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Stripe order at low temperatures in $La_{2-x}Sr_xNiO_4$ with $0.289 \lesssim x \lesssim 0.5$

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The stripe order in $La_{2-x}Sr_xNiO_{4+\delta}$ with $0.289 \lesssim x \lesssim 0.5$ was studied with neutron-scattering technique. At low temperatures, all samples exhibit hole stripe order. Incommensurability ϵ of the stripe order is approximately linear in the hole concentration $n_h = x + 2\delta$ up to $x = 1/2$, where δ denotes the off stoichiometry of oxygen atoms. The charge and spin ordering temperatures exhibit maxima at $n_h = \frac{1}{3}$, and both decrease beyond $n_h > \frac{1}{3}$. For $\frac{1}{3} \leqslant n_h \lesssim \frac{1}{2}$, the stripe ordering consists of the mixture of the $\epsilon = \frac{1}{3}$ stripe order and the $n_h = \frac{1}{2}$ charge/spin order.

The stripe order formed by linearly segregated holes in the oxygen-doped and Sr-doped La_2NiO_4 system is studied in detail in a series of works by Tranquada and co-workers.[1–6] When the spins in this compound form the ordering at low temperatures, a hole stripe separates the antiferromagnetic Ni spin order as an antiphase domain boundary. It was suggested that such characteristic stripe order may persist for a larger hole concentration n_h up to $n_h \approx \frac{1}{2}$ with keeping the linear relation between the hole concentration n_h and the incommensurability ϵ of the stripe order, i.e., $\epsilon \sim n_h$.[5,6] According to the resistivity and electron-diffraction studies,[7] on the other hand, commensurate charge order is speculated for two Sr concentrations $n_h = \frac{1}{3}$ and $\frac{1}{2}$. In fact, very recent experimental studies have established that the $n_h = \frac{1}{3}$ sample exhibits the stripe-type charge order below $T \sim 240$ K, and it accompanies anomalies in optical conductivity and Raman spectra.[8–10]

So far, the hole stripe order in the nickelate is confirmed in the O-doped $La_2NiO_{4+\delta}$ samples with $\delta = 0.105, 0.125, \frac{2}{15}$ (Refs. 1–4) and the Sr-doped $La_{2-x}Sr_xNiO_4$ samples with $x = 0.135, 0.20, 0.225$ and $x = \frac{1}{3}$ (Refs. 5,6,9) by neutron diffraction. For a small hole concentration $n_h = x + 2\delta$, the distance between the hole stripes is wide enough to accommodate three or more Ni chains in between, and this situation allows for Ni chains to form antiphase antiferromagnetic spin ordering across the hole stripes. In contrast, for the samples with larger n_h of $\frac{1}{3} \leqslant n_h \leqslant \frac{1}{2}$, the distance of the hole stripes is small, and only one or two Ni chains are accommodated between the hole stripes provided that the hole stripes reside on the Ni sites. Hence it would be interesting to study whether samples with $\frac{1}{3} \leqslant n_h \leqslant \frac{1}{2}$ can form essentially the same stripe ordering, or they exhibit qualitatively different charge ordering. The information on spin/charge ordering for $\frac{1}{3} \leqslant n_h \leqslant \frac{1}{2}$ would also be very useful to understand the behavior of the resistivity. In order to elucidate the effects of the higher hole doping to the hole stripe order, we have carried out a neutron-diffraction study on $La_{2-x}Sr_xNiO_4$ samples with the Sr concentration x for $0.289 \lesssim x \lesssim 0.5$. The preliminary results have been reported elsewhere.[11]

Some of the important findings in the present study are that the incommensurability ϵ in the Sr-doped nickelate is approximately linear in n_h up to $n_h \approx \frac{1}{2}$, in sharp contrast with the $La_{2-x}Sr_xCuO_4$ system.[12,13] A careful examination of the n_h dependence of ϵ further revealed that there is a systematic deviation from an $\epsilon \sim n_h$ law around $n_h = \frac{1}{3}$, and that such deviation strongly influences transport properties.[14] We also observed that the charge ordering temperature T_{CO} and the spin ordering temperature T_N exhibit maxima at $n_h = \frac{1}{3}$, and they decrease beyond $n_h = \frac{1}{3}$. In addition, the stripe order at low temperatures is of two-dimensional (2D) character, and it consists of a mixture of the $n_h = \frac{1}{3}$-type stripe order and the $n_h = \frac{1}{2}$-type charge order within the 2D NiO_2 planes for $\frac{1}{3} \leqslant n_h \leqslant \frac{1}{2}$.

