Hole concentration dependence of the ordering process of the stripe order in $La_{2-x}Sr_xNiO_4$

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Ordering process of stripe order in $La_{2-x}Sr_xNiO_4$ with x being around 1/3 was investigated by neutron-diffraction experiments. When the stripe order is formed at high temperature, incommensurability ϵ of the stripe order has a tendency to show the value close to 1/3 for the samples with x at both sides of 1/3. With decreasing temperature, however, ϵ becomes close to the value determined by the linear relation of $\epsilon = n_h$, where n_h is a hole concentration. This variation of the ϵ strongly affects the character of the stripe order through the change of the carrier densities in stripes and antiferromagnetic domains.

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A unique feature of stripe order in high-T_c cuprates[1] has been drawing considerable attention of a number of experimentalists as well as theorists. A similar stripe order observed in a hole-doped nickelate $La_{2-x}Sr_xNiO_{4+\delta}$ makes this compound a good candidate for a study of the stripe order because of its isomorphic crystal structure with high-T_c cuprates and further stability of the stripe order compared with cuprates. With decreasing temperature, the charge stripe is formed first at $T = T_{CO}$, and then the spins order antiferromagnetically with antiphase domains at the charge stripes at the lower temperature T_N.[2–6] The modulation vector of the spin order is given by $\mathbf{g}_{spin} = \mathbf{Q}_{AF} \pm (\epsilon,0,0)$, where $\mathbf{Q}_{AF} = (1,0,0)$ is the wave vector for a simple antiferromagnetic order, while that of the charge order is $\mathbf{g}_{charge} = (2\epsilon,0,0)$ in the orthorhombic cell.

Although the stripe order in nickelates has been well studied for the low-doped region for $n_h \leqslant 1/3$, where n_h is the hole concentration,[2–5,7,8] little work has been reported so far for the highly doped region with $n_h > 1/3$. Very recently we have extended the study of the stripe order with the neutron-diffraction technique toward the higher-doping region up to $n_h = 1/2$.[6] Surprisingly, we have observed that the stripe order persists up to $n_h = 1/2$ and the incommensurability ϵ is approximately linear against n_h. From the n_h dependence of the onset temperatures of the charge stripe and spin order, T_{CO}, T_N, and the correlation length of the stripe order, we argued that the stripe is most stable at $n_h = 1/3$. In order to further elucidate the nature of the stripe order in nickelates, especially, its ordering process and the influence of the commensurability at $n_h = 1/3$, we have performed a detailed neutron diffraction study on the three Sr-doped nickelate samples $La_{2-x}Sr_xNiO_4$ with $x < 1/3$, $x = 1/3$, and $x > 1/3$.

The central result reported in this paper is that three distinct temperature regions are identified in the ordering process of the charge stripe order. The variation of the incommensurability of the charge stripe order plays a crucial role to determine the character of the stripes by the variation of the carrier density in the charge stripes. The character of the stripes also depends on the hole concentration, and it shows symmetrical behavior around $n_h = 1/3$ due to the strong influence of the commensurability at this concentration. The preliminary results have been reported elsewhere.[9]

Single crystal samples studied in the present study were grown by the floating zone method. The crystal structure is pseudotetragonal. The oxygen off-stoichiometry δ as well as the hole concentration $n_h = x + 2\delta$ were characterized in detail as previously reported.[10] The calibrated hole concentration n_h for the present samples are 0.289, 0.339, and 0.39. We denote the samples by n_h throughout this report.

The neutron-diffraction experiments were performed using triple-axis spectrometer GPTAS installed at the JRR-3M reactor in JAERI, Tokai, Japan with a fixed incident neutron momentum of 2.57 $Å^{-1}$. We chose a combination of horizontal collimators of 40′-80′-40′-80′ (from monochromator to detector) for most of scans except for profile scans for $n_h = 0.39$, which were measured with 20′-40′-40′-40′. The crystals were mounted in Al cans filled with He gas, and were attached to a cold head of a closed-cycle He gas refrigerator. The temperature was controlled within an accuracy of 0.2 K. We employ the orthorhombic setting for convenience of easier comparison with preceding works. All the measurements were performed on the $(h,0,l)$ scattering plane.

