First time determination of the microscopic structure of a stripe phase:
Low temperature NMR in La$_2$NiO$_{4.17}$

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The experimental observations of stripes in superconducting cuprates and insulating nickelates clearly show the modulation in charge and spin density. However, these have proven to be rather insensitive to the harmonic structure and (site or bond) ordering. Using $^{139}$La NMR in La$_2$NiO$_{4.17}$ with $\delta = 0.17$, we show that in the 1/3 hole doped nickelate below the freezing temperature the stripes are strongly solitonic and site ordered with Ni$^{3+}$ ions carrying $S = 1/2$ in the domain walls and Ni$^{2+}$ ions with $S = 1$ in the domains.

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Stripe phases have by now been observed in a variety of doped Mott-insulators, like cuprates, nickelates and manganites [6,10,11]. Nevertheless there is still a remarkable lack of knowledge on the details of the charge- and spin distributions in these novel electronic phases. At the same time there is a growing body of theoretical literature dealing with the microscopic origin of stripe formation, predicting stripes starting from rather different physical perspectives [1–5]. Given its potential connections for instance to the mechanism of superconductivity, it is a matter of high urgency to find out how the stripes look like in detail. In this regard the various theories lead to quite different predictions. Because the spin- and charge distributions are inhomogeneous, NMR with its microscopic sensitivity could in principle yield important information. However, in cuprates attempts in this direction have been frustrated due to the anomalous, glassy ordering dynamics obscuring the static signal. Neutron scattering shows that both in cuprates and nickelates the correlation length of the stripe order is relatively small. This disorderly nature comes to play in NMR [6,11] in the form of a peculiar loss of signal intensity (wipe-out) [6–11] explained by a spread in very short spin-dephasing times $T_2$ [6–11]. Even at the lowest temperatures the signal recovery is only partial indicating that this dynamics is still at work at temperatures as low as 0.3 K in the cuprates, prohibiting attempts to deduce information about the static order from the NMR data [6–11]. We demonstrate here that in a nickelate stripe system the nature of the stripe order (established by neutron scattering) can be deduced in detail from NMR, despite the strong similarities with the cuprate NMR at higher temperatures. We find the stripe structure to be strongly solitonic, with sharply defined charge stripes with a width which is not exceeding the lattice constant by much. Surprisingly, they look quite like the site centered stripes predicted by early mean-field calculations for the nickelate system [4].

Before analyzing the low temperature line shape, which is the central issue of this Letter, we first introduce the main features of the NMR line shape, derive the value of the hyperfine coupling and explain the partial recovery of the signal intensity from the relaxation data.

The NMR measurements were performed on the same La$_2$NiO$_{4.17}$ crystals as measured before [6–11], by sweeping the external field $B$ at various frequencies. The crystal symmetry is almost tetragonal [14], which makes the $^{139}$La-spectra ($I = 7/2$) strongly dependent on the direction of the magnetic field with respect to the crystallographic axes.

FIG. 1. Ordering of excess oxygen, holes and spins. Open circles refer to the ordered excess oxygen sites at $z = 0.217c$, which introduce holes assumed to be Ni$^{3+}$ with $S = 1/2$ (gray circles, site-order scenario). The arrows refer to the Ni$^{2+}$ spins with $S = 1$. Black circles indicate the $^{139}$La sites at $z = 0.14c$. The dotted lines are the in-plane boundaries for the unit cell before doping. The drawn tilted rectangle is the enlarged unit cell after doping.
In La$_2$NiO$_4$$_{1.8}$, with hole doping very close to La$_2$NiO$_4$_{$1.7$}, details about the excess oxygen positions are available. The interstitial oxygen sites are at (0,183a, 0,183b, 0,217c) or equivalent positions. A scenario for the excess oxygen ordering is shown in Fig. 1. There is one excess oxygen atom for each six unit cells. The number of $^{139}$La sites, which are far from the excess oxygen atoms, is twice as large as the number closest to the excess oxygen atoms. For La$_2$NiO$_4$_{$1.7$}, using simple point charge calculations, we expect the interstitial oxygen to change the electrical field gradient (EFG) around the La-sites and to split the $^{139}$La NMR line into two: an A-line due to A-sites with the main component of the EFG (V$_{zz}$) along the c-axis and a B-line due to two times less abundant B-sites with the crystal field gradient in the (ab)-plane. This prediction is in agreement with the experimental intensity ratio of line A to B.

Below 15 K, when the signal starts to regain some of its intensity, the NMR lines are largely broadened. In Figs. 3 and 4 the spectra are shown for $B || c$ and $B \perp c$. Simulations of the spectra taking into account the quadrupolar and Zeeman contributions are shown in the lower panels. The spectra can be decomposed into 2 La sites, one with resolved satellites and the other with overlapp-
ping lines due to much stronger magnetic broadening. Magnetic freezing or ordering is also visible in the bulk magnetic susceptibility, which starts to deviate from the Curie law and peaks at $T = 17 \pm 3$ K. The peak in $-d\chi/dT$ indicates a series of cusps at different spin freezing temperatures close to $17$ K and can be due to spin frustration or spin clusters.

We first show that contrary to the observation in the cuprates, the low temperature line pattern in the nickelate is not due to motional narrowing. In case of two lines separated by $\delta \omega$ the condition for motional narrowing is that the correlation time $\tau$ for the (spin) fluctuations is much less than $1/\delta \omega$. The splitting $\delta \omega$ is given by $\gamma_n$ times the value of the internal field $h_0$: $\delta \omega = \gamma_n < h_0 >$. The value of $\tau$ is coupled to the relaxation rate via $\tau \sim \gamma_n^2 < h_0^2 > T_1/\omega^2$. Hence the condition can be rewritten as $R_m = \gamma_n^3 < h_0^2 >^{3/2} T_1/\omega^2 \ll 1$. Using typical values for $h_0 = 1.5$ T, $\omega = 2\pi \times 40$ MHz and $T_1 = 50$ $\mu$s, $R_m \sim 10^2$.

