Magnetism of Stripe-Ordered $La_{5/3}Sr_{1/3}NiO_4$

Y. Yoshinari,[1] P. C. Hammel,[1] and S-W. Cheong[2]
[1]*Los Alamos National Laboratory, Los Alamos, New Mexico 87545*
[2]*Lucent Technologies, Bell Laboratories, Murray Hill, New Jersey 07974*
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^{139}La nuclear magnetic resonance studies reveal markedly different magnetic properties of the two sites created by the charged domain wall formation in $La_{5/3}Sr_{1/3}NiO_4$. Nuclear magnetic resonance is slow compared to neutron scattering; we observe a 30 K suppression in magnetic ordering temperature indicating glassy behavior. Applied magnetic field reorients the in-plane ordered moments with respect to the lattice, but the relative orientation of the spins among themselves is stiff and broadly distributed. [S0031-9007(99)08997-8]

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Since the discovery of high temperature superconductivity in the cuprates, the behavior of holes added to a strongly correlated two dimensional (2D) antiferromagnet (AF) has been a subject of intense interest. One important aspect of this system is its tendency toward inhomogeneous charge distribution [1]. In particular, segregation of doped holes into periodic arrays of charged stripes separating hole-free domains has been predicted [2]. Stripe ordering has been observed in doped La_2NiO_4 [3–6] which remains semiconducting up to very high Sr content [7]. The recent observation of similar elastic superlattice peaks in the isostructural [8,9] high-T_c superconductor $La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$ [10] indicates the existence of similar charge-ordered structures, and suggests that these structures may be relevant to cuprate superconductivity [11–14]. Similarities between these elastic superlattice peaks and the incommensurate peaks observed in inelastic neutron studies of $La_{2-x}Sr_xCuO_4$ [15] have been noted [16]. Hence, these incommensurate peaks are being reconsidered as possible evidence for the presence of dynamic charged stripes in the cuprate [16].

There is clear evidence for stripe formation in doped 2D AF systems [3–6], but detailed microscopic studies of their low energy dynamic and static magnetic properties are lacking. A detailed elastic neutron diffraction study of the title compound [6] has demonstrated charge ordering at $T_{co} = 240$ K [6,17,18] into domain walls or "stripes." The stripes run along two equivalent diagonal directions $\vec{e} = (1,1)$ or $(1,\bar{1})$ in the tetragonal unit cell with dimensions $a_t \times a_t$ in the basal plane, where a_t is the lattice parameter corresponding to the Ni-Ni spacing. The stripe period perpendicular to the stripes is $3a_t/\sqrt{2}$. At $T_{so}^{NS} = 190$ K, spin-superlattice peaks appear, indicating ordering of the spins between the stripes. Three temperature regions were evident, the highest between T_{so}^{NS} and T_{co} exhibited elastic charge-order peaks with weaker intensity and significantly reduced correlation lengths compared to lower temperatures. The authors proposed the existence of a "stripe glass" in this temperature regime, but were unable to study the very important issue of orientational order due to the dominant affect of short stripes. Below T_{so}^{NS}, the charge-stripe order was found to improve.

In this Letter we report a single crystal ^{139}La NMR study of the two magnetically distinct sites observed below T_{co}, the first located in the domain walls and the second in the hole-free domains. Although the two regions are spatially proximate and strongly interacting, their static and dynamic magnetic properties are quite different. The NMR provides specific evidence in support of the stripe-glass hypothesis and reveals pronounced and unusual spin disorder arising from stripe defects. A hallmark of glassy systems is sensitivity of the transition temperature to measurement time scale; we find that the onset of spin ordering at $T_{so}^{NMR} = 160$ K in the NMR measurement is 30 K lower than T_{so}^{NS}, as a consequence of its slower characteristic time scale (μsec compared to psec for the neutron measurement). At low temperature where charge order becomes very good, the static spin order exhibits a continuous distribution of moment magnitudes and in-plane orientations. The $H_0 \perp c$ lineshape demonstrates that the ordered moments rotate in response to the applied field such that the most probable spin orientation is perpendicular to the applied field. However, the broad continuous distribution reveals the "stiffness" of the spin texture: Defects in the charge order (stripe ends or bifurcations) frustrate the spin order, causing the orientation of the in-plane ordered moments to rotate relative to each other. Finally, the NMR measurements rule out the motion of domain walls below T_{co}.