Let us begin with the profiles of charge/spin stripe order. In order to characterize the stripe order in the ab plane, we performed scans along the [100] direction. Figure 1 shows typical profiles of the charge and spin superlattice peaks measured along the $(h,0,1)$ line for $n_h = 0.39$, which has a larger hole concentration than $n_h = 1/3$. At 170 K, only the charge-order peak is visible, reflecting that the charge-ordering temperature T_{CO} is higher than the spin-ordering temperature T_N for a sample with $n_h > 1/3$ similar to those with $n_h < 1/3$. At somewhat lower T, a peak of the spin order appears and its intensity grows with decreasing T. At 8 K well-defined charge- and spin-order peaks are observed at $(4-2\epsilon,0,1)$ and $(3+\epsilon,0,1)$ with $\epsilon \simeq 0.36$, respectively. Furthermore, a careful inspection of the profiles of the charge-order peak reveals that the incommensurability ϵ has a small T dependence.

To examine the ordering process of the stripe order in more detail, we have carried out a systematic study of the T dependence of the charge and spin stripe-superlattice peaks in samples that have the hole concentration $n_h < 1/3$ and $n_h > 1/3$. The T dependences of intensity ϵ and width for the two selected samples with $n_h = 0.289$ and 0.39 are summarized in Fig. 2.

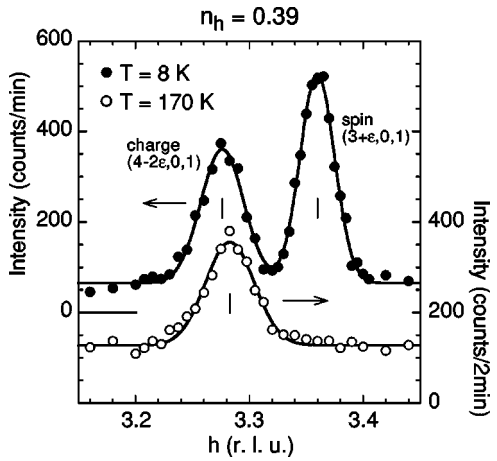

FIG. 1. Profiles for the charge and spin superlattice peaks observed along $(h,0,1)$ for $n_h=0.39$ measured at $T=10$ K (open symbols) and 170 K (closed symbols). Solid lines are the fits to the Gaussian and vertical bars indicate the peak positions.

Figures 2(a) and 2(d) show the T dependences of the intensities of the $(4-2\epsilon,0,1)$ charge order peak and those of the $(1+\epsilon,0,1)$ spin order peak. As mentioned above, T_{CO} is higher than T_N for both samples.[6] The T dependence of the intensity exhibits a distinct anomaly at T_L, below which the intensity of the charge order peak saturates. As shown in Figs. 2(b) and 2(e), the incommensurability ϵ continuously varies through the spin-ordering temperature T_N, but locks in at T_L. Notice that the lock-in temperature of ϵ is well correlated with the saturation temperature of the intensity of the charge order peak, T_L. As for the correlation lengths of the charge and spin orders, the width of the charge stripe peak continues to decrease below T_{CO}, but saturates around T_N as shown in Figs. 2(c) and 2(f), indicating that, once spin domains between charge stripes establish an antiferromagnetic (AF) spin order below T_N, the correlation length of the charge stripe order ceases to grow. In other words, the charge stripe order is short ranged for $T_N<T<T_{CO}$, but forms quasi-long-range order below T_N. This fact strongly indicates that AF spin correlations are essential to stabilize charge/spin stripe order, and implies that they are also responsible for the anomalous behavior of ϵ and the peak intensity for $T_L<T<T_{CO}$.

A closer examination of behavior of ϵ will provide rich information on the physics of charge/spin stripe order with n_h around 1/3. To visualize the behavior of ϵ of the *off-concentration* samples with $n_h=0.289$ and $n_h=0.39$ against the *commensurate* value of $n_h=1/3$, their T dependences are replotted together with that of the commensurate $n_h=0.339\simeq 1/3$ sample in Fig. 3. The commensurate $n_h=1/3$ sample is unique because ϵ exhibits practically no temperature dependence and stays at $\epsilon=1/3$ $(=n_h)$ for all T. By contrast, one can clearly see that the behavior of ϵ for two *off-concentration* samples is symmetric around $\epsilon=1/3$.