Single-crystal samples studied in the present study were cut from the same crystals used in the previous measurements of optical and Raman spectra as well as transport properties. They were grown by the floating zone method, and the oxygen off stoichiometry as well as the hole concentration $n_h = x + 2\delta$ were characterized in detail as previously reported.[8,10,14] All the samples are denoted by the calibrated hole concentration n_h throughout this report.

The neutron-scattering experiments were performed using triple axis spectrometers HQR and GPTAS installed at the JRR-3M reactor in JAERI, Tokai, Japan. To optimize the visibility of the weak signal from the charge ordering, we chose a combination of horizontal collimators of open-sample-40′-analyzer-open (from monochromator to detector) for the HQR spectrometer which is installed at the thermal guide tube with a fixed incident neutron momentum of 2.57 $Å^{-1}$. The crystals were mounted in an Al can filled with He gas. Following the preceding works, we denote the reciprocal space by the orthorhombic notation, and all the measurements were performed on the $(h0l)$ scattering plane.

In order to characterize the charge and spin ordering in the highly Sr-doped nickelate samples, we first studied the ordering in the NiO_2 planes. We found that the samples with $0.289 \lesssim n_h \lesssim 0.5$ show very similar superlattice reflections of the stripe order with those observed in the Sr-doped and O-doped samples with smaller n_h. Figure 1 shows the profiles of the charge and spin superlattice peaks observed along the $(h01)$ line, on which the superlattice reflections of the

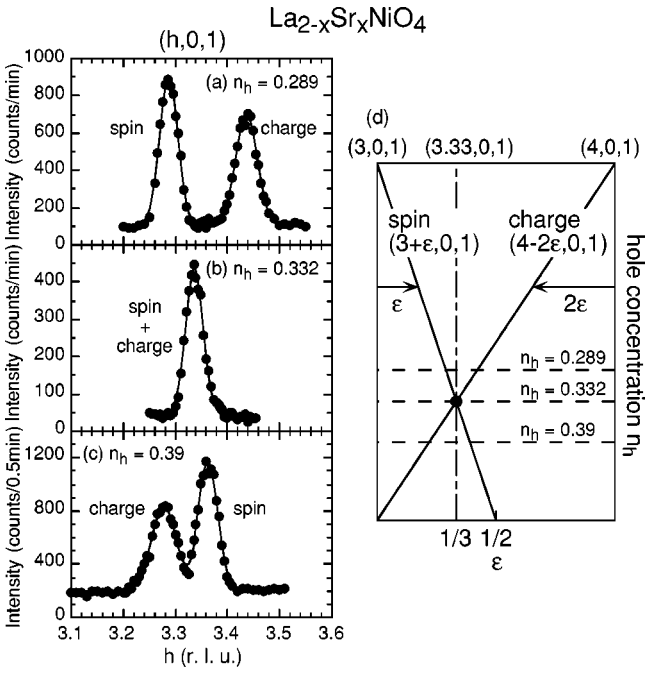

FIG. 1. In-plane scan profiles for the spin and charge superlattice peaks observed along $(h01)$ for (a) $n_h=0.289$, (b) $n_h=0.332$, and (c) $n_h=0.39$ samples. The right panel (d) illustrates the shift of the spin and charge superlattice peaks on the $(h01)$ line from the fundamental Bragg reflections (301) and (401) as a function of n_h.

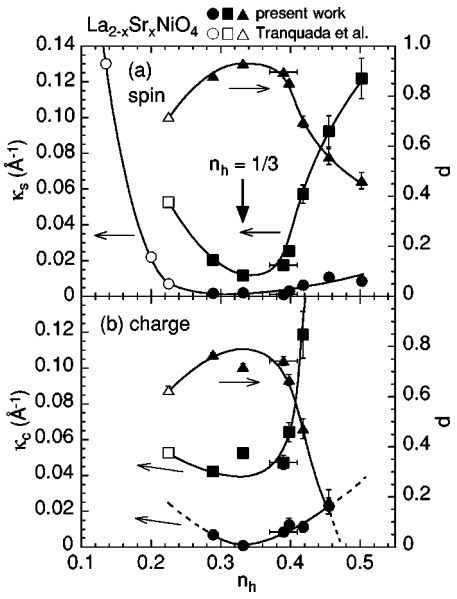

FIG. 2. Inverse correlation length of the spin order κ_s (upper panel) and of the charge order κ_c (lower panel) at low temperatures. The circles and squares denote the in-plane and out-of-plane inverse correlation lengths, while triangles denote p defined in Eq. (1). Filled symbols are for the present work, open symbols for Refs. 5 and 6. κ_c of $n_h=\frac{1}{3}$ is estimated from the data at 170 K.

