

Optical spectroscopy of the charge-ordering transition in $\text{La}_{1.67}\text{Sr}_{0.33}\text{NiO}_4$

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Optical spectra of a single crystal of $\text{La}_{1.67}\text{Sr}_{0.33}\text{NiO}_4$, which undergoes a charge-ordering transition at $T_{\text{CO}} \sim 240$ K, have been investigated for wide ranges of photon energy (0.008–3 eV) and temperature (10–480 K). The opening of a charge gap as well as change of the gap magnitude (2Δ) with temperature is clearly observed below T_{CO} , with an anomalously large ratio of $2\Delta(T=0)/k_B T_{\text{CO}}$ (~ 13). Conspicuous spectral change with temperature is also observed above T_{CO} over the energy region up to 2 eV, which suggests persistent fluctuation of the charge ordering or formation of small polarons above T_{CO} . [S0163-1829(96)51244-0]

Physical properties of two-dimensional (2D) doped Mott insulators have been a subject of various theoretical and experimental studies because of their relevance to the high- T_c cuprate superconductors. Some of the theoretical studies based on the 2D single-band¹ or two-band Hubbard Hamiltonian² indicate that doped holes tend to order in a stripe, which acts as a domain wall of antiferromagnetic domains. This is a new type of charge and spin ordering driven by the electron-electron interaction, and has experimentally been observed in Ni oxides with the K_2NiF_4 structure. For example, the neutron scattering measurement of $\text{La}_2\text{NiO}_{4.125}$,³ in which the number of holes per Ni site (n_h) is $1/4$, has revealed that holes and spins simultaneously order below 110 K in a pattern consistent with the theories. For $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ with $x=1/3$ ($n_h=1/3$), on the other hand, ordering of the doped holes has been observed by electron diffraction measurement,⁴ and anomalies associated with the charge-ordering transition at ~ 240 K are observed in resistivity, magnetic susceptibility, sound velocity, and specific heat.⁵ In this paper, we clarify the conspicuous change of the electronic structure over a wide energy region in the course of the charge-ordering phase transition in this Ni-oxide system.

Measurement of optical spectra is useful for the investigation of the electronic structures of the compounds with strong electron correlation and their change upon an electronic phase transition, such as a Mott transition,⁶ an antiferromagnetic transition,⁷ or a double-exchange ferromagnetic transition.⁸ We have spectroscopically investigated the charge-ordering transition with use of a single crystal of $\text{La}_{1.67}\text{Sr}_{0.33}\text{NiO}_4$. The spectra below the transition temperature (T_{CO}) clearly show a temperature-dependent evolution of the charge gap, and even those above T_{CO} show an anomalous change with temperature.

For the optical measurement, we have grown a single crystal of $\text{La}_{1.67}\text{Sr}_{0.33}\text{NiO}_4$ by the floating zone method.⁹ The ab plane and ac plane were cut from the crystal ingot, and was polished to the optical flatness with alumina powder. Reflectivity measurements were carried out between 0.008 eV and 40 eV, using a Fourier-transform interferometer (0.008–0.8 eV) and grating spectrometers (0.6–40 eV). Synchrotron radiation at INS-SOR, University of Tokyo, was utilized for the measurements between 6 and 36 eV. Mea-

surements with changing temperature (T) were carried out using a temperature-variable cryostat between 0.008–3 eV. Optical conductivity spectra [$\sigma(\omega)$] were obtained by Kramers-Kronig analysis of the reflectivity data at respective temperatures that were extrapolated with the room-temperature data for the higher-energy region (≥ 3 eV). We also measured the anisotropic dc resistivity of the same sample by the conventional four-probe technique.