A local probe of electronic properties, nuclear magnetic resonance is well suited to determining the microscopic properties of inhomogeneous structures. ^{139}La NMR is employed because ^{61}Ni NMR is not readily performed. In $La_{2-x}Sr_xNiO_4$ a given ^{139}La nucleus ($I = 7/2$, gyromagnetic ratio $\gamma = 601.44$ Hz/Oe) directly probes the magnetic properties of only one Ni electronic spin moment. This is because the transferred hyperfine coupling of the ^{139}La nuclear spin to the single Ni site that shares the La-apical O-Ni bond is an order of magnitude larger than its coupling to any of its four other Ni neighbors.

In the Ni^{2+} ($3d^8$) ionic state, the two unpaired spins occupy the in-plane $3d_{x^2-y^2}$ and the out-of-plane $3d_{3z^2-r^2}$ atomic orbitals. The latter spin is particularly strongly coupled to the La nuclear moment through an orbital hybridization mediated by the apical oxygen. The magnitude of the hyperfine field at the La site due to the Ni moment was determined from a plot of our data for the Knight shift K in the paramagnetic state vs the magnetic susceptibility χ with temperature as an implicit parameter [19] (see also [20]). The Knight shift $K = A\chi$, where A is the hyperfine coupling and χ is the local electronic susceptibility. The hyperfine coupling to a moment oriented parallel (perpendicular) to the c axis is $A_c = 23 \pm 5$ kOe/μ_B ($A_{ab} = 20 \pm 2$ kOe/μ_B). These fields are 1 order of magnitude larger than the classical dipole fields of the same magnetic moments [21], so the transferred coupling to the single Ni dominates.

The 700 mg single crystal of $\mathrm{La}_{5/3}\mathrm{Sr}_{1/3}\mathrm{NiO}_4$ used in this study was prepared by the floating zone method [6]. The spectrum taken at 220 K shown in Fig. 1(b) shows the quadrupole split ^{139}La NMR field-swept spectrum [22]. The central ($-\frac{1}{2} \leftrightarrow +\frac{1}{2}$) nuclear Zeeman transition is least affected by the distribution of nuclear quadrupole frequencies ν_Q and so produces the most narrow and intense peak [23]. The Knight shift K and spin-lattice relaxation time T_1 were measured on this peak. T_1 was measured by monitoring the spin-echo intensity as a function of time after a single saturation pulse was applied. All relaxation curves were best fit by the ($I = 7/2$) theoretical expression for magnetic coupling as opposed to quadrupolar coupling [24]. For poorly resolved peaks at lower T, the measurements were performed at the value of applied field, where the distinct peaks appeared at the lowest T for which they were clearly resolved.

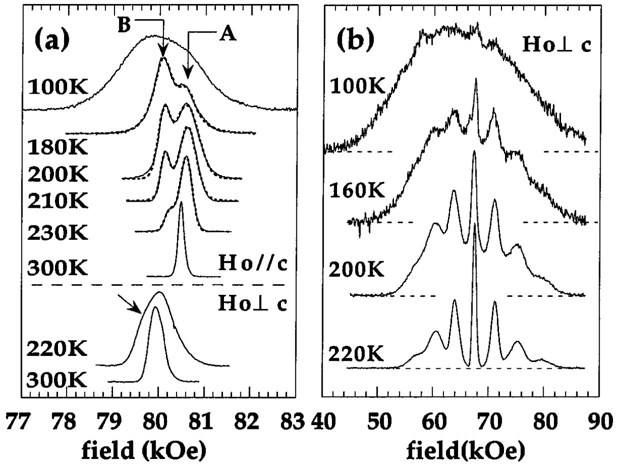

FIG. 1. Quadrupole split ^{139}La NMR spectra in $\mathrm{La}_{5/3}$-$\mathrm{Sr}_{1/3}\mathrm{NiO}_4$. All spectra were taken using a $\frac{\pi}{2}$–30 μsec–π spin-echo sequence. (a) Central transition ($-\frac{1}{2} \leftrightarrow +\frac{1}{2}$) spectra with $H_0 \parallel c$ (upper) and $H_0 \perp c$ (lower) taken at 48.5 MHz. Dotted lines are fits (see text). (b) Full spectra including quadrupole satellites taken at 41.0 MHz with $H_0 \perp c$.