spin order were observed at $(2n+1\pm\epsilon,0,1)$, while those of the charge order were observed at $(2n\pm2\epsilon,0,1)$ with n integer, respectively. Note that, due to the $\epsilon\sim n_h$ law, an increase of n_h switches the relative positions of the spin and charge superlattice peaks, as schematically shown in Fig. 1(d). At $n_h=\frac{1}{3}$, the superlattice peak of the spin order exactly coincides with that of the charge order as seen in Fig. 1(b), which strongly enhances the stability of the $n_h=\frac{1}{3}$ stripe order and gives rise to a distinct anomaly in the resistivity.[7]

The reasonably sharp peaks observed in the present samples indicate that the well-developed stripe order is established within the NiO_2 planes up to $n_h\lesssim0.5$. We subsequently examined the stacking of the stripe order perpendicular to the NiO_2 planes, by observing the profiles along the l direction (not shown). We found that the scattering profiles are centered at $l=$integer with stronger intensity at $l=$odd, being similar to the results observed in the less Sr-doped samples.[5,6] Consequently, the inverse correlation length κ of the stripe order along the stacking direction was evaluated by fitting to the formula suggested by Tranquada *et al.*,[6]

$$I(l)\sim\frac{1-p^2}{1+p^2-2p\cos\pi l}, \tag{1}$$

where $p=e^{-c/2\xi_l}=e^{-c/2\kappa_l}$. For $\xi_l/c\gg1$, it converges to a conventional Lorentzian form. The fact that the l dependence is well described by Eq. (1) means that the correlation of the stacking of the hole stripes decays exponentially but they are pinned to the lattice at low temperatures even for $\frac{1}{3}\lesssim n_h\lesssim\frac{1}{2}$. The profiles observed by h scans are also fitted to Lorentzian, and all the results are summarized in Fig. 2. The circle symbols denote the in-plane κ, while squares denote κ perpendicular to the NiO_2 planes which is evaluated from p.

As a function of n_h, we can identify three regions for the stripe order. For $n_h\lesssim\frac{1}{4}$, the correlation length is short both within and perpendicular to the NiO_2 planes, and the stripe order is essentially three-dimensional (3D) short-range order (SRO). For $n_h\gtrsim0.4$, on the other hand, the stripe order is well developed within the NiO_2 planes, but is less correlated between the NiO_2 planes, being quasi-2D long-range order (LRO). Near $n_h\sim\frac{1}{3}$, κ shows a minimum, and the stripe order is quasi-3D LRO, demonstrating the stability of the stripe order at $n_h\sim1/3$.

The stability of the $\epsilon=\frac{1}{3}$ stripe order is also evident in the n_h dependence of the charge and spin ordering temperatures T_{CO} and T_N, and they are summarized in the upper panel of Fig. 3. In earlier works,[5–7] T_{CO} and T_N were speculated to increase linearly in n_h as indicated by a dashed line for T_{CO}. We found, however, that they peak at $n_h=\frac{1}{3}$. We confirmed that the transition temperatures determined in the present work are in excellent accord with the anomalies of the temperature dependence in the resistivity along the c axis $(\mathbf{E}\|c)$.[8] As pointed out earlier,[2,5,6] T_{CO} and T_N are different for all the samples we studied with $0.289\lesssim n_h\lesssim0.5$, indicating that the hole stripe order is established first at T_{CO}, and then the antiphase spin order is formed at the lower temperature T_N for $n_h\lesssim\frac{1}{2}$.

Now, we examine the incommensurability ϵ of the stripe order for $0.289\lesssim n_h\lesssim0.5$ in detail. Since ϵ is weakly temperature dependent, ϵ of the low-temperature limit is plotted at the bottom panel of Fig. 3.[15] We confirmed that ϵ is approximately linear in n_h up to the limit of the stripe order, $n_h\approx\frac{1}{2}$. This is in strong contrast to the doped cuprate superconductor $La_{2-x}Sr_xCuO_4$ and to the O-doped nickelate. For