Figure 1 shows the T dependence of resistivity in the ab plane ($\mathbf{E} \perp c$) and along the c axis ($\mathbf{E} \parallel c$). Both the ab plane and c axis resistivity show rather sharp increase at 240 K, as indicated by arrows in Fig. 1. We have also found that the magnetic susceptibility slightly drops at the corresponding temperature. According to the studies on the relating polycrystalline samples,^{4,5} these anomalies are due to the charge-ordering transition, where the doped holes order in stripes along the diagonal direction of the Ni square lattice.

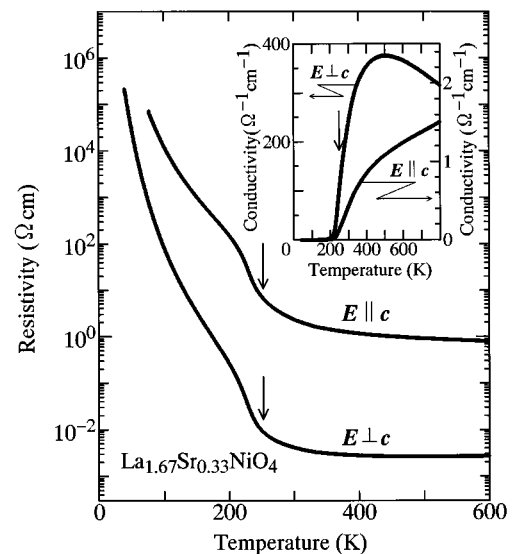


FIG. 1. Temperature dependence of resistivity for a single crystal of $\text{La}_{1.67}\text{Sr}_{0.33}\text{NiO}_4$ within the ab plane ($\mathbf{E} \perp c$) and along the c axis ($\mathbf{E} \parallel c$). Arrows show the transition temperature for charge ordering (T_{CO}) at which resistivity sharply increases and the magnetic susceptibility decreases. The inset shows the inverse of the same data (i.e., conductivity) drawn on a linear scale.

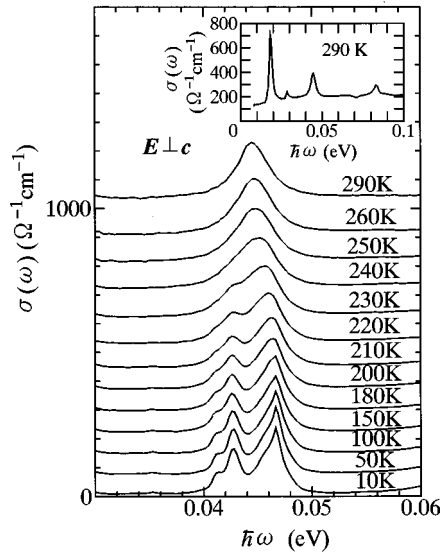


FIG. 2. Temperature dependence of a phonon spectrum around 0.044 eV in the ab plane $\sigma(\omega)$ spectra. The inset shows the overall feature of the phonon spectrum in the ab -plane $\sigma(\omega)$ spectrum at 290 K.

The present resistivity measurement with use of a single crystal has shown that the ratio of the ab plane and c axis resistivity (ρ_c/ρ_{ab}) is ~ 500 at room temperature, which is comparable in size to the value of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.¹⁰ In spite of such a large anisotropy, similar anomalies are observed in both the ab plane and c axis resistivity at T_{CO} , which is consistent with the observation of the charge-ordering correlation along the c axis as well as in the ab plane.⁴ The T dependence of the resistivity for the both directions below T_{CO} is not of the thermal activation type, but follows the variable-range-hopping (VRH) relation, $\rho(T) = \rho_0 \exp(T_0/T)^{1/4}$, below 150 K.¹¹

To see the anisotropic transport property above T_{CO} in more detail, we plot in the inset of Fig. 1 the T dependence of the conductivity (i.e. inversed resistivity) on a linear scale. The ab -plane conductivity ($\mathbf{E} \perp c$) goes through a maximum at $T_{\text{max}} \sim 500$ K, and below T_{max} it decreases with decrease of T even above $T_{\text{CO}} \sim 240$ K. The semiconducting behavior above T_{CO} is accompanied by a gradual change of the electronic structure over a large energy scale, as shown in the following. On the other hand, the c -axis conductivity ($\mathbf{E} \parallel c$) keeps on decreasing with decrease of T at least below 800 K.

