarized. However, in contrast to K_2NiF_4 and La_2CuO_4, where the ordered moments in the $\hat{\mathbf{c}}$ and $\hat{\mathbf{b}}$ directions,[9,14] respectively, La_2NiO_4 is characterized by ordered moments parallel to $\hat{\mathbf{a}}$. Figure 1(b) also shows the temperature dependence of the (011) intensity. The Néel temperature for $\delta=0.05$ is seen to be $T_N=70$ K.

To measure the magnetic fluctuations in the ordered state of $La_2NiO_{4+\delta}$, we have performed a variety of inelastic constant-Q and constant-$\hbar\omega$ scans, some of which are displayed in Fig. 2. Room-temperature and 12-K data are shown for $\delta=0$ and 0.05, respectively; the presence of a gap in the inelastic spectrum indicates that the $\delta=0$ sample is magnetically ordered at room temperature, which is well above T_N (70 K) for $\delta=0.05$. At $Q=(1,0,0)$ and (3,0,0) the spectra have the same shape, but the intensity is lower for the larger of the two magnetically equivalent momentum transfers [left-hand side of Fig. 2(a)]. It is therefore safe to conclude that the strong scattering at $Q=(1,0,0)$ is of magnetic origin. A further issue is the dependence of the data on the component η of the momentum transfer along $[010]\parallel\hat{\mathbf{c}}$. As can be found from comparison of data for $Q=(1,0.4,0)$ and (1,0.9,0) [see left-hand side of Fig. 2(b)], the spectra are virtually independent of η. Thus the fluctuations in the 3D ordered state are primarily of 2D character, a result which is hardly surprising given the structure of the compound.

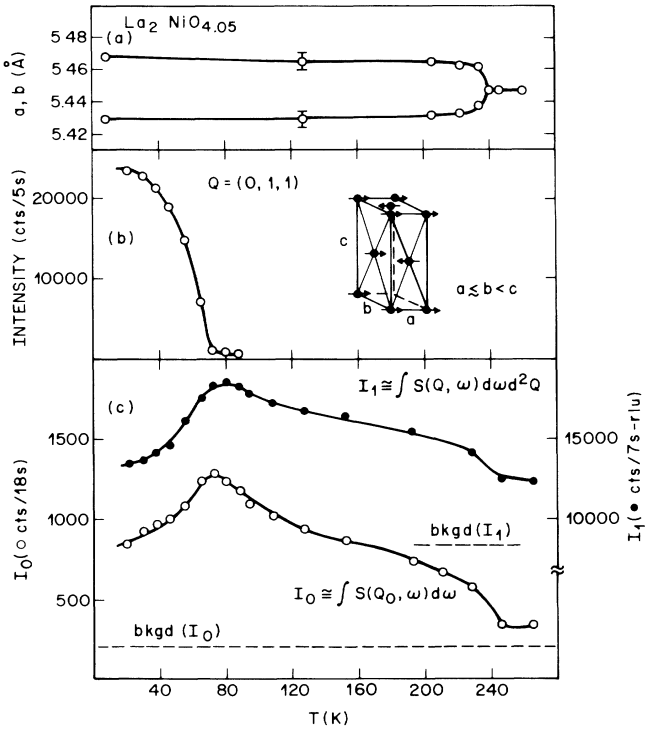

FIG. 1. Temperature dependence of (a) in-plane lattice parameters, (b) magnetic Bragg intensity, and (c) quasielastic (see text) intensities collected for $E_i=42$ meV. Inset in (b): Magnetic structure; filled circles denote Ni atoms. Atoms on the hidden faces of the unit cell are not shown.

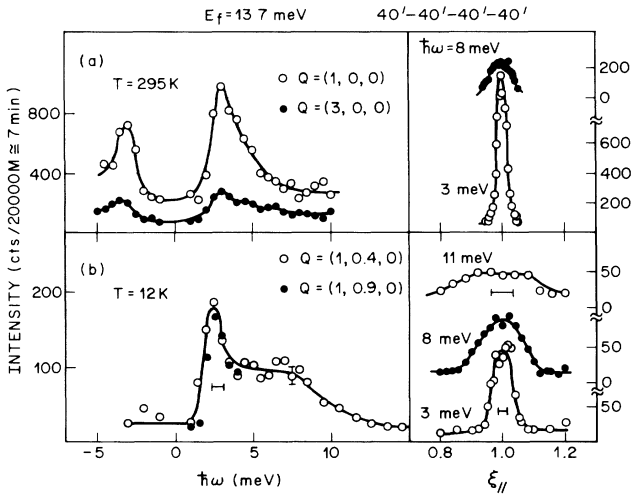

FIG. 2. Constant-momentum-transfer (left-hand frames) and energy-transfer (right-hand frames) scans for (a) $\delta=0$ and (b) $\delta=0.05$. The instrumental resolution (full-width at half maximum) is indicated by the horizontal bars. No attempts have been made to correct the data for the small background signal ($\simeq$2.5 counts/min).

