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Commensurability effect on the charge ordering of $La_{2-x}Sr_xNiO_4$

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Measurements of Hall coefficients, thermoelectric power, and optical conductivity spectra were done for single crystals of $La_{2-x}Sr_xNiO_4$ ($x=0.27-0.50$) showing prototypical charge ordering. We found that the character of the carriers in the charge-ordered state changes from electronlike to holelike when the hole concentration p crosses 1/3, and that the correlation gap in the optical spectrum for $p=1/3$ is collapsed when p is away from 1/3. These results indicate that the deviation of p from 1/3 can be regarded as electron or hole doping into the commensurate charge-ordered state at $p=1/3$. [S0163-1829(99)50732-7]

Charge ordering is a generic phenomenon for the strongly correlated electron system whose band filling deviates away from integer value. In this state, doped carriers are localized and order periodically (usually accompanied by spin ordering) at low temperature. Recent studies on transition metal oxides have shown a variety of examples of charge ordering for two-dimensional (2D) nickelates (with K_2NiF_4 structure),[1–5] 2D and 3D (perovskite) manganites,[6–8] and perovskite ferrates.[9] Among them, $La_{2-x}Sr_xNiO_4$ is a prototypical example of charge ordering. In this compound, charge and spin ordering occurs over a wide hole-concentration (p) range ($0<p\leqslant 0.5$), and the wave vectors of the charge ordering, $(\pm\epsilon,\pm\epsilon)$, and spin ordering, $(\frac{1}{2}\pm\epsilon/2,\frac{1}{2}\pm\epsilon/2)$, vary continuously with p, almost following the trend that $\epsilon\sim p$.[1–4] These results suggest a picture in which doped holes in this 2D nickelate line up along the diagonal direction of the Ni square lattice, and the period of these ''charge stripes'' varies continuously in accordance with the hole concentration.[5] It should be noted that similar variations of the charge-stripes period with carrier concentration are also observed in perovskite manganites,[7] and that several theoretical studies[10,11] can reproduce this phenomenon and the relation of $\epsilon=p$.

Concerning such charge ordering over a wide carrier-concentration range, it is an interesting issue whether the commensurability effect exists for a specific carrier concentration. In fact, a previous study[12] reported an anomaly at $p=1/3$, where the resistivity jumps most clearly at the transition temperature of the charge ordering (T_{co}), compared with other hole concentrations. This suggests the importance of the commensurate vs incommensurate issue in the charge and spin ordering of 2D nickelates. In this paper, we demonstrate that $p=1/3$ is a special hole concentration for this system and transport properties and electronic structures are critically affected by the deviation of the hole concentration from this value. We propose a picture in which the commensurate charge-ordered state for $p=1/3$ is analogous to a Mott insulator, and the deviation from $p=1/3$ ($p>1/3$ or $p<1/3$) can be regarded as hole or electron doping, respectively, into such a Mott insulator.

All the samples studied in this work are single crystals grown by a floating-zone method. Taking account of the oxygen of stoichiometry (δ) in the samples, we determined the hole concentration ($p=x+2\delta$) of each sample by the iodometric analysis, and the determined values of p are as follows: $p(x)=0.289$ (0.27), 0.301 (0.30), 0.332 (0.33), 0.353 (0.36), 0.398 (0.39), and 0.502 (0.50). The results thus indicate only a minor amount of of stoichiometry in the grown crystal. For the Hall-coefficient and thermoelectric-power measurements, we cut the samples into a rectangular shape (typically $2\times0.2\times4$ mm for the Hall measurement, and $2\times1\times4$ mm for the thermoelectric-power measurement), and made electrical contacts using gold paint cured at 800 °C. Measurements of in-plane Hall coefficients were carried out by applying a magnetic field (7 T) parallel to the c axis (perpendicular to the NiO_2 plane). We checked the linearity of the Hall coefficient against the magnetic field at several temperatures, and found no anomalous part. We also measured the in-plane and out-of-plane thermoelectric power by applying a temperature gradient of ~0.2 K. Reflectivity measurements were carried out over a wide photon energy range between 0.01 and 6 eV and optical conductivity spectra were derived by the Kramers-Kronig transformation.[13] The wave vector of the charge and spin ordering was determined by neutron-scattering measurements, and details are described elsewhere.[2,14]

