

Optical study of the $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ system: Effect of hole doping on the electronic structure of the NiO_2 plane

T. Ido,* K. Magoshi, H. Eisaki, and S. Uchida

Department of Applied Physics, The University of Tokyo, Yayoi, Tokyo 113, Japan

(Received 26 August 1991)

The optical spectra of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ are systematically investigated from the infrared to ultraviolet energy range and over a wide compositional range, $0 \leq x \leq 0.5$. La_2NiO_4 is a charge-transfer (CT) insulator with a CT energy gap of about 4 eV, twice as large as that in the isostructural La_2CuO_4 . Introduction of holes into the NiO_2 plane induces broad absorption in the infrared region below the CT gap energy, similar to the case of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. The induced absorption consists of two distinct bands centered at 0.6 and 1.5 eV. The total spectral weight of the two absorption bands increases proportionately to the dopant concentration x . Notable differences from the cuprates are that these bands do not shift with increasing x and that a Drude-type absorption centered at $\omega=0$ does not appear up to $x=0.5$ in the case of the nickelate. They might arise from different symmetries of the doped holes and/or different spin quantum number of the Ni^{2+} ion.

The $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (La-Sr-Cu-O) system with a K_2NiF_4 -type structure has been studied extensively, because it is a prototypical high-temperature superconductor with $T_c=39$ K at $x=0.15$.¹ The starting compound La_2CuO_4 is a two-dimensional antiferromagnetic insulator with $S=\frac{1}{2}$ (Cu^{2+}). Hole doping by substitution of divalent Sr for trivalent La suppresses the antiferromagnetic order and causes an insulator-metal transition at $x\sim 0.05$. Superconductivity simultaneously appears and is observed up to $x\sim 0.25$. An analogous system $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ (La-Sr-Ni-O), which has a similar K_2NiF_4 structure, has also attracted much attention.²⁻⁴ La_2NiO_4 is an antiferromagnetic insulator with $S=1$ (Ni^{2+}),⁵ but in this system the insulating phase persists up to $x\sim 1.0$. The metallic phase, reported to be realized for $x > 1.0$, has so far exhibited no superconductivity. In order to understand the factor(s) crucial for high- T_c superconductivity it would be helpful to study differences and/or similarities in the electronic structure between these two systems.

In this paper, we report the optical spectra of single-crystalline $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ over a wide energy range 0.01–6 eV. We measured optical reflectivity for various Sr contents from $x=0$ to 0.50 with both polarizations, parallel and perpendicular to the NiO_2 planes, $\text{E}\perp c$ and $\text{E}\parallel c$. The present data have revealed the overall features of the effect of hole doping in the La-Sr-Ni-O system more clearly than the previous report.⁶ Furthermore, the comparison with the result of the optical spectra of La-Sr-Cu-O extensively studied by our group⁷ enables us to discuss the difference in the dynamics of holes and/or in the doped hole state between both compounds.

Single-crystalline samples of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ were grown by the floating zone method using a halogen-lamp-image furnace. Polycrystalline rods were prepared by the following processes. The stoichiometric mixtures of La_2O_3 , SrCO_3 , and NiO were ground and calcined three times at 1100°C for 10–30 h each time. The obtained powders were then pressed into rods and sintered at 1450°C for 24 h. The seed crystal (La_2NiO_4) and the polycrystalline rod were rotated in the opposite direction to each

other and zone-melted downward at a rate of 3–6 mm/h in flowing air. The results of electron-probe-microanalysis (EPMA) showed that the Sr contents in the grown crystals are almost identical to the nominal ones. The crystals were cut in the ac plane as checked by the backreflection Laue photographs. A reflectivity measurement was done on this plane with a typical diameter of 5 mm.

It is well known that $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ with low Sr content has a large amount of excess oxygen ($+\delta$).³ To reduce it, the samples with $x=0, 0.1$, and 0.2 were vacuum sealed in a silica tube together with Cu metal powder and annealed at 800°C for 30, 10, and 10 h, respectively. On the other hand, the samples with high Sr content, $x=0.4$ and 0.5 , were annealed in O_2 flow at 1000°C for 10 h to fill the oxygen vacancies. All of the obtained samples show activation-type resistivity with a typical activation energy of 0.1 eV.

