Commensurate-Incommensurate Crossover of Charge Stripe in $La_{2-x}Sr_xNiO_4$ ($x \sim 1/3$)

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The temperature (T) dependence of the charge-stripe order in $La_{2-x}Sr_xNiO_4$ has been investigated in the vicinity of $x \sim 1/3$ by synchrotron radiation x-ray diffraction measurements. With decreasing T, a prominent commensurate-incommensurate (C-IC) crossover is observed in the $x < 1/3$ region, while for the $x > 1/3$ region the IC order is dominant over the whole T range. Such a C-IC crossover is interpreted as the entropy-driven self-doping of the charge stripes, and its x dependence indicates the clear electron-hole asymmetry with the $x = 1/3$ compound as the Mott insulator.

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Throughout the decade, complex spin-charge-orbital ordering phenomena in a wide range of materials have been an important topic in physics of correlated electron systems [1]. The stripe order is one of the most well-known examples, where doped holes (or electrons) align themselves in one dimension to form a charge stripe that acts as a domain wall of antiferromagnetic (AFM) domains. Incommensurate (IC) superstructures indicative of such stripe orders have been experimentally observed in several materials with the K_2NiF_4-type (layered perovskite) structure, such as the high-T_c superconducting $(La, Nd)_{2-x}Sr_xCuO_4$ [2] and orbital-ordered $Nd_{1-x}Sr_{1+x}MnO_4$ [3]. Among them, the layered nickelate $La_{2-x}Sr_xNiO_4$ (LSNO) is a prototypical system to show a firm spin-charge stripe order, which is known to occur over a wide hole concentration region, likely up to $x \sim 0.7$ [4–8]. In the relatively low-doped region ($x < 1/2$), the stripe order is characterized by a set of modulation vectors for charge and spin along the diagonal direction of the tetragonal NiO_2 sheet, which are given as $\vec{q}_c = (\epsilon\epsilon)$ and $\vec{q}_s = (\frac{1-\epsilon}{2}\frac{1-\epsilon}{2})$, respectively. The incommensurability ϵ, which corresponds to the inverse of the hole-stripe period, continuously varies with hole doping while holding the relation that $\epsilon \sim x$. Such an x dependence of a stripe order period is what is expected theoretically [9] and is also similarly observed in the cuprates and manganites mentioned above.

In LSNO, the stripe order is significantly stabilized at $x = \epsilon = 1/3$. In fact, the transition temperature (T_{co}) of the quasi-long-range charge ordering is maximized ($T_{co} \sim 240$ K) at $x = 1/3$ [7]. Around this fixed point of the spin-charge stripe order, various kinds of experiments have been extensively carried out so far. The measurements of resistivity [10,11] and sound velocity [12] showed the clearest anomalies at $x = 1/3$. The optical gap (Δ), which evolves below T_{co} as the order parameter, also takes the maximum at $x = 1/3$ with $\Delta \sim 0.26$ eV [11,13]. The Hall and Seebeck coefficients below T_{co}, on the other hand, change their sign from negative to positive when x traverses 1/3 [11]. These results indicate that the deviation of x from 1/3 can be regarded as an electronlike ($x < 1/3$) or holelike ($x > 1/3$) carrier doping into the $\epsilon = 1/3$ charge-ordered insulator. At the vicinity of such a prominent fixed point, recent diffraction studies [6,14,15] reported the T dependence of ϵ, which showed a tendency to approach 1/3 as increasing T. In the present Letter, we have performed the synchrotron radiation x-ray diffraction experiments to investigate such a commensurate-incommensurate (C-IC) crossover, using nine single crystals in total whose Sr concentrations are finely varied covering both the *under* and *overdoped* regions around $x = 1/3$. From such detailed measurements, it has become clear that there is a striking asymmetry of the C-IC crossover between the under and overdoped regions. To elucidate a possible origin of the C-IC crossover, we propose here a simple model that takes account of the variable band filling (doping) in the stripe, and we discuss the "electron-hole asymmetry" at around the $x = 1/3$ commensurate insulator.

Single crystals of LSNO with varying Sr content ($x =$ 0.25, 0.27, 0.29, 0.31, 0.33, 0.333, 0.35, 0.39, and 0.45) were grown by a floating-zone method as described elsewhere [11,16]. Throughout this Letter, we use the tetragonal ($I4/mmm$) unit cell notation ($a \approx b \approx 3.8$ Å, $c \approx 12.8$ Å) to describe the results of the diffraction study. The synchrotron x-ray diffraction measurements were carried out using a six-axis spectrometer at the BL-4C in Photon Factory, KEK, Japan. The incident x-ray energy was mostly tuned at $E_i = 13$ keV.