Figure 1 shows the temperature dependence of the in-plane Hall coefficient (R_H) for $x=0.27$, 0.30, 0.33, 0.36, and 0.39, together with the in-plane resistivity for the same samples in the inset. The resistivity for $x=0.33$ in the inset (the solid line) clearly shows anomaly at 230 K, which corresponds to T_{co} determined by neutron-scattering measurements.[2] A similar anomaly is also observed for $x=0.36$, but it is unclear for other compositions. These results are consistent with previous work on polycrystals.[12] We stress again that all these compounds ($x=0.27-0.39$) undergo charge-ordering transition, and the transition temperatures are between 200 and 230 K, as verified by neutron-scattering measurements.[2]

On the other hand, the Hall coefficient R_H shows characteristic behaviors depending on the hole concentration. R_H at

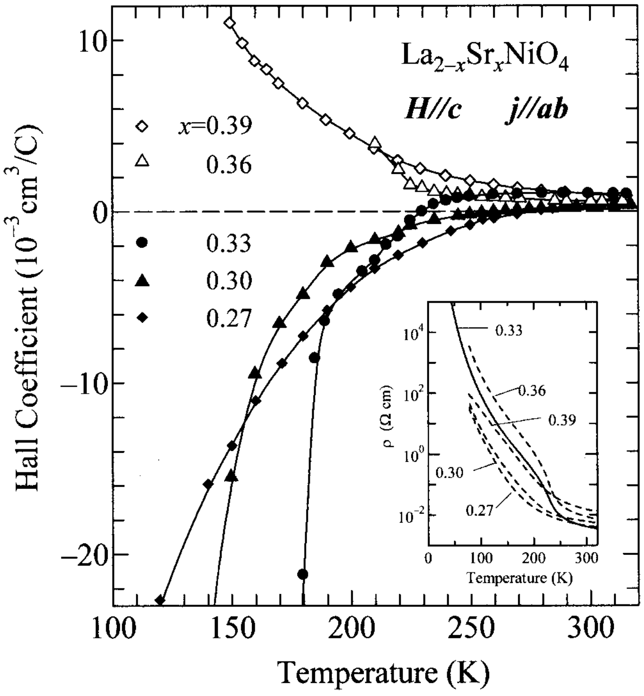

FIG. 1. Temperature dependence of the in-plane Hall coefficient for $La_{2-x}Sr_xNiO_4$ crystals with $x=0.27$, 0.30, 0.33, 0.36, and 0.39. Closed symbols correspond to the hole concentration less than 1/3 whereas open symbols correspond to greater than 1/3. The inset shows the temperature dependence of the in-plane resistivity.

300 K (above T_{co}) has small positive values between 0.2 and 1×10^{-3} cm^3/C for all samples. These values correspond to the order of one carrier per Ni site ($R_H=0.6\times10^{-3}$ cm^3/C in the simplest model). When temperatures are decreased below T_{co}, however, R_H decreases down to large negative values for $x=0.27,30,33$, whereas it increases up to large positive values for $x=0.36$ and 0.39. We measured R_H at lower temperatures for $x=0.33$ and 0.30, and found that it keeps on decreasing to -100×10^{-3} cm^3/C (which corresponds to less than 0.01 carriers per Ni site) for both samples, though we cannot measure it further because of a poor S/N ratio.

The behavior of the Hall coefficient for $0.27\leqslant x\leqslant0.39$ is summarized in the following way: (i) at $T>T_{co}$, R_H is a small positive value, (ii) at $T<T_{co}$, the absolute value of R_H increases with decreasing temperature, and (iii) the sign of R_H at $T<T_{co}$ is negative for $p<1/3$, whereas it is positive for $p>1/3$. (i) and (ii) can be explained by a simple picture in which the compound is metallic and has a large Fermi surface above T_{co},[15] whereas the charge gap opens up below T_{co} and the number of carriers is reduced. Similar behaviors were observed in some charge-density-wave (CDW) systems.[16] However, the systematic sign change in R_H with hole concentration p across 1/3 is unusual in the present system.