Figure 1(a) shows ^{139}La NMR central transition spectra. A low field peak (the B peak) emerges from the main A peak below T_{co}. The distinct peaks are expected since the magnetic environment of Ni sites in or near the charged domain walls is very different from that of the intervening hole-free regions. As we will show below, an internal field due to static-ordered moments contributes to the shift of the B peak at low temperature, demonstrating the assignment of the B peak to the AF-ordered, hole-free regions between domain walls; the A peak corresponds to domain wall sites.

With cooling, intensity is smoothly shifted from the A to the B peak, as shown in Fig. 2(a), and the spectra broaden increasingly rapidly; below ~100 K the two lines merge into a broad Gaussian peak [25]. The T dependence of I_B, the intensity of the B peak relative to the total central transition intensity, is displayed in Fig. 2(a) [26]. The nuclear spin-spin relaxation time T_2, was found to be quite different for the two peaks; I_B is corrected for T_2. Thus, I_B quantitatively represents the number of nuclear sites in the "B environment." For 210 K $< T < T_{\mathrm{co}}$, $I_B \approx \frac{1}{4}$, less than either $\frac{1}{3}$ or $\frac{2}{3}$, values expected for narrow, sharply defined ordered stripes at $\frac{1}{3}$ hole doping. With decreasing T, I_B increases steadily, saturating at ≈0.93 at about 160 K, indicating that essentially all sites are situated in the B environment.

The internal field due to static spin ordering is apparent in the field dependence of the shift of the B peak in the $H_0 \parallel c$ central transition spectra. Because the ordered

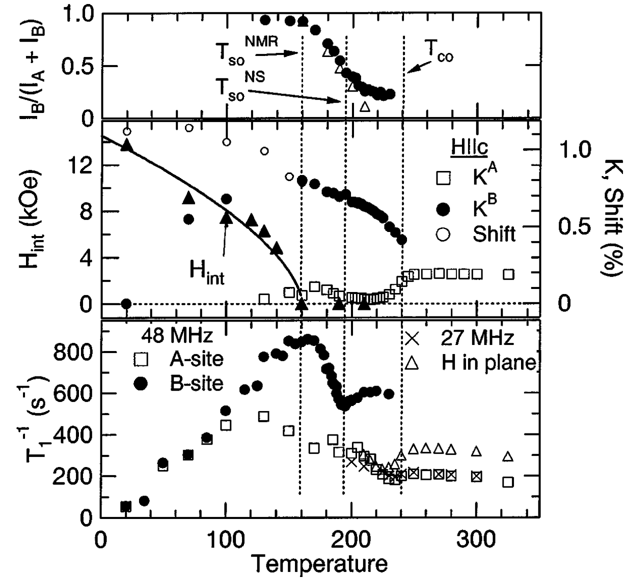

FIG. 2. (a) The T dependence of I_B, the B-peak fraction of the total intensity with $H_0 \parallel c$ (●), and of the broad peak fraction for $H_0 \perp c$ (△). (b) The T dependencies of the ^{139}La Knight shifts K for $H_0 \parallel c$ (plotted against the right-hand axis): A peak (□) and B peak (●). The open circles indicate the total shift of the B peak below $T_{\mathrm{so}}^{\mathrm{NMR}}$. H_{int} is plotted against the left-hand axis. The solid line is a guide to the eye. (c) T dependencies of the ^{139}La T_1^{-1} for $H_0 \parallel c$: A peak (□) and B peak (●); $H_0 \perp c$ (△); all measured at 48.5 MHz. T_1^{-1} for the A peak with $H_0 \parallel c$ at 27 MHz (×) is also shown.