The charge-ordering transition at ~ 240 K is also evidenced by the T dependence of optical-phonon structures in the $\sigma(\omega)$ spectra as shown in Fig. 2. $\text{La}_{1.67}\text{Sr}_{0.33}\text{NiO}_4$ has the tetragonal K_2NiF_4 structure with the space group $I4/mmm$ at room temperature,¹¹ in which there should be seven optical-allowed phonon modes; four are the in-plane (E_u) modes, and three the out-of-plane (A_{2u}) ones. In the $\sigma(\omega)$ spectrum for $\mathbf{E} \perp c$ at room temperature, four peaks arising from the four E_u modes can be observed at 0.018 eV, 0.028 eV, 0.044 eV, and 0.083 eV as shown in the inset of Fig. 2. Among them, the 0.044 eV phonon, which is a Ni-O bending mode by the analogy with the phonon assignment of La_2CuO_4 ,¹² appears to split into four peaks below 240 K. The charge ordering gives rise to the formation of a super-

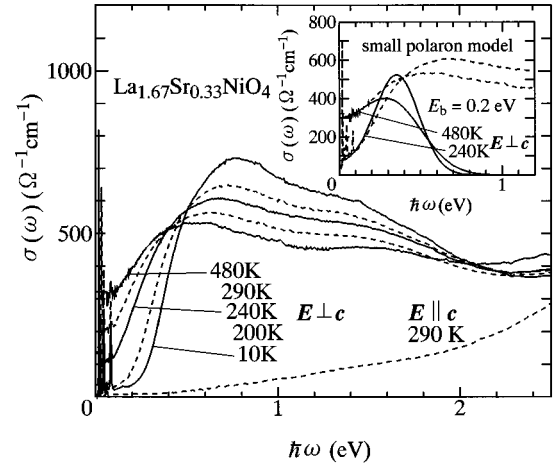


FIG. 3. The $\sigma(\omega)$ spectra of $\text{La}_{1.67}\text{Sr}_{0.33}\text{NiO}_4$ below 2.5 eV for $\mathbf{E} \perp c$ at 480 K, 290 K, 240 K, 200 K, and 10 K, and for $\mathbf{E} \parallel c$ at 290 K. The inset shows the fitting result of the 480-K and 240-K spectra for $\mathbf{E} \perp c$ by a small polaron model (see text).

lattice and lowers the crystal symmetry. The former effect would lead to folding of phonon-dispersion branches and the appearance of new Γ -point modes as in the case of the CDW transition, whereas the latter to lifting of the doubly degenerated E_u phonon modes. The experimentally observed multiplet structure of the optical phonon at low temperature seems consistent with this picture, though the detailed assignment of the split phonon modes is yet to be made.

Figure 3 shows the $\sigma(\omega)$ spectra for $\mathbf{E} \perp c$ (ab -plane spectra) below 2.5 eV at several temperatures. The ab -plane spectrum at 290 K is nearly identical to the one previously reported for the $x=0.30$ crystal by Ido *et al.*⁹ According to Ref. 9, there is little spectral weight below 3 eV in the ab -plane spectrum for $x=0$ (La_2NiO_4), which is a $3d^8$ Mott insulator, whereas the spectral weight is induced in the inner-gap region by hole doping (x). We also plot the $\sigma(\omega)$ spectrum for $\mathbf{E} \parallel c$ (the c -axis spectrum) at 290 K by a dashed line. There is much less spectral weight in the c -axis spectrum than in the ab -plane spectrum below 2.5 eV,^{9,13} indicating that the anisotropic electronic structure below 2.5 eV is responsible for the anisotropic charge dynamics of this compound as shown in Fig. 1.