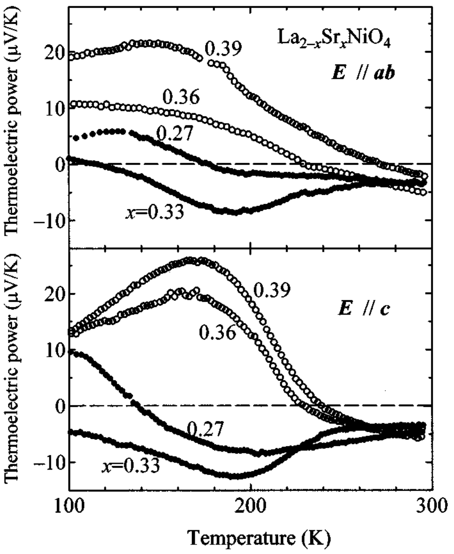

FIG. 2. Temperature dependence of the in-plane (upper panel) and out-of-plane (lower panel) thermoelectric power for $La_{2-x}Sr_xNiO_4$ crystals with $x=0.27$, 0.33, 0.36, and 0.39.

A similar implication for the sign change of carriers is also obtained by the measurement of thermoelectric power S, as shown in Fig. 2. At room temperature, S is of the order of ~-5 μV/K for $x=0.27-0.39$, both within the plane (upper panel) and perpendicular to the plane (lower panel). Such a small absolute value is typical of a metal. With decreasing temperature below T_{co}, however, S shifts in the negative direction for $x<1/3$ and in the positive direction for $x>1/3$, for both in-plane and out-of-plane components. S has the maximum or minimum at a certain temperature and comes back to zero with further reducing temperature. This maximum or minimum seems to relate to the spin-ordering temperature, where the spin entropy (and thermoelectric power, as a result) is suppressed. Despite the existence of a maximum or minimum in S with temperature, which is missing in R_H, and the difference of the sign above T_{co} between R_H and S, overall p-dependent features and temperature dependence look very similar in these two values. This indicates that the change of the sign apparently comes from the change of the character of the carriers, i.e., from electronlike to holelike carriers when p crosses the 1/3 point.

As a summary of the Hall-coefficient and thermoelectric-power measurements, in Fig. 3 are plotted the R_H (circles) and S (triangles) values for the in-plane direction at 300 K ($>T_{co}$, open symbols) and 210 K ($<T_{co}$, closed symbols) against the hole concentration p. The values at 300 K are almost independent of p for both R_H and S, indicating that the electronic structure above T_{co} does not change very much for the p range of 0.27 – 0.50.[17] On the other hand, both R_H and S values at 210 K clearly show different signs for $p<1/3$ (negative) and $p>1/3$ (positive), and the absolute values are larger than those at 300 K. Therefore, the charge ordering induces the change from the high-temperature phase with a large number of carriers to the low-temperature phase with a small number of electronlike ($p<1/3$) or holelike ($p>1/3$) carriers.

For the charge-ordering state with $\epsilon=1/3$, there are three Ni sites in the unit cell. Thus, when $p=1/3$, there is one hole per unit cell, and this state is a sort of half-filled state. Half-filled states can be insulating by electron correlation, and in fact, the charge gap (Hubbard gap) for $p=1/3$ was clearly demonstrated by the previous optical measurement.[13] If ϵ is exactly the same as p, the system remains half-filled and the charge gap would not be changed against the deviation of p