moments lie in the $\mathrm{NiO_2}$ planes [5], their internal field adds to the applied field in quadrature ($H_{\mathrm{eff}}^2 = H_0^2 + H_{\mathrm{int}}^2$). Thus, they do not produce the large shift one would expect based on the value of $A_{ab} = 20\ \mathrm{kOe}/\mu_B$. The $\nu_0 (= \gamma H_0)$ dependence of the shift is shown at several temperatures for $H_0 \parallel c$ in Fig. 3. Understanding the field dependence requires taking into account the quadrupole interaction which produces a large negative shift at low applied fields ($\propto -\nu_Q^2/\nu_0^2$). Exact diagonalization of the Hamiltonian

$$\frac{\mathcal{H}}{h} = (1 + K)\nu_0 I_z + \frac{\nu_Q}{2}\left[I_z^2 - \frac{I(I+1)}{3}\right] + \nu_{\mathrm{int}} I_x \qquad (1)$$

(with $z \parallel c$, and assuming that the moment lies in the plane) provides excellent fits (solid lines) to the measured field-dependent shifts. The quadrupole frequency ν_Q was monitored and varies by less than 10%; this has a negligible effect on the determination of ν_{int}. The T dependence of the internal magnetic field ($H_{\mathrm{int}} = \nu_{\mathrm{int}}/\gamma$) deduced from these fits is shown in Fig. 2(b). We observe no internal field in the 30 K region between $T_{\mathrm{so}}^{\mathrm{NS}}$, where superlattice peaks are first observed, and $T_{\mathrm{so}}^{\mathrm{NMR}}$, below which an internal field is observed. At 20 K, $H_{\mathrm{int}} \simeq 14$ kOe at the La site, implying a Ni spin polarization $\langle S \rangle \mu_B = H_{\mathrm{int}}/A_{ab} \approx 0.7\ \mu_B$. The growth of H_{int} below $T_{\mathrm{so}}^{\mathrm{NMR}}$ is unusually slow; this indicates a suppression of the ordered moment by strong magnetic fluctuations.

At higher temperatures, in the absence of an internal field, the Knight shift K is given by Eq. (1) with $\nu_{\mathrm{int}} = 0$. Above $T_{\mathrm{so}}^{\mathrm{NMR}}$ the $H_0 \parallel c$ shifts for the A and B sites are essentially independent of ν_0, demonstrating that they are both exclusively magnetic in origin. The T dependence of K is shown in Fig. 2(b). K^A for the A sites decreases below T_{co}, while K^B for the B sites increases strongly, reaching ~0.8% at $T_{\mathrm{so}}^{\mathrm{NMR}}$. This large increase in K^B cannot be attributed to a variation in the hyperfine coupling since a shift in A would have a much more dramatic effect on T_1^{-1} ($\propto A^2$) which is not observed; furthermore, the variation of the lattice parameter is smooth across T_{co} and elsewhere [27]. Therefore, the large magnetic shift of the B sites indicates an anomalously large susceptibility in the magnetic domains between stripes. When the contribution of the static field to the shift is taken into account we find that K^B decreases significantly below $T_{\mathrm{so}}^{\mathrm{NMR}}$, indicating a hardening of the ordered spins to a field applied perpendicular to the orientation of the ordered moments.

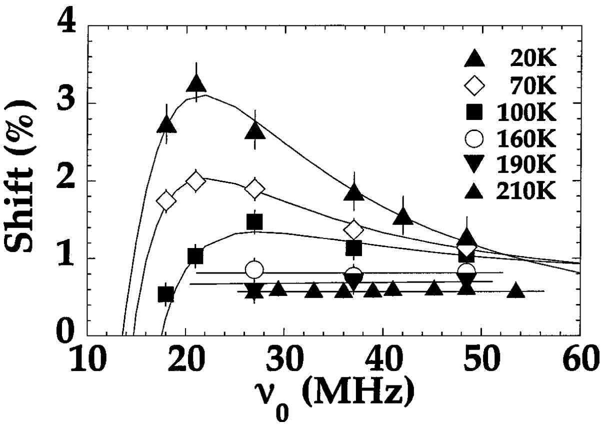

FIG. 3. The ν_0 dependence of the B-peak shift is shown for $H_0 \parallel c$ for various T. The lines show fits to a model incorporating quadrupole interactions and an internal field lying in the planes ($\perp c$); see Eq. (1) and text.