Figure 1 shows the temperature (T) dependence of the superlattice peak profiles for $x = 0.31$, 0.333, and 0.35. The peak corresponds to the reflection at $(2 - \epsilon\ 2 - \epsilon\ 1)$

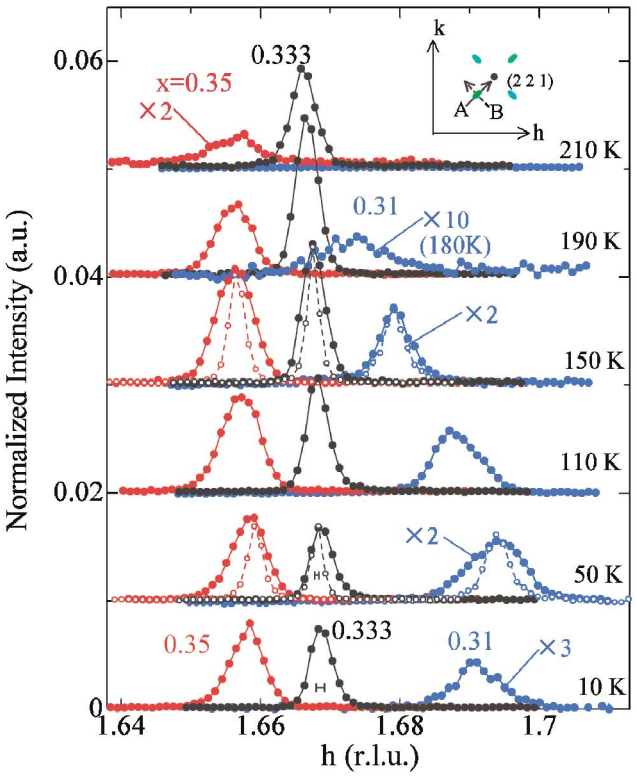

FIG. 1 (color). Superlattice peak profiles at $(2-\epsilon\ 2-\epsilon\ 1)$ due to the formation of the charge stripe order in $La_{2-x}Sr_xNiO_4$. The curves with solid (open) circles correspond to the profiles for the A (B) scan, as shown in the inset [the reciprocal $(h\,k\,1)$ plane]. The resolution limits for the A and B scans are indicated at 10 and 50 K profiles, respectively.

due to the charge-stripe order. The curves depicted with solid and open circles are the profiles of $(h\,h\,1)$ and $(h\ 4-2\epsilon-h\ 1)$ scan, respectively, as shown in the inset of Fig. 1 as A and B scans. Each of them reflects the correlation in real space along the perpendicular or parallel direction to the charge stripe. The sharpest and most symmetric profile is observed for $x = 0.333$ (black curve), indicating the special stability of the $\epsilon = 1/3$ stripe order. The resolution limits for the A and B scans are 0.0021 and 0.0010 $Å^{-1}$, as each of them show at the 10 K and 50 K profiles of $x = 0.333$, respectively. The correlation lengths for the direction perpendicular and parallel to the stripe are $\xi_\perp \sim 300$ Å and $\xi_\parallel \sim 460$ Å, for $x = 0.333$ at 10 K. These values are close to the results of preceding neutron and x-ray diffraction studies [7,17,18]. The T dependence of the peak position reflects that of the stripe incommensurability ϵ, or the inverse of the stripe period. For $x = 0.333$ and 0.35, the peak positions are nearly T independent with $\epsilon \sim 0.333$ and 0.342, respectively. For $x = 0.31$, by contrast, the peak position strongly depends on T; ϵ moves from $\sim$0.325 at 180 K to $\sim$0.305 at 50 K. In other words, the stripe order for $x = 0.31$ tends to take the form of $\epsilon = 1/3$ pattern, rather than the $\epsilon \sim x$ IC stripe, when T is increased.