The ab -plane spectrum shows a conspicuous change with T as shown in Fig. 3. At 480 K, which approximately corresponds to the temperature for the maximum conductivity, a broad peak at ~ 0.5 eV is observed together with finite $\omega \rightarrow 0$ conductivity ($\sim 300 \Omega^{-1} \text{cm}^{-1}$), which nearly agrees with the value of dc conductivity at this temperature. However, a Drude-like feature of a metallic state, namely sharp increase of conductivity with decrease of $\hbar\omega$, is not discernible. When T is decreased down to 240 K, which is immediately above T_{CO} , the low-energy spectral weight below 0.4 eV is suppressed and transferred to the higher energy up to 2 eV. In the charge-ordered phase at 10 K, there is little spectral weight below 0.2 eV, indicating that the ground state of this compound is insulating with a finite energy gap, and the missing spectral weight is also distributed over the higher energy region up to ~ 2 eV.

At first, let us focus on the behavior below $T_{\text{CO}} \sim 240$ K. The magnified $\sigma(\omega)$ spectra below 0.6 eV are shown in Fig.

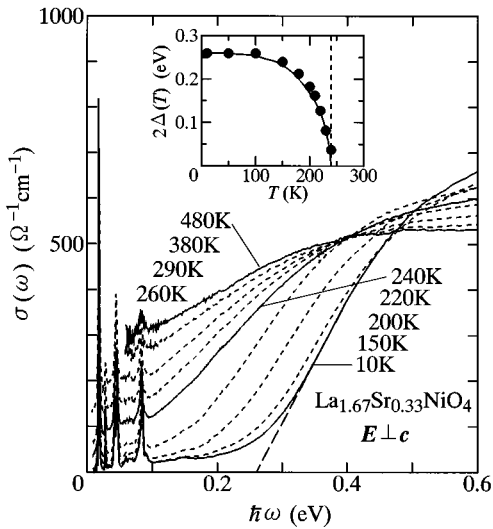


FIG. 4. The $\sigma(\omega)$ spectra of $\text{La}_{1.67}\text{Sr}_{0.33}\text{NiO}_4$ for $\mathbf{E} \perp c$ below 0.6 eV at various temperatures. The inset shows the temperature dependence of the magnitude of the energy gap estimated from the spectra. The solid line represents the BCS function.

4 at various temperatures. The $\sigma(\omega)$ spectrum at 10 K shows an onset of increase at 0.2–0.3 eV. We have estimated the magnitude of the charge gap (2Δ) by extrapolating the increasing part linearly to the base line of $\sigma(\omega) = 0$, as shown by the dashed line for the 10 K spectrum, and have found that $2\Delta \sim 0.26$ eV at 10 K. Slight residual conductivity inside the energy gap is observable even in the 10 K spectrum. This may arise from remnant charge carriers showing incoherent motion, which are perhaps responsible for the VRH-type behavior of the dc resistivity.

The $\sigma(\omega)$ curves show a nearly parallel shift under variation of T below $T_{\text{CO}} \sim 240$ K, as seen in Fig. 4. The T dependence of the estimated gap magnitude [$2\Delta(T)$] is plotted in the inset of Fig. 4 by closed circles. The energy gap is approximately zero at $T_{\text{CO}} \sim 240$ K, then gradually increases with decrease of T , and is saturated at 0.26 eV. Such a T dependence of 2Δ suggests that the energy gap 2Δ is a relevant order parameter for the charge-ordered phase. One such example is the charge-density-wave (CDW) or spin-density-wave (SDW) transition,¹⁴ where both the amplitude of CDW/SDW and the energy gap shows BCS-like T dependence. The T dependence of the energy gap of the present compound also appears to be in good agreement with the BCS function as shown by the solid line in the inset of Fig. 4. However, the ratio of the energy gap at $T=0$ K [$2\Delta(0)$] to the transition temperature ($k_B T_{\text{CO}}$) is ~ 13 in this compound, which is significantly larger than the theoretical value for the conventional CDW/SDW transition,¹⁴ $2\Delta(0)/k_B T_c \sim 3.5$. Such a large value of $2\Delta(0)/k_B T_{\text{CO}}$ implies that the charge gap in the charge-ordered phase is affected by electron-correlation effect, or otherwise that the T_{CO} is suppressed due to the fluctuation arising from the low dimensionality.