In our previous study, we established that although the low T value of ϵ follows a linear law, i.e., $\epsilon=n_h$, there was a small systematic deviation of ϵ.[6] From Fig. 3, we find that such a systematic deviation in the off-concentration samples is further enhanced at high T near T_{CO}: In either case, ϵ exhibits a closer value to 1/3. These deviations from the $\epsilon=n_h$ law at high T for off-concentration samples indicate that the charge stripe itself prefers $\epsilon=1/3$ by tuning the carrier density within the stripes. We would like to emphasize here that the self-tuning behavior of ϵ toward 1/3 at high T in the present Sr-doped samples should not be confused with a similar lock-in behavior of ϵ in the oxygen-doped samples.[3] In the excess-oxygen samples, it is driven by the ordering of the interstitial oxygen atoms and associated buckling of NiO_6 octahedra, whereas the amount of the excess oxygen is negligible in the present Sr-doped samples. Thereby, the tendency of charge stripes favoring $\epsilon\simeq 1/3$ at high T is intrinsic to the stripe ordering in the Sr-doped system, and we tentatively call it as a *commensurability effect*.

Next, we discuss the T dependence of ϵ. With decreasing T, ϵ decreases for $n_h=0.289$ whereas it increases for $n_h=0.39$, and is locked below T_L for both samples. Namely, ϵ becomes closer to n_h at low T. To describe the effect of the change of ϵ, we shall introduce the nominal hole density within charge stripes n_{st}. From the observed value of ϵ, one can evaluate n_{st} by $n_{st}\equiv n_h/\epsilon$. In terms of n_{st}, the observed behavior of ϵ indicates that n_{st} strongly deviates from unity at $T\sim T_{CO}$ due to the commensurability effect at $\epsilon=1/3$, but it shows a tendency to approach unity upon decreasing T.

When $n_{st}=1$, all the doped holes are accommodated within the charge stripes and the stripes become half-filled Mott insulators, and there are no excess carriers in the system.[10] On the contrary, when $n_{st}\neq 1$, there are excess electrons $(n_{st}<1)$ or holes $(n_{st}>1)$ in the system to form half-filled stripes. In this situation, there are two possibilities concerning the location of the excess carriers: one is they enter the charge stripe and the other is they are distributed in a NiO_2 matrix separated by the stripes. Considering the fact that the stripes are in a short-ranged glassy state at $T\sim T_{CO}$ where n_{st} strongly deviates from unity, it would be natural to assume that the excess carriers enter both NiO_2 matrix and stripes because it is difficult to distinguish between the two in the high-T glassy-stripe state. To simplify the discussion, we shall describe such a situation by $n_{st}\neq 1$ in this paper, although in the strict sense of the definition this quantity is only relevant to the stripes.

The T-dependent variation of n_{st} is intimately related to the development of the AF spin correlations. It was reported that the AF spin correlations develop dynamically in the NiO_2 matrix imediately below T_{CO}, though T_N is well below T_{CO}.[4,14] When $n_{st}\neq 1$, carriers distributed in the NiO_2 matrix may cause local disturbances of the AF exchange interactions in the AF spin domains. On the other hand, when $n_{st}=1$, there is no disturbance to the AF spin correlation. From this consideration, we suggest that the observed T dependence of n_{st} is driven by the development of the AF spin correlations at low T's. By confining doped holes within charge stripes and by adjusting the distances between the stripes, the AF spin correlations gain the exchange energy, and concomitantly favor the half-filled stripe with $n_{st}=1$.

The variation of n_{st} driven by AF spin correlations has a strong influence on the lattice distortions caused by the stripe