What is the information we might extract from the lineshape data? The high $T$ data will be sensitive for the EFG parameters and the low $T$ data in addition for the internal or local field. Since the internal field lies in the $ab$-plane, the spectra for $B \parallel c$ will be rather insensitive to the local field. For $B \parallel ab$ the antiferromagnetic alignment of the electron spins we expect to lead to a splitting of the lines. The simulations of the spectra are shown in the lower panels. The principal axes of the EFG with respect to the crystal axes are described by Eulerian angles $(\alpha, \beta, \gamma)$ and the external magnetic field is described by polar angles $(\theta, \varphi)$ with respect to crystallographic axes.

For $B \parallel c (\theta = 0)$ the high $T$ data (e.g. at 75 K) at $\nu = 38.2$ MHz are well reproduced by a quadrupolar splitting $\nu_Q = eQV_{zz}/4hI(2I-1)$ (with $Q$ the electric quadrupole moment of the $^{139}$La-nucleus) of 4.5 MHz. The anisotropy parameter $\eta = (V_{xx} - V_{yy})/V_{zz} = 0$. The width of the satellites in the spectra can be simulated by introducing a spread in the EFG parameter $\Delta \nu_Q = 0.5$ MHz, while the width of the main line requires a (dipolar) field distribution of 0.05 T at the La-site. For the La(B)-site these values are $\nu_Q=8.5$ MHz, $\eta = 0.75$, $\Delta \nu_Q = 1.0$ MHz and $\Delta_B = 0.05$ T. The other parameters are for the A-site: $\alpha = 0$, $\beta = 0$, $\gamma = 0$; for the B-site: $\alpha = 0$, $\beta = \pi/2$, $\gamma = -\pi/6$. According to the simulation of the low temperature data the main effect of the magnetic freezing is the increase of the magnetic broadening $(\Delta B)$ to 0.5, resp. 0.15 T. The spectra shown use internal fields of 1.5 T at the A-site and 0.5 T at the B-site. These internal field values follow from the simulations for $B \perp c$, where the values are much more restricted. For the $B \perp c$ orientation simulation of the 107 K data with the same parameter set as for $B \parallel c$ reproduce the data well $(\varphi = \pi/6)$. For the 4.2 K data the antiparallel alignment of the internal field leads to a splitting of the lines and is described by polar angles $(\theta = \pi/2, \varphi = \pi/3 \pm \pi/2)$ with respect to crystallographic axes.

To explain these remarkable differences, let us assume that we deal with site centered stripes. These stripes naturally lead to two kinds of Ni-ions: Ni$^{2+}$ (A-sites) and Ni$^{3+}$ (B-sites) with two kinds of spins $S = 1$ and $S = 1/2$ respectively. As a consequence the La sites will experience different hyperfine fields. The internal dipolar magnetic field arising from the Ni-spins at the La-sites
will be of the order of 0.2 T. However, the La nuclei just above and below Ni$^{2+}$ in addition will have an exchange coupling via the oxygens. This hyperfine field due to the overlap of the Ni 3d$_{2z}$ and La 6s orbitals through the 2p$_z$ orbital of apical oxygen, is about 1.8 T in the undoped samples and is almost doping independent [27]. Due to the different occupation of the 3d$_{2z}$ orbital of Ni$^{3+}$ the exchange coupling between the $S = 1/2$ Ni$^{3+}$ spins and the La sites will be weaker [28,29]. The ratio between the different occupation of the 3d$_{2z}$ orbitals is almost doping independent [27].

Due to the orbital of apical oxygen, is about 1.8 T in the undoped above and below Ni$^{2+}$ in addition will have an exchange coupling via the oxygens. This hyperfine field due to the finite size of the correlated magnetic regions.

Reason for the extra broadening might be found in the overlap of the Ni 3d$_{2z}$ and La 6s orbitals through the 2p$_z$ orbital of N$_{i}$ and Ni$^{2+}$ will be close to 1:2. This difference in intensity ratio and hyperfine field are indeed the main characteristics of the line shape and hence are well accounted for by this scenario. Can bond centered stripes explain the observations as well? The hyperfine fields will have the same maximum, but the distribution will be different. The line shapes for $B \perp c$ puts a limit to the field on the B sites of at most 0.3 T, which rules out this possibility.

The experiments show that apart from the internal field we need to introduce an appreciable magnetic broadening. Part of the broadening might be due to canting of the spins in the ordered phase in the NiO$_2$-plane away from the charge and spin stripe direction [21], which effect we have not included into this calculation. Another reason for the extra broadening might be found in the finite size of the correlated magnetic regions.

Summarizing, in La$_2$NiO$_{4.17}$ interstitial oxygens determine the line profile above the wipe-out temperature. The NMR intensity loss above the spin freezing or ordering temperature around 20 K is linked to a spread in spin-dephasing as in the cuprates. From the angular and temperature dependence of the La line profiles, we show that the distribution of the internal fields is in agreement with two kinds of Ni-sites with different ionicity and hence different hyperfine interaction with the visible La sites. Site centered stripes of the kind predicted by mean-field theory [2] fit the low temperature data of the visible La nuclei remarkably well.

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