Substantial disordering of the in-plane orientation of the static moments is evident from the broad $H_0 \perp c$ line [Fig. 1(b)]. The internal field due to the antiferromagnetically ordered moment can vary from parallel to antiparallel orientation relative to the field applied in the plane, causing shifts comparable to the internal field. The half-width of the $H_0 \perp c$ line is consistent with the ~12 kOe ordered moment detected in $H_0 \parallel c$ measurements. An orientationally ordered moment would produce discrete lines with shifts determined by the orientation of the ordered moment relative to the applied field; on the other hand, a completely random distribution of in-plane orientations would generate a two-dimensional powder pattern spectrum with singularities at its extrema [distribution $P(\Delta\nu)$ of frequency shifts $\sim 1/\sqrt{(\gamma H_{\mathrm{int}})^2 - (\Delta\nu)^2}$]. Neither is seen; instead, the broad spectrum peaked at a very small shift indicates that the most probable in-plane spin orientation is perpendicular to the applied field. This is the usual response of an ordered antiferromagnet since this allows a slight canting of the moments in response to the field. However, the broad width demonstrates a broad distribution of orientations around the perpendicular orientation. Thus, an applied field easily rotates the moments in the plane with respect to the lattice (and, hence, the ordered-stripe structure), but the broad distribution of orientations of the moments relative to one another is unchanged by the applied field. This is not due to a fortuitous choice of field orientation: The twinning of the stripe orientation would produce two populations of ordered moments rotated 90° with respect to each other, but the spectrum shows no evidence of a second, rotated spin population. This in-plane "twisting" of the spin texture by stripe defects presumably occurs over length scales comparable to the spin coherence length observed with neutrons (~100 Å [6]).

The temperature dependencies of T_1^{-1} for the two environments [shown in Fig. 2(c)] are very different; two transitions occur in the hole-free domains (B line) with little effect on spin dynamics in the domain walls (A line). At all temperatures, signal recoveries demonstrate a single T_1 and no signal intensity is lost. Below T_{co}, T_1^{-1} at the A sites is monotonic in the temperature down to 100 K. In contrast, T_1^{-1} at the B sites shows a distinct and unusual *negative-going* cusp at $T_{\mathrm{so}}^{\mathrm{NS}}$ that clearly signals the transition at which spin-superlattice peaks appear in the neutron measurements [6]. This demonstrates that the suppression of spin ordering in NMR is not a consequence of sample variability since the transition at $T_{\mathrm{so}}^{\mathrm{NS}}$ is clearly observed in our NMR measurements. A typical magnetic ordering transition would generate a *positive* cusp or divergence in T_1^{-1} at the ordering temperature (see, e.g., Ref. [28]). The increase of T_1^{-1} toward a strong peak at the lower temperature $\sim$160 K indicates a rapid slowing of collective spin fluctuations, indicative of long-range, 3D magnetic order at this temperature. The appearance of the internal field at the same temperature would naturally be interpreted as a magnetic transition, were it not for the fact that the spin-superlattice peak in neutron scattering occurs at the higher temperature.

This contrast in apparent ordering temperatures suggests sensitivity to measurement time scale. Rotation of the ordered moment (which is slow compared to the inverse of the energy resolution of the neutron measurement) could motionally average and, thus, reduce the measured $H_{\rm int}$. $T_{\rm so}^{\rm NMR}$ would then correspond to the temperature at which this motion becomes slow on the NMR time scale ($\sim$ microseconds corresponding to < 0.1 μeV). Our results rule out motion of domain walls below $T_{\rm co}$ even on the NMR time scale, as we observe distinct relaxation rates for the two sites immediately below $T_{\rm co}$ [25,29]. A second possibility is that the magnetic order is sufficiently sensitive to the applied magnetic field so that it is suppressed between 160 and 195 K.

In summary, the onset of magnetic order in charge-stripe ordered $La_{5/3}Sr_{1/3}NiO_4$ is suppressed by 30 K when detected on the μsec time scale of NMR compared to psec for neutron diffraction; this provides strong and specific evidence in support of the glassy character of the stripe order. The interplay between spin and charge order is evident in the very broad NMR line found at low temperature, where the stripes are relatively well ordered. This probably arises from the strong spin disordering effects of defects (stripe ends and bifurcations) in the charge-stripe pattern. These defects induce a distribution of *relative* spin orientations. However, the collection of spins as a whole is easily reoriented with respect to the lattice by an applied magnetic field. Finally, below the charge ordering temperature, the ordered charge stripes themselves are static on the NMR time scale.

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