Reflectivity data of $\text{E}\parallel c$ and $\text{E}\perp c$ were collected at room temperature using polarized light at near-normal incidence to the ac plane polished by aluminum powder of 0.1- μm particle size. Two spectrometers were used with various detectors and polarizers: a rapid-scanning Michelson interferometer covering 0.01–1 eV and a grating-type monochromator covering 0.5–6 eV. The accuracy of reflectivity in this measurement is less than 2% over the energy range covered here.

Figure 1(a) shows the reflectivity spectra of La-Sr-Ni-O on a logarithmic energy scale for the polarization in the NiO_2 planes ($\text{E}\perp c$). The spectrum of undoped La_2NiO_4 exhibits several peaks in the far-infrared region due to optical phonons and a weak feature at 4 eV. The spectrum of optical phonons is in agreement with previous reports.^{6,8}

On Sr substitution a reflectivity edge suddenly appears at about 1.0 eV. Similar spectral change was observed in La-Sr-Cu-O.⁷ In the case of La-Sr-Ni-O the position of the edge seems to shift to higher energies as the doping proceeds to $x=0.3$, whereas the edge is almost fixed at ~ 1.0 eV in the case of La-Sr-Cu-O. In the far-infrared region the optical phonons are somewhat screened by dop-

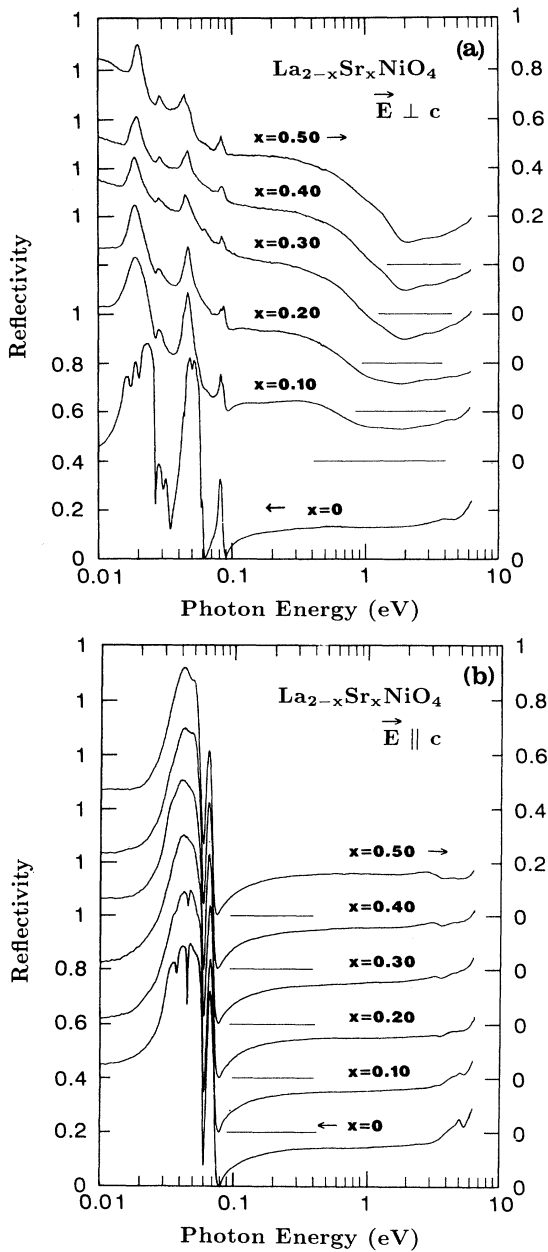


FIG. 1. Reflectivity spectra for various compositions of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ single crystals measured at room temperature (~ 300 K). The incident light was polarized (a) in the NiO_2 plane ($E \perp c$) and (b) along the c axis ($E \parallel c$). Note that the energy is plotted on a logarithmic scale.

ing, but the screening is not complete even at $x=0.5$ unlike the case for La-Sr-Cu-O , where the optical phonons are almost entirely screened for $x > 0.10$.⁷

Figure 1(b) shows the reflectivity spectra of the same set of samples for the light polarization along the c axis ($E \parallel c$). The most significant feature in this polarization is a peak at 5 eV, which is presumably due to the charge-transfer (CT) excitation from so-called apical $\text{O } 2p_\sigma$ to $\text{Ni } 3d_{3z^2-r^2}$ state. Because $\text{Cu } 3d_{3z^2-r^2}$ is filled in cuprates, this absorption is not seen in La_2CuO_4 .⁷ The doping

effect on the optical spectrum is much smaller in $E \parallel c$ than in $E \perp c$. The optical phonons are screened less and the CT excitation persists up to $x=0.5$ though it slightly shifts to lower energies. Such strongly anisotropic spectra were also observed in La-Sr-Cu-O , reflecting two-dimensional electronic structure inherent to the K_2NiF_4 crystal structure.