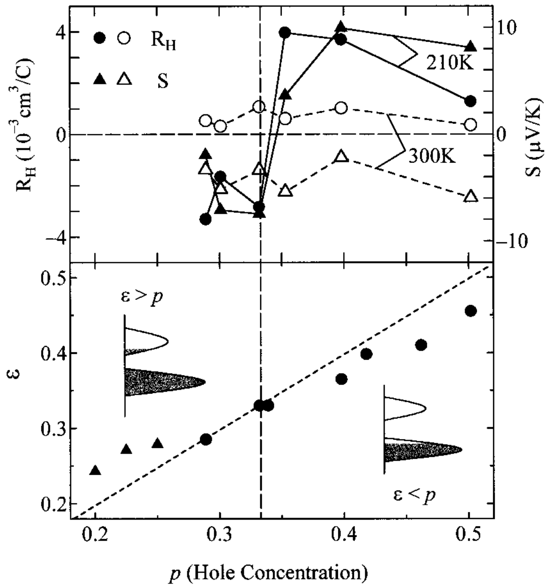

FIG. 3. Upper panel: Hole-concentration (p) dependence of Hall coefficient (R_H, circles) and thermoelectric power (S, triangles) at 300 K ($>T_{co}$, open symbols) and at 210 K ($<T_{co}$, closed symbols). Lower panel: p dependence of the wave vector (ϵ) of the charge ordering in $La_{2-x}Sr_xNiO_4$ (closed circles and triangles are from Refs. 2 and 4, respectively).

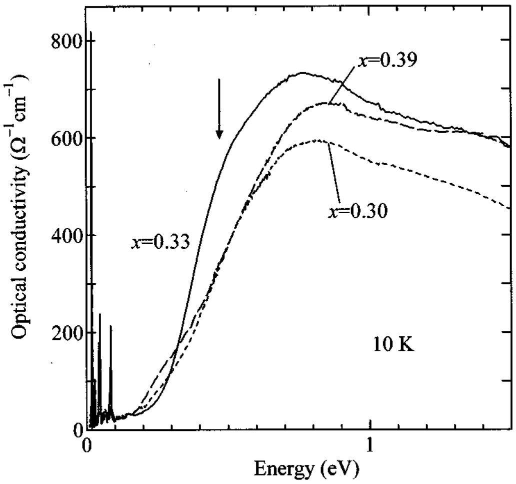

FIG. 4. Optical conductivity spectra at 10 K for $x=0.30$ (dotted line), 0.33 (solid line), and 0.39 (dashed line).

from 1/3. However, if one carefully looks at the p-ϵ relation shown in the lower panel of Fig. 3, where ϵ was determined by the neutron-scattering measurements,[2,14] one can see the tendency of $\epsilon>p$ for $p<1/3$ and $\epsilon<p$ for $p>1/3$. This means that ϵ is exactly 1/3 when p is 1/3, but if p deviates from 1/3, ϵ does not shift so much as to follow the change of p but tends to stick to 1/3.[19] As a result, when p is less than 1/3, the number of holes are deficient for filling up the Hubbard-split band and additional electrons are introduced in the conduction (upper Hubbard) band (as shown in the lower panel of Fig. 3), and vice versa when p is greater than 1/3. This model explains why the sign for R_H and S changes when x goes across 1/3. In other words, the deviation of p from 1/3 acts as electron or hole doping into the commensurate charge-ordered state at $p=1/3$.

Such a model is also supported by the study of the electronic structures. Figure 4 shows the optical conductivity spectra at 10 K for $x=0.30$, 0.33, and 0.39. For $x=0.33$, there is a clear shoulder at 0.5 eV (shown by the arrow) and a gap feature below 0.25 eV, which were reported previously.[13] For $x=0.30$ and 0.39, however, the shoulder becomes unclear and the intensity in the lower-energy region (<0.3 eV) increases compared with $x=0.33$. These results clearly demonstrate the anomaly in the electronic structure at $p=1/3$. The change of the spectra associated with the deviation of p from 1/3 is similar to the case of doped Mott insulators. In $R_{1-x}Ca_xTiO_3$,[18] for example, the gap structure existing in the undoped compound collapses and the in-gap state evolves with doping. In this analogy, the 0.5 eV shoulder for $x=1/3$ corresponds to the excitation between the Hubbard-split band of the commensurate charge ordering, but such a feature collapses with the deviation of p from 1/3 in either direction. It should be noted that hole doping and electron doping has a similar effect on the change of optical conductivity spectra as demonstrated in the case of cuprates,[20] and this is also consistent with the similarity of the spectra between $x=0.30$ (electron doping) and 0.39 (hole doping) in the present compounds.