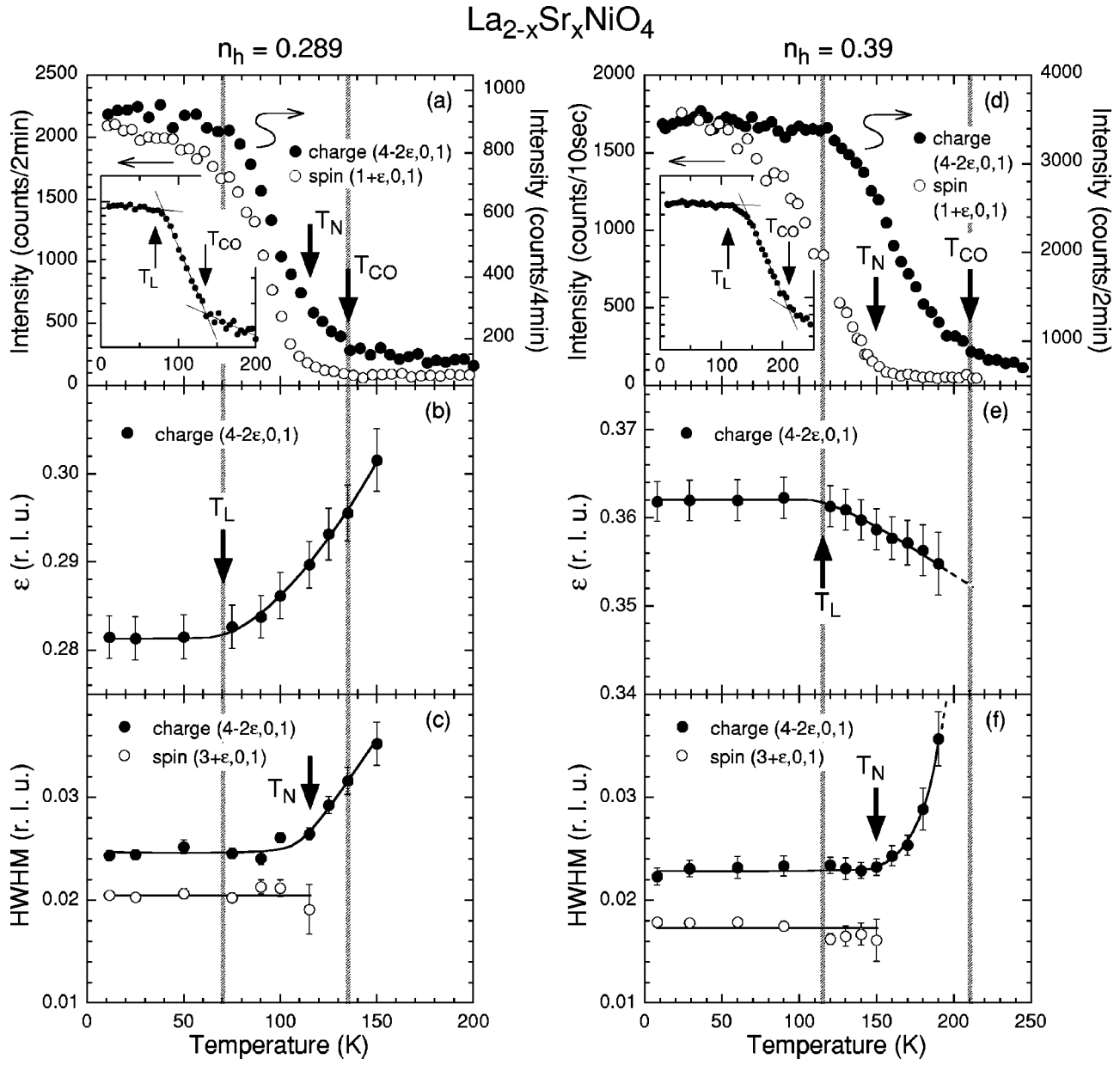

FIG. 2. Temperature dependence of the scattering intensity [(a), (d)], the incommensurability ϵ [(b), (e)], and the peak width (half width at half maximum) [(c), (f)] of the charge order peak (closed symbols) and the spin order peak (open symbols) for $n_h=0.289$ [(a)–(c)] and $n_h=0.39$ [(d)–(f)]. The intensities of the charge order peaks are replotted in logarithmic scale as insets in (a) and (d).

order. The extra electrons or holes supplied to the AF spin domains must cause local atomic displacements and disturb the lattice distortions induced by the charge stripe order, thereby reducing the intensity of the charge order peak, because it is proportional to the square of the coherent component of the amplitude of the displacements. Consequently, the behavior of ϵ shows a strong correlation with the intensity of charge stripe peaks, as shown in Figs. 2(a), 2(b), 2(d), and 2(e). In particular, the continuous shift of ϵ gives rise to a Debye-Waller-like T dependence of the intensity of the stripe order, i.e., $I\sim e^{-2T/T_0}$ for $T_L<T<T_{CO}$, as depicted in the insets of Figs. 2(a) and 2(d). On the analogy of the Debye-Waller factor, one can interpret that such T dependence indicates the existence of strong fluctuations in the charge stripe order, being consistent with the continuous change of n_{st} as well as the correlation length of the stripe order. A similar behavior is also observed in the charge order peak as well as the field-induced magnetic order peak in $La_2NiO_{4+\delta}$ with $\delta=2/15$.[3,11]