At the two-dimensional zone center [i.e., momentum transfers of form $Q=(1,\eta,0)$], the inelastic scans are characterized by a sharp excitation above a gap of 2.5 meV, followed by a long tail extending to high energies. For $\delta=0.05$, the intensity begins to decay rapidly for $\hbar\omega\gtrsim 8$ meV, while for $\delta=0$ the spectrum remains relatively intense to at least 10 meV. The constant-energy scans, shown on the right-hand side of the Fig. 2, make the differences between $\delta=0$ and 0.05 even clearer. For example, at $\hbar\omega=8$ meV, the scans have half widths at half maximum of 0.04 and 0.08 reciprocal-lattice units (r.l.u.) for $\delta=0$ and 0.05, respectively. If we associate the scattering with unresolved spin waves (for $\hbar\omega$ well above the energy gap) whose dispersion is given by $\omega=cq$, the corresponding values for $\hbar c$ are $\gtrsim 0.2$ and 0.1 eV-Å. Thus, the effective *in-plane* exchange constant, as established from the excitation spectrum in the ordered state, changes by at least a factor of 2 upon our changing the oxygen content of $La_2NiO_{4+\delta}$ by $\simeq 1\%$.

To survey the temperature dependence of the magnetic correlations we have used the spectrometer without an analyzer in the mode where an integral is performed over outgoing neutron energies such that the in-plane component, $\xi_\parallel$, of the momentum transfer is held fixed. The results are proportional to

$$I=\int_{-\infty}^{E_i}\left(\frac{E_i-\hbar\omega}{E_i}\right)^{1/2}|F(\mathbf{Q}_\omega)|^2 S(\mathbf{Q}_\omega,\omega)d\omega,$$

where $\mathbf{Q}_\omega=(\xi_\parallel,\eta(\omega),0)$,

$$\frac{\hbar c^*}{(2m^{1/2})}\eta(\omega)=(E_i-\hbar^2\xi_\parallel^2/2m)^{1/2}-(E_i-\hbar\omega)^{1/2},$$

$S(\mathbf{Q},\omega)$ is the Fourier transform in space and time of the two-spin correlation function, m is the mass of the neutron, F, is the form factor of the magnetic ions, and E_i is the (fixed) incident neutron energy. While, in general, $I\neq\int_{-\infty}^{E_i}S(\mathbf{Q}_\omega,\omega)d\omega$, for the present experiment, where $E_i=42$ meV, $I\approx\int_{-20\,\mathrm{meV}}^{20\,\mathrm{meV}}S(\mathbf{Q}_\omega,\omega)d\omega$. If the magnetic layers were truly decoupled, we would have $S(\mathbf{Q}_\omega,\omega)=S(\mathbf{Q}_\parallel,\omega)$ where $\mathbf{Q}_\parallel=(\xi_\parallel,0,0)$, so that as long as the characteristic energies of the spin system are well below 20 meV, I represents a good measure of the equal-time spin correlation function $\tilde{S}(\mathbf{Q})$. Figure 3 shows data collected as functions of $\xi_\parallel$ for a variety of temperatures below room temperature. At 246 K, the magnetic diffuse scattering is relatively broad, with a width corresponding to a magnetic correlation length of roughly 10 Å. Between 246 and 228 K, where the structural transition occurs, the diffuse scattering narrows greatly, to a width which exceeds that associated with the resolution (0.05 r.l.u. FWHM) by only 30%. The corresponding magnetic correlation length exceeds 50 Å. Further reductions in temperature lead to gradual further sharpening in $S(Q)$. Even for T well below T_N, substantial 2D scattering remains; however, the large $|\xi_\parallel-1|$ tails are somewhat suppressed. Figure 1(c) shows the peak (I_0) and q-integrated ($0.8<\xi_\parallel<1.2$) (I_1) quasielastic intensities. Both quantities vary most rapidly with T near the tetragonal-to-orthorhombic transition. Furthermore, I_0 has a discernible maximum at the 3D ordering temperature, a result which suggests that the 3D ordering at T_N is associated with ordering in the (2D) layers. Nonetheless, the 2D scattering measured by I_1 for $T\ll T_N$ accounts for as many moments as that yielding the 3D Bragg reflection.