The $\sigma(\omega)$ spectra show considerable T dependence even above T_{CO} , as can be seen in Figs. 3 and 4: The spectral weight below 0.4 eV is transferred to the higher-energy region with decrease of T , forming an isosbetic point at ~ 0.4 eV. This is in contrast to a nearly rigid shift of $\sigma(\omega)$ as

observed below T_{CO} . The spectral weight transfer with change of T above T_{CO} is extended up to 2 eV, which is about two orders of magnitude larger than the corresponding energy scale of temperature. In the following, we argue two possible explanations for the temperature dependence of the $\sigma(\omega)$ spectra above T_{CO} . One is that the doped holes form small polarons above T_{CO} . A previous optical study^{15,16} of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ indicates that the $\sigma(\omega)$ spectra can be fitted with the following functional form for the small polaron,¹⁷

$$\sigma(\omega, T) = \frac{A}{kT(2E_b kT)^{1/2}} \exp(-E_b/2kT) \frac{\sinh(\hbar\omega/2kT)}{\hbar\omega/2kT} \times \exp[-(\hbar\omega)^2/8E_b kT], \quad (1)$$

where E_b corresponds to the polaron binding energy. Note that this functional form is only valid at high temperature ($k_B T \geq \frac{1}{2}\hbar\omega_0$; ω_0 is the phonon frequency). We have attempted the fitting of the present spectra with Eq. (1), where we choose common values of two fitting parameters in Eq. (1), the binding energy E_b ($=0.2$ eV) and the coefficient A , for all the spectra. The results for the 480-K and 240-K spectra are shown in the inset of Fig. 3. The agreement between the experimental and calculated curve is satisfactory below 0.2 eV. However, the calculated curve cannot reproduce the observed spectral change extending up to 2 eV. This disagreement in the high-energy region suggests that electron-electron interaction would play an important role for the formation of small polarons,¹⁸ which is not taken into account in Eq. (1).

Another explanation of the high-temperature behavior is to consider the fluctuation of the charge ordering above T_{CO} . In the case of the quasi-one-dimensional CDW transition,¹⁹ for example, the real transition temperature becomes much lower than the mean-field transition temperature due to the strong fluctuation arising from the low dimensionality. In such a case, the ordering with finite correlation length persists well above the transition temperature, which gives rise to a pseudogap in the density of states. If this is the case for the present compound that is electronically two-dimensional, then we have to consider *fluctuating charged stripes* in the NiO_2 plane. Accordingly, the opening of a pseudogap would be expected above T_{CO} , which would decrease the low-energy conductivity as observed in the present experiment.

In summary, optical conductivity spectra are investigated for a single crystal of $\text{La}_{1.67}\text{Sr}_{0.33}\text{NiO}_4$, which undergoes the charge-ordering transition at 240 K. Splitting of the optical phonon structures is observed below 240 K due to a lattice-structural change upon the charge-ordering transition. Below T_{CO} , opening of a charge gap is observed in the $\sigma(\omega)$ spectrum. The magnitude of a charge gap (2Δ) changes with T following the BCS function, but the $T \rightarrow 0$ K value is significantly large as compared to $k_B T_{\text{CO}}$ [$2\Delta(0)/k_B T_{\text{CO}} \sim 13$]. Spectral changes with T extending up to 2 eV are observed even above T_{CO} , which suggest fluctuating charged stripes or formation of small polarons.