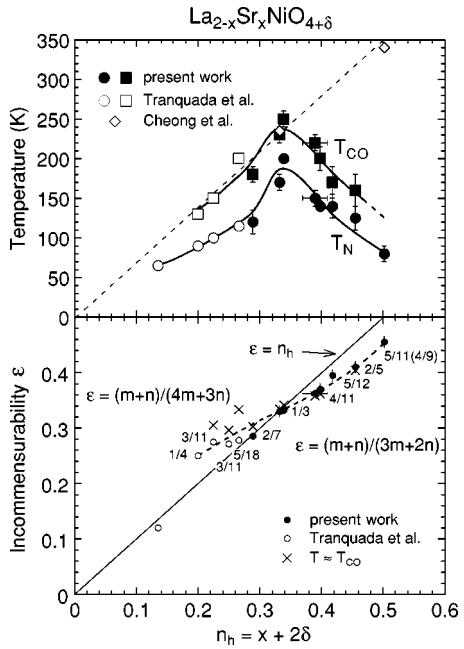

FIG. 3. Upper panel: T_{CO} (square and diamond symbols) and T_N (circles). Lower panel: Hole concentration n_h dependence of the incommensurability ϵ for $n_h \leq \frac{1}{2}$ determined at the lowest temperature studied. The cross symbols indicate the high temperature initial values of ϵ. ($\diamond$ is taken from Ref. 7, and $\bigcirc$, $\square$ from Refs. 1–6).

instance, ϵ saturates at $\epsilon \sim \frac{1}{8}$ beyond the optimum doping in the cuprate.[12,13] In the Sr-doped nickelate, on the other hand, the formation of the $\frac{1}{3}$ stripe order is clearly stable, and the region of the stripe order extends to the higher hole concentration.

The analysis of ϵ further provides important information on the structure of the stripe order. For the O-doped $La_2NiO_{4+\delta}$ samples, ϵ is often locked at a rational value given by $\epsilon=(m+n)/(4m+3n)$ (Refs. 1–3) because the interstitial oxygen ordering stabilizes the commensurate $\epsilon=\frac{1}{4}$ and $\frac{1}{3}$ stripe orders and introduces the competition between them. In the present study, we found that the low-temperature limit of ϵ can be expressed by the same relation for $n_h<\frac{1}{3}$, but it changes to

$$\epsilon=(n+m')/(3n+2m') \quad \text{for} \quad n_h \geq \tfrac{1}{3}, \tag{2}$$

as tabulated in Table I. To explain the meaning of this formula, the model of the $\epsilon=\frac{1}{3}$ stripe order and the $n_h=\frac{1}{2}$ charge order are depicted in Figs. 4(a) and (b). The fact that

TABLE I. Incommensurability ϵ observed in the present work. See the text for details.

n_h	ϵ^{obs}	$\frac{m+n}{4m+3n}$	$\frac{n+m'}{3n+2m'}$
0.289	0.285	(1,1)	
1/3	0.332		(1,0)
0.398	0.365		(3,1)
0.425	0.398		(1,1)
0.462	0.410		(2,3)
1/2	~0.455		(1,3) or (1,4)

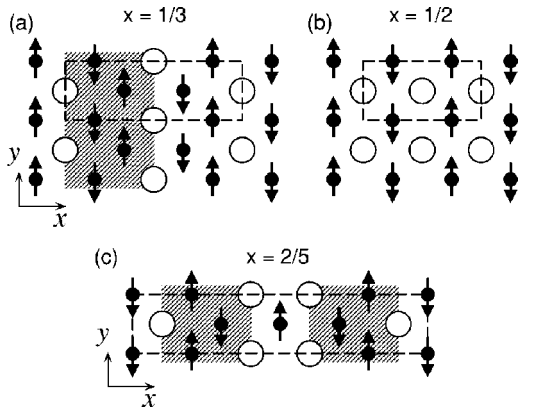

FIG. 4. Models of stripe order for $n_h=1/3$ (a), 1/2 (b), and $n_h=2/5$ (c), respectively. Dashed lines indicate the magnetic unit cell, while the shaded area denotes the $\frac{3}{2}a$-width unit of the $\epsilon=\frac{1}{3}$ stripe order.

ϵ is given by Eq. (2) for $\frac{1}{3} \leq n_h \leq \frac{1}{2}$ can be interpreted that the stripe order in this range of hole concentration consists of a combination of the $\frac{3}{2}a$-width unit of the $\epsilon=\frac{1}{3}$ stripe order and the a-width unit of the $n_h=\frac{1}{2}$ charge order, separated by discommensuration. An example observed in the $n_h=0.425$ sample is depicted in Fig. 4(c), in which the shaded regions correspond to the $\frac{3}{2}a$-width unit. m, n, and m' in Eq. (2) and Table I give the numbers of the $2a$-, $\frac{3}{2}a$-, and a-width units in the long-period commensurate unit cell. For $\frac{1}{3} \leq n_h \leq \frac{1}{2}$, an increase of m' relative to n in Table I indicates that the fraction of the $n_h=\frac{1}{2}$ charge order progressively increases in the stripe ordering pattern. We caution here that, although the model patterns in Fig. 4 are depicted for the case of Ni-centered stripes, both Ni-centered and O-centered stripes exist in the nickelate. The O-centered stripes are presumably dominant at high temperatures immediately below T_{CO}, but the fraction of the Ni-centered stripes increases as T is lowered.[3] The present data do not exclude the O-centered stripes, and Eq. (2) can be interpreted by using the O-centered blocks.