To see such a C-IC crossover in a wider x region, the T dependencies of the incommensurability are plotted in Fig. 2 for all the samples. The curve with open circles is the result of the previous neutron diffraction measurement [14]. All the other data were obtained by the x-ray diffraction in the same condition, except for $x = 0.33$ which was measured using the $E_i = 8.3$ keV x ray. At the first glance, striking asymmetry is recognized between the over $(x > 1/3)$ and the underdoped $(x < 1/3)$ region. In the underdoped region, the crossover of the incommensurability from $\epsilon \sim 1/3$ to $\epsilon \sim x$ as lowering T is commonly observed. By further decreasing T below 50 K, the slight recovery of ϵ toward $\epsilon = 1/3$ is also discerned, especially at the vicinity of $x = 1/3$. For $x = 1/3$ and in the overdoped region, by contrast, the T dependence of ϵ is very little. The origin of such a C-IC crossover is attributed to the robustness of the $\epsilon = 1/3$ C stripe order. When $x \neq 1/3$, the excess holes or electrons may be introduced into the $\epsilon = 1/3$ C stripe, giving rise to excess entropy. At the ground state, however, the half-filled stripe order is rather favored, which satisfies $\epsilon \sim x$. The competition between these two effects may give rise to the T dependence of the incommensurability on the C-IC crossover.

Based on this idea, we propose a simple model that can account semiquantitatively for the C-IC crossover. For simplicity, we here assume that holes reside on Ni sites and the valence of Ni ions to be exclusively +2 or +3, taking the $U \gg k_BT$ limit (U represents effective on site Coulomb potential). First, let us describe the underdoped $(x < 1/3)$ case. Here we use p for hole concentration in the analysis to discriminate it from the nominal Sr content x for each sample. We define δ as the concentration of the electrons doped into hole stripes (Ni^{3+}), which are schematically shown in Fig. 3(a) as the encircled sites. The incommensurability of the stripe can be written as $\epsilon = p + \delta$. Now we consider the entropy of the charge configuration per Ni, s, which arises from the degree of

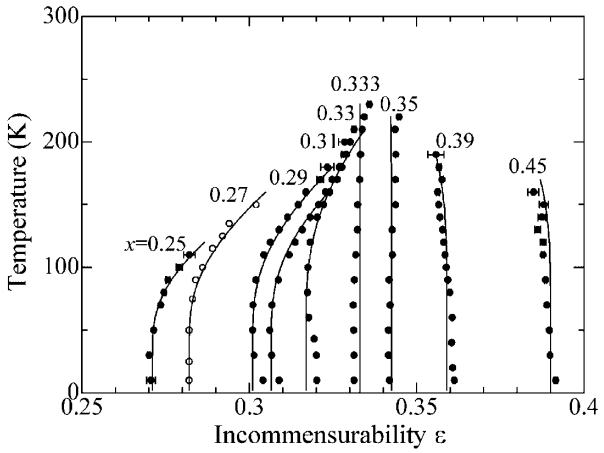

FIG. 2. Temperature dependencies of the incommensurability ϵ of the stripe order for $La_{2-x}Sr_xNiO_4$ $(0.25 \leq x \leq 0.45)$. The curves are the results of fitting (see the text).

freedom of the doped electrons on hole stripes. In the $t \ll k_B T$ limit (t represents transfer energy),

$$s = S/N = (k_B/N)\ln({}_{\epsilon N}\mathrm{C}_{\delta N}) \approx k_B[\epsilon \ln\epsilon - (\epsilon - p)\ln(\epsilon - p) - p \ln p].$$

Here S is the total entropy for the N-site system. If we simply neglect the Coulombic interaction among the charge stripes, the energy term per Ni depends solely on δ as $e = E_g\delta = E_g(\epsilon - p)$. Here E_g is the energy required to dope an electron onto a hole stripe. Thus the solution to minimize the free energy $f = e - Ts$ is deduced as below:

$$\epsilon_{\mathrm{under}} = \frac{p}{1 - \exp(-E_g/k_B T)}.$$

For the overdoped case, by contrast, the excess holes reside on the AFM domain [see Fig. 3(b)]. Thus, there is some difference in the entropy term which comes from the degree of freedom of excess holes in the AFM domain. With E_g, the energy required for hole doping in this case, the $\epsilon(T)$ for the overdoped region is given as

$$\epsilon_{\mathrm{over}} = \frac{p - \exp(-E_g/k_B T)}{1 - \exp(-E_g/k_B T)}.$$

Using these solutions of $\epsilon(T)$, the results of fitting for the respective curves are plotted in Fig. 2. There are only two parameters, p and E_g, in the fitting procedure, with which most of the ϵ-T curves are quite well reproduced. The hole concentration p is taken to be the saturated value of ϵ at low T. On the other hand, E_g, the energy required for doping an electron or a hole into the half-filled stripe state, is responsible for the T scale ($\sim E_g/5k_B$) of the C-IC crossover. Incidentally, ϵ shows a slight turn back for $0.29 \leq x \leq 0.33$ without any locking behavior, which is beyond the present simplified model. Since such a turn back shows up below 50 K, it may be related to the change of the magnetic state previously observed by a polarized neutron diffraction study [19], yet remains to be elucidated in the future study.