To make more quantitative the discussion on the infrared absorption of $E \perp c$, the Kramers-Kronig (KK) transformation was carried out on the reflectivity spectrum. In this analysis we assumed a constant reflectivity for $\hbar\omega \leq 0.01$ eV, and extrapolated the spectrum by connecting it with the higher-energy data up to 35 eV measured using synchrotron radiation at the Institute for Solid State Physics, the University of Tokyo.⁹

The KK transformed optical conductivity spectra are shown in Fig. 2 for two representative compositions $x=0$ and 0.3 together with that for La_2CuO_4 for comparison. The 4-eV feature, which corresponds to the optical gap in this polarization, is assigned to the charge-transfer excitation from in-plane $\text{O } 2p$ to the $\text{Ni } 3d$ state. Since the Ni on-site Coulomb repulsive energy is estimated to be 6 eV or larger, La_2NiO_4 can be classified as a CT-type insulator similar to La_2CuO_4 .¹⁰ This means that the band gap is formed between the $\text{Ni } 3d$ and $\text{O } 2p$ bands, not between the Mott-Hubbard split $\text{Ni } 3d$ bands. The CT energy of 4 eV is larger than 2 eV in La_2CuO_4 , but identical to that in NiO .¹¹

Figure 2 indicates that the 4-eV CT peak becomes smeared, whereas an absorption appears on doping. Thus, it is possible that the spectral weight of the infrared absorptions is transferred from the CT excitation as in the case of La-Sr-Cu-O . As will be anticipated in Fig. 3, the amount of the transferred spectral weight is comparable with that in La-Sr-Ni-O . However, the total spectral weight in the infrared region seems too large to be transferred solely from the 4-eV CT excitation in La_2NiO_4 . This is suggestive of the transfer from other excitations in the higher-energy

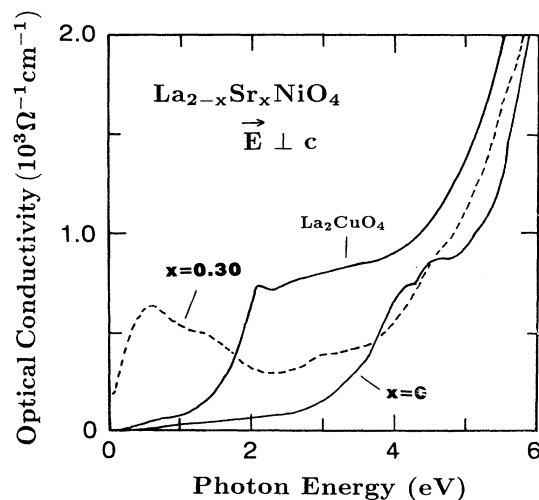


FIG. 2. Optical conductivity spectra ($E \perp c$) of La_2NiO_4 and $\text{La}_{1.7}\text{Sr}_{0.3}\text{NiO}_4$, obtained from the Kramers-Kronig transformation of the reflectivity spectrum in Fig. 1(a). The spectrum of La_2CuO_4 is also shown for comparison.

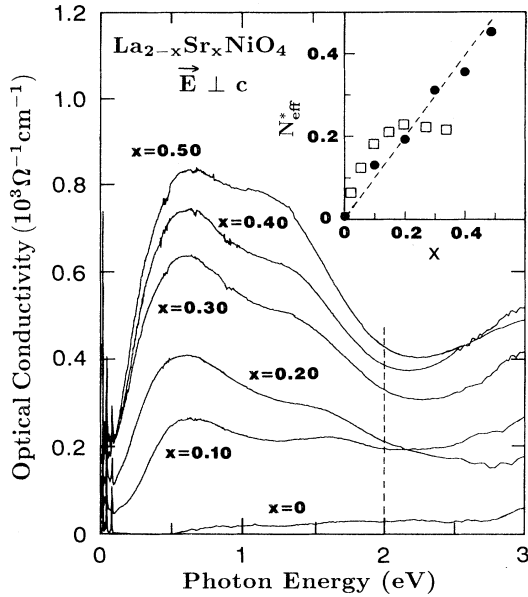


FIG. 3. Optical conductivity spectra ($E \perp c$) below 3 eV for various compositions of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ at room temperature, obtained from the Kramers-Kronig transformation of the reflectivity spectra in Fig. 1(a). The integrated spectral weight of the optical conductivity $N_{\text{eff}}^*(\omega)$ is defined by