The high density of hole concentration drastically influences the two ordering temperatures, T_{CO} and T_N, for $n_h > \frac{1}{3}$. (1) Up to $n_h=\frac{1}{3}$, the spin order is essentially an antiferromagnetic order which is separated by an antiphase domain boundary of hole stripes. For the $n_h=\frac{1}{2}$ ordering pattern, however, the spin order is actually a 2D checkerboard pattern as depicted in Fig. 4(b), and all the nearest-neighbor sites of the spins are occupied by holes. The existence of holes reduces the effective exchange interactions between spins, and lowers T_N, being consistent with studies of spin dynamics in O-doped nickelates.[16,17] (2) As seen in the right column of Table I, the discommensuration of the stripe order progressively increases the fraction of the $\epsilon=\frac{1}{2}$ pattern for $\frac{1}{3} \leq n_h \leq \frac{1}{2}$. In the matrix of the $\epsilon=\frac{1}{3}$ stripe order, intervening $n_h=\frac{1}{2}$ patterns strongly disturb the spin/charge correlation within and between the NiO_2 planes as manifested by the n_h dependence of κ in Fig. 3. These effects in turn cause the suppression of T_{CO} and T_N for $n_h > \frac{1}{3}$.

Finally, we point out that ϵ was slightly shifted towards $\epsilon=\frac{1}{3}$ for both sides of $n_h=\frac{1}{3}$ as indicated by a dashed curve as shown in Fig. 3. One can see that the farther the distance of n_h from $n_h=\frac{1}{3}$, the larger the deviation of ϵ from the ϵ

$\sim n_h$ law. This behavior has an interesting implication in the transport properties.[14] In the stripe model, the hole density in a stripe n_{st} is always $n_{st}=1$ for all ϵ when the $\epsilon \sim n_h$ law holds. Here, the hole density in a stripe n_{st} is defined as $n_{st} \equiv$ {number of holes/Ni site}/{number of domain walls (DW)/Ni site}$=n_h/\epsilon$. Because one hole exists per each Ni site, hole stripes are half filled and they are Mott insulator-like. The deviation of ϵ from the $\epsilon \sim n_h$ law indicates that the hole density deviates from 1 for both sides of $n_h=\frac{1}{3}$. For $n_h<\frac{1}{3}$, $n_{st} \lesssim 1$ and the carriers are expected to be electron-like, while for $n_h>\frac{1}{3}$, $n_{st} \gtrsim 1$ and the carriers are holelike. This consideration is fully consistent with the change of the sign of the Hall coefficient R_H at $n_h=\frac{1}{3}$.[14]

In summary, we have presented that the region of the stripe order extends up to $n_h \sim \frac{1}{2}$ at low temperatures ~ 10 K in $La_{2-x}Sr_xNiO_4$. Incommensurability ϵ shows the $\epsilon \sim n_h$ law with systematic deviation around $n_h=\frac{1}{3}$, which controls the nature of carriers in hole stripes. The stripe order consists of combination of the $\epsilon=\frac{1}{3}$ stripe order and the $n_h=\frac{1}{2}$ charge order, and ϵ is given by $(m+n)/(4m+3n)$ for $n_h<\frac{1}{3}$ or by $(n+m')/(3n+2m')$ for $n_h>\frac{1}{3}$. The $n_h=\frac{1}{3}$ stripe order is stabilized by the coincidence of the periodicities of the charge and spin order, and as a result, it forms quasi-3D LRO, while it forms 3D SRO for $n_h<\frac{1}{4}$, and quasi-2D LRO for $0.4 \lesssim n_h \lesssim 0.5$.

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[15] ϵ is temperature dependent, and the high temperature values of ϵ determined at T slightly below T_{CO} are indicated by cross symbols in Fig. 3. The present samples with $n_h \gtrsim 0.289$ exhibited a shift of $0.01-0.02a^*$, but it was much smaller than those of the samples reported in earlier works (Refs. 2, 3, and 6).

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