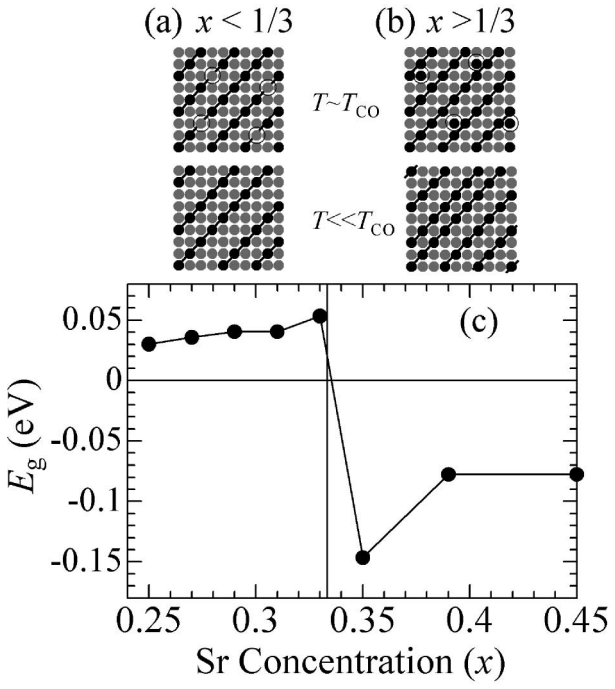

FIG. 3. (a) and (b) show the schematics for the microscopic process of the temperature-induced crossover for the $x < 1/3$ and $x > 1/3$ regions, respectively. Open circles denote the self-doped electrons and holes. (c) shows the x dependence of E_g, the energy required for doping an electron ($x < 1/3$) and a hole ($x > 1/3$) into the half-filled stripe state and into the AFM domain region off the stripe, respectively, obtained by the fitting analysis. Its sign is taken to be positive for electron doping.

Summarizing the model, the C-IC crossover is ascribed to the self-doping effect of the stripe across the energy gap E_g, which appears at high T because of the entropy term. Since there is no large difference in the entropy term for electron and hole doping, E_g is expected to govern the asymmetry of the C-IC crossover around $\epsilon \approx p \approx x \approx 1/3$. The x dependence of E_g, as obtained in the fitting procedure for Fig. 2, is plotted in Fig. 3(c). The sign of E_g is taken to be positive for electrons. For the $x < 1/3$ region, $|E_g|$ is at most $\sim$0.053 eV ($x = 0.33$). For $x = 0.35$, however, a larger value such as $|E_g| > 0.15$ eV is necessary to produce the observed T-independent behavior of ϵ for the whole T region below T_{co}. Thus, the experimental result indicates that the energy cost for hole doping is nearly 3 times as large as that for electron-doping. The jump of E_g at $x = 1/3$, which is equivalent to the energy cost for taking an electron out of the domain and placing it onto a hole stripe, can be considered as a minimum charge gap of the $x = \epsilon = 1/3$ charge-ordered state. From the result shown in Fig. 3(c), the approximate energy jump is estimated to be $E_g(0.33) - E_g(0.35) \gtrsim 0.21$ eV. This is well in accord with the optical gap energy as reported, $\Delta \sim 0.26$ eV [13].

Now let us go back to the superlattice peak profiles depicted in Fig. 1. For 150 and 50 K, the both profiles for the A and B scans are shown. The A scan profiles are broader and more asymmetrically distorted than the B scan profiles, even when the resolution limits are properly taken into account. The line shape for the B scan profile is nearly symmetric and well fitted with a single Gaussian peak. It indicates that the charge stripe is better ordered along its running direction. To discuss the T dependence in detail, the full widths at half maxima (FWHMs) of the superlattice peaks for various samples, $\kappa_\perp$ (A scan) and $\kappa_\parallel$, are plotted in Fig. 4. The resolution function, for which we used the Bragg reflection at (1 1 2), was deconvoluted using Gaussian approximation. As for $\kappa_\parallel$, T dependence is not clearly observed, except for the thermal broadening at high T near T_{co}. By contrast, $\kappa_\perp$ shows a distinct broadening behavior as lowering T, especially in the slightly underdoped region ($x = 0.33$ and 0.31). Such a T-dependent anisotropic broadening is not observed at all for $x = 0.333$, indicating it cannot be