It becomes clear so far that charge ordering in $La_{2-x}Sr_xNiO_4$ tends to be commensurate ($\epsilon=1/3$), and the deviation of p from 1/3 can be regarded as electron or hole doping to the commensurate charge ordering with $\epsilon=1/3$. It is not self-evident why ϵ tends to be locked at such a specific commensurate value as $p=1/3$, and not at 1/4 or 1/2. It should be noticed, however, that the wave vector of the charge ordering, $(\pm\epsilon,\pm\epsilon)$, coincides with that of the spin ordering, $(\frac{1}{2}\pm\epsilon/2,\frac{1}{2}\pm\epsilon/2)$, only when $\epsilon=1/3$. This specific condition, together with the electron-lattice coupling, may further stabilize the charge ordering.

It is interesting to compare the 2D nickelates with other compounds showing similar charge and spin ordering. One is the 2D cuprates showing the so-called 1/8 anomaly. An analogous charge and spin ordering to the 2D nickelate is observed in the neutron-scattering measurement of the 2D cuprates with 1/8 hole concentration,[21] suggesting that the stripe formation is relevant to the 1/8 anomaly. There are several measurements of R_H and S for these compounds. In a single crystal of $La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$,[22] for example, both R_H and S show positive values above the transition temperature for the charge ordering, whereas it decreases down to the negative values below the transition temperature. This seems parallel to the present case of the 2D nickelates for $p<1/3$. However, the hole-concentration dependence of S for $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$,[23] does show a simple sign change across $x=1/8$, which might be due to another structural phase transition occurring in the 2D cuprates. Another example is perovskite manganites and their 2D analogs. In $La_{1-x}Ca_xMnO_3$, for example, charge ordering occurs for $x>0.5$, accompanied by the ordering of e_g orbitals.[7] Because of this orbital ordering, the position of the superlattice peak $(\epsilon,\epsilon,0)$ is given by $\epsilon=\frac{1}{2}(1-x)$ in the pseudocubic setting.[7] In other words, the period of this ordering is governed by the number of e_g electrons $(=1-x)$. However, charge and orbital ordering also occurs in $Pr_{1-x}Ca_xMnO_3$ even for $0.3 \leqslant x \leqslant 0.5$, but ϵ is fixed to the commensurate value for $x = 0.5$ ($\epsilon = 1/4$).[8] This might suggest that 1/2 is special for the manganites just as 1/3 is for the 2D nickelates.

In summary, we have found that the character of the carriers in the charge-ordering phase of $La_{2-x}Sr_xNiO_4$ is changed from electronlike to holelike across $p = 1/3$. We have also found that the correlation gap between the Hubbard-split bands of the commensurate charge ordering for 1/3 is collapsed when p is away from 1/3. These results indicate that the deviation of hole concentration from 1/3, such as $p < 1/3$ or $p > 1/3$, can be regarded as electron or hole doping into the commensurate charge-ordered state at $p = 1/3$, which is analogous to the doping into a Mott insulator.

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[15] The magnitude of resistivity above T_{co} is fairly low ($< 10^{-2}$ cm^{-1}) compared with that below T_{co}, but is still high as a simple metal with a large Fermi surface. For this issue, the formation of small polarons, or fluctuations of charge ordering, are proposed based on optical study (Ref. 13). It should be noted that such a ''dirty'' metal is a generic feature for the compounds showing charge ordering, e.g., perovskite manganites [Y. Okimoto *et al.*, Phys. Rev. B **57**, R9377 (1998)], Fe_3O_4 [S. K. Park *et al.*, *ibid.* **58**, 3717 (1998)], and $La_{1/3}Sr_{2/3}FeO_3$ [T. Ishikawa *et al.*, *ibid.* **58**, R13 326 (1998)].

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