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- ¹D. Poilblanc and T. M. Rice, *Phys. Rev. B* **39**, 9749 (1989); H. J. Shulz, *J. Phys. X* **50**, 2833 (1989); M. Kato, K. Machida, H. Nakanishi, and M. Fujita, *J. Phys. Soc. Jpn.* **59**, 1047 (1990); M. Inui and P. B. Littlewood, *Phys. Rev. B* **44**, 4415 (1991).
- ²J. Zaanen and O. Gunnarsson, *Phys. Rev. B* **40**, 7391 (1989); J. Zaanen and P. B. Littlewood, *ibid.* **50**, 7222 (1994).
- ³J. M. Tranquada, D. J. Butterly, and D. E. Rice, *Phys. Rev. Lett.* **70**, 445 (1993); J. M. Tranquada, J. E. Lorenzo, D. J. Buttrey, and V. Sachan, *Phys. Rev. B* **52**, 3581 (1995).
- ⁴C. H. Chen, S-W. Cheong, and A. S. Cooper, *Phys. Rev. Lett.* **71**, 2461 (1993).
- ⁵S-W. Cheong, H. Y. Hwang, C. H. Chen, B. Batlogg, L. W. Rupp, Jr., and S. A. Carter, *Phys. Rev. B* **49**, 7088 (1994); A. P. Ramirez, P. L. Gammel, S-W. Cheong, D. J. Bishop, and P. Chandra, *Phys. Rev. Lett.* **76**, 447 (1996).
- ⁶G. A. Thomas, D. H. Rapkine, S. A. Carter, A. J. Millis, T. F. Rosenbaum, P. Metcalf, and J. M. Honig, *Phys. Rev. Lett.* **73**, 1529 (1994); T. Katsufuji, Y. Okimoto, and Y. Tokura, *ibid.* **75**, 3497 (1995).
- ⁷T. Katsufuji, Y. Okimoto, T. Arima, Y. Tokura, and J. B. Torrance, *Phys. Rev. B* **51**, 4830 (1995).
- ⁸Y. Okimoto, T. Katsufuji, T. Ishikawa, A. Urushibara, T. Arima, and Y. Tokura, *Phys. Rev. Lett.* **75**, 109 (1995).
- ⁹T. Ido, K. Magoshi, H. Eisaki, and S. Uchida, *Phys. Rev. B* **44**, 12 094 (1991).
- ¹⁰Y. Nakamura and S. Uchida, *Phys. Rev. B* **47**, 8369 (1993).
- ¹¹S. H. Han, M. B. Maple, Z. Fisk, S-W. Cheong, A. S. Cooper, O. Chmaissem, J. D. Sullivan, and M. Marezio, *Phys. Rev. B* **95**, 1347 (1995).
- ¹²R. Feile, *Physica C* **159**, 1 (1989) and references therein.
- ¹³J. M. Bassat, P. Odier, and F. Gervais, *Phys. Rev. B* **35** 7126 (1987).
- ¹⁴A. W. Overhauser, *Phys. Rev.* **128**, 1437 (1962); *ibid.* **167**, 691 (1968).
- ¹⁵X-X. Bi and P. C. Eklund, *Phys. Rev. Lett.* **70**, 2625 (1993).
- ¹⁶D. A. Crandles, T. Timusk, J. D. Garret, and J. E. Greedan, *Physica C* **216**, 94 (1993).
- ¹⁷M. I. Klinger, *Phys. Status Solidi* **11**, 499 (1965); **12**, 765 (1965); H. G. Reik and D. Heese, *J. Phys. Chem. Solids* **28**, 581 (1967).
- ¹⁸According to the theoretical studies on the 2D Hubbard Hamiltonian (Refs. 1 and 2), the holes tend to form small magnetic polarons rather than the charged stripe in the case of sufficiently large electron correlation.
- ¹⁹P. A. Lee, T. M. Rice, and P. W. Anderson, *Phys. Rev. Lett.* **31**, 462 (1973).