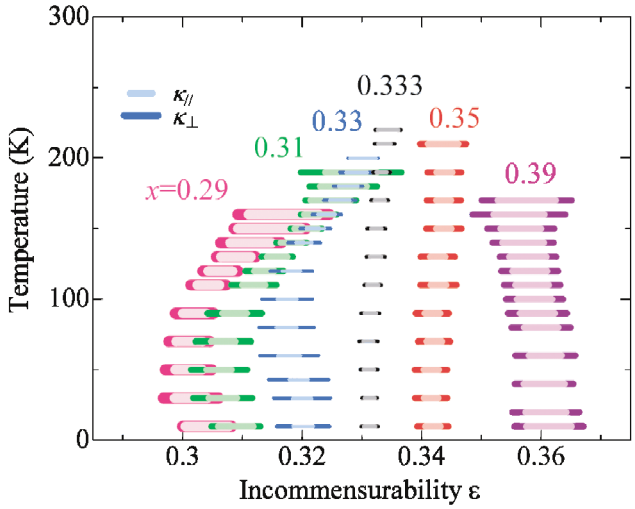

FIG. 4 (color). Full width at half maximum for each superlattice peak as a function of temperature for various x around $x = 1/3$ in $La_{2-x}Sr_xNiO_4$. $\kappa_\perp$ and $\kappa_\parallel$ represent the FWHMs along the A and B scans (see the inset of Fig. 1), respectively.

solely ascribed to the distribution of ϵ induced by some mesoscopic Sr inhomogeneity in the crystals. It is worth noting that similar phenomena are also observed in such C-IC transitions as in helical magnets [20] and modulated ferroelectric materials with impurities [21]. When the deviation of ϵ from the C state is small enough in the course of the C-IC crossover, we may consider the situation where the discommensuration line (DCL) is present and possibly ordered with a small wave vector $\delta\epsilon$ $(= 1/3 - \epsilon)$ in the DCL-vacuum $(\epsilon = 1/3)$ state. In the $x \lesssim 1/3$ region, the number of the DCL keeps increasing as lowering T from T_{co}. The ordering process of the DCL may thus suffer from the random potential due to the La/Sr alloying, which tends to randomly pin down the DCL. When the inter-DCL interaction is weak enough, for example, in the case of small $\delta\epsilon$, the long-range order of DCL can hardly evolve. We speculate that such a random potential effect on the sparsely populated DCLs is an origin of anomalous broadening of the IC peak in the lower-doped region near $x = 1/3$.

In conclusion, we have performed the synchrotron radiation x-ray diffraction study on $La_{2-x}Sr_xNiO_4$ crystals ($x = 0.25$–0.45) with stripe order. Commensurate-incommensurate (C-IC) crossover of the charge-stripe order is observed with lowering temperature (T) in the $x < 1/3$ region. In $x \gtrsim 1/3$, on the other hand, the crossover is much less distinct. We proposed a simple model considering the entropy-driven electron transfer between the on- and off-stripe regions, which reproduces the observed T- and x-dependent C-IC crossover quite well. The result and its fitting analysis confirm that there is the electron-hole asymmetry at around $x = \epsilon = 1/3$ charge-ordered state that is a commensurate Mott insulator with a well-defined charge gap of ≈ 0.2 eV. The broadening of the in-plane superlattice peaks as lowering T is also observed in the $x < 1/3$ region, which is indicative of a glassy state of the discommensuration lines of the stripe due to the pinning effect.

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[16] The deviation of the Sr concentration from the prescription was estimated by the inductively coupled plasma atomic emission spectroscopy measurement to be $\Delta x \lesssim 0.01$. Since the observed stripe incommensurability ϵ at low temperature for every sample shows a fairly good correspondence to the ϵ-p diagram reported before [7], the amount of the nonstoichiometric oxygen (δ_{ox}) seems to be not so large as to significantly change the hole concentration $p = x + 2\delta_{ox}$ from x. (The δ_{ox} as estimated by the iodmetric titration analyses [11] was at most 0.01.)
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