We now comment on the relation between two- and three-dimensional order in layered compounds. For Heisenberg systems, the in-plane correlation length $l(T)$ grows until the *effective* interplane coupling $l^2(T)J'$ (J' represents the coupling between neighboring spins in adjacent planes) becomes comparable to kT, whereupon the system order three dimensionally. Note that even if $l(T)-l_0$ is temperature independent because of disorder, for sufficiently large l_0, a reduction in T can still yield a 3D magnetic ordering transition at $kT_N\approx J'l_0^2$, while for small l_0, a spin-glass-like transition will occur. It appears that both antiferromagnetic and spin-glass phases are found in compounds derived from La_2Cu-

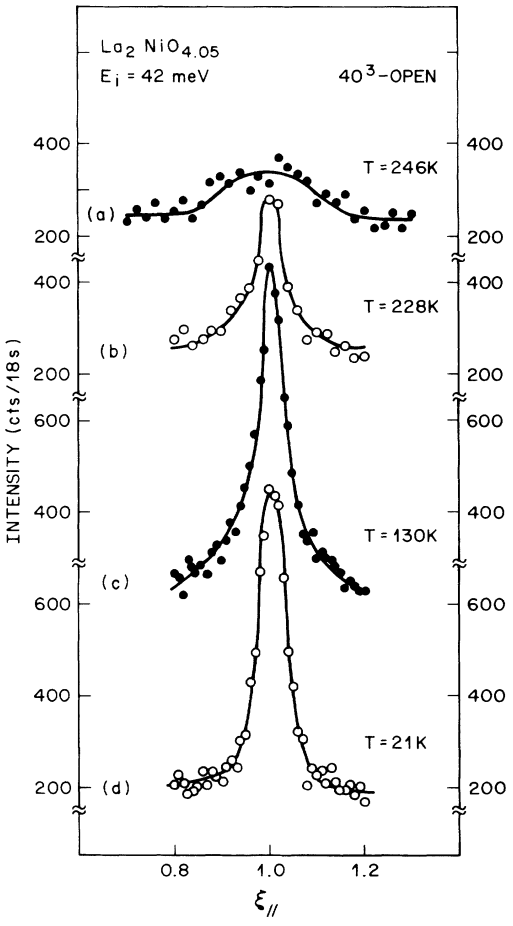

FIG. 3. Quasielastic scans collected as functions of basal plane component $\xi_\parallel$ of momentum transfer.

O_4.[14-16] The extent to which the 3D transition is driven by changing 2D correlations can be determined from the 2D quasielastic scattering (I_0). For example, for $La_2NiO_{4+\delta}$ with $\delta=0.05$, there is an obvious maximum in I_0 at T_N, which implies that $l(T)$ is still evolving for $T\sim T_N$. In contrast, Shirane *et al.*, have noted[10] that for one sample of La_2CuO_4 with $T_N=200$ K, there is a considerably less pronounced maximum in the 2D quasielastic scattering (I_0) at the 3D Néel temperature. Of course, it is unclear whether a $La_2NiO_{4+\delta}$ sample with $T_N=200$ K will behave more like the sample used in the present work or the La_2CuO_4 sample of Ref. 10.

In many respects, a possible exception being that considered in the previous paragraph, $La_2NiO_{4+\delta}$ behaves similarly to La_2CuO_4, which is considered the parent of the high-T_c superconductors. For both the Ni and Cu compounds, there is three-dimensional magnetic order with a Néel temperature highly dependent on oxygen stoichiometry.[5,9] Furthermore, above T_N, there is an extended temperature range characterized by relatively strong two-dimensional magnetic correlations.[10] Both of these results are not surprising in view of the highly anisotropic and face-centered nature [see inset in Fig. 1(b)] of the crystal structure. The tetragonal version of the lattice is frustrated in the sense that there is no unique way in which to stack consecutive square antiferromagnetic layers, so that even a small concentration of defects in the (slightly) orthorhombic version can reduce T_N substantially. More remarkable are the influence of δ on the estimated in-plane spin-wave velocity c and the considerable increase of the *in-plane* correlation length at the tetragonal-to-orthorhombic transition. It will be interesting to see whether similar results hold for $La_2CuO_{4+\delta}$; the latter effect may be harder to identify for the Cu compound where the tetragonal-to-orthorhombic transition is second order.

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