The variation of n_{st} also affects the transport property in the nickelate system. When $n_{st}\neq 1$, it indicates that charge stripes and AFM spin domains become doped insulators. In our previous study,[6] we found that $n_{st}<1$ for $n_h<1/3$ whereas $n_{st}>1$ for $n_h>1/3$. This means that the character of carriers changes from electronlike to holelike when n_h crosses the value 1/3, as was evidenced by the previous Hall-coefficient study.[10] The doped carriers give rise to a relatively high conductivity in the high-T region. As n_{st} gradu-

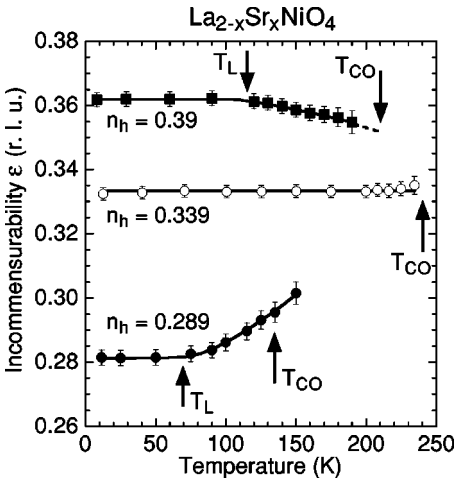

FIG. 3. Temperature dependence of the incommensurability ϵ for $n_h=0.289$ (closed circles), $n_h=0.339$ (open circles), and $n_h=0.39$ (closed squares).

ally becomes unity with lowering T, however, the half-filled stripes segregate within the AF spin-ordered NiO_2 matrix and the conductivity is continuously reduced. This picture explains well the fact that the resistivity of the nickelate system does not exhibit a steep upturn at T_{CO} but rather shows crossover behavior except for the $n_h=1/3$ sample.[10,12]

From the results observed in the present study and discussions presented above, we conclude that the distance of stripes and the incommensurability ϵ are determined by two competing effects: the commensurability effect, which favors $\epsilon=1/3$, and the AF spin correlation, which favors $\epsilon=n_h$. The former is important just below T_{CO} while the latter becomes dominant as the AF spin correlation develops. This competition leads to three distinct T regions that can be identified in the ordering process of charge/spin stripe order as indicated by vertical dashed lines in Fig. 2: (i) a disordered stripe with no static order for $T>T_{CO}$, (ii) a fluctuating charge/spin stripe order with a continuous shift of ϵ for $T_L<T<T_{CO}$, and (iii) a frozen quasi-long-range charge/spin stripe order with fractional ϵ below T_L. Right below T_{CO}, ϵ shows a tendency of having a value close to 1/3 for the samples with x at both sides of 1/3 due to the commensurability effect for $\epsilon=1/3$. This effect takes place at the expense of a deviation of the stripe carrier density n_{st} from unity. With decreasing T, however, AF spin correlations favor half-filled stripes to gain the exchange energy. Consequently, ϵ becomes close to the value determined by the linear relation of $\epsilon=n_h$, and n_{st} recovers the value of the half-doping, namely, $n_{st}\sim 1$. The competition of aforementioned two effects is responsible for the temperature and hole-concentration dependences of the character of the stripe order shown in the present study as well as in Refs. 6,10 and 12 through the change of the amount of the excess carriers.

In contrast, when $n_h=1/3$, the above two effects complement each other and ϵ is locked at 1/3 with the whole T range below T_{CO} as shown in Fig. 3. This makes the transition of the stripe order for $n_h=1/3$ sharp: the intensity of the charge order peak does not show the Debye-Waller-like behavior (not shown); the resistivity shows a distinct step at T_{CO} (Refs. 10,12 and 13); and a clear charge gap is formed below T_{CO}.[13,14]

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