$$N_{\text{eff}}^*(\omega) = \frac{2m_0V_{\text{unit cell}}}{\pi e^2} \int_0^\omega \sigma(\omega') d\omega',$$

where $N_{\text{eff}}^*(\omega)$ is normalized per Ni atom, assuming the free-electron mass m_0 . N_{eff}^* (2 eV) in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ (solid circles) and N_{eff}^* (1 eV) in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (open squares) are shown in the inset as a function of Sr content x .

region. Unfortunately, much stronger absorption, assigned to the excitations in the La (Sr) O planes extending over a wide energy range from 3–12 eV,⁹ dominates and overlaps the CT absorption. So the quantitative analysis of the strengths of the CT and higher-energy excitations is difficult in the present case.

Figure 3 demonstrates in more detail how the optical conductivity evolves with x . As Sr concentration increases, two broadbands centered near 0.6 and 1.5 eV grow. A Drude-type absorption expected in metals does not appear even up to the highest Sr content of $x=0.5$, which is in agreement with semiconducting resistivity behavior. It turns out that the reflectivity edge appearing first at 1 eV is associated with the 0.6-eV absorption band, while that at 2 eV for $x \geq 0.3$ arises from both the 0.6- and 1.5-eV absorption bands.

In the case of La-Sr-Cu-O as well as other high- T_c cuprates,^{12–14} a similar broad absorption band is seen with a peak located at energy in the midinfrared region; so it is called “mid-ir absorption.” In our earlier paper⁷ it was clearly demonstrated that the mid-ir absorption shows up by transferring the spectral weight from the CT excitation observed at 2 eV in the undoped compound. In addition, another Drude-type absorption band centered at zero energy also develops. The intensities of both absorptions rapidly increase and simultaneously the center of the

mid-ir absorption shifts toward zero energy. The optical conductivity of La-Sr-Cu-O for $x > 0.10$ shows no well-separated peaks at finite energies; so it appears that the two absorption bands merge into one strong absorption centered at zero energy. This is consistent with the good metallic resistivity observed in the high- T_c compositions. From this result, we suggested that the doping creates a band of states within the CT gap where the quasiparticles move quite itinerantly. The doping-induced ir absorptions which extend to 1 eV or higher seem to indicate a similar change in the electronic structure of the CT insulator La_2NiO_4 , supposedly the formation of the states within the CT gap.

There should be a great difference in the character of the “mid-ir absorption,” judging from the fact that the center of the ir absorptions do not go soft with the increase of x and the Drude-type absorption does not develop even at $x=0.5$. Furthermore, the ir absorption in La-Sr-Ni-O has apparently two components peaked at 0.6 and 1.5 eV. The CT energy is related to the energy difference between Ni (Cu) 3d and O 2p orbitals and scales to the degree of hybridization ($\sim t_{pd}^2/\Delta^2$, t_{pd} being the transfer integral between 3d and 2p) between these orbitals. The difference in the CT energy, 4 eV in La_2NiO_4 and 2 eV in La_2CuO_4 , would then indicate the different degree of the d - p hybridization between the two systems. This might account, to some extent, for the fact that the doped charges are less itinerant and the insulating phase persists to much higher dopant concentration in La-Sr-Ni-O. However, the observed doping dependence of the spectrum seems essentially different between the two systems to be explained by the difference in the CT energy. It is found in the inset of Fig. 3 that the total strength of the ir absorptions induced by doping increases proportionately to the Sr content x in La-Sr-Ni-O, unlike the case of La-Sr-Cu-O and other cuprates, where the strength of the mid-ir absorption increases much more rapidly with x and saturates at $x \sim 0.2$.

On considering the difference in the doping effect between La-Sr-Ni-O and La-Sr-Cu-O, another important issue is the symmetry of the doped holes in La-Sr-Ni-O. In La_2NiO_4 , two holes reside on the $3d_{x^2-y^2}$ and $3d_{3z^2-r^2}$ orbitals in the Ni^{2+} (d^8) state and they are ferromagnetically coupled to form a high-spin state ($S=1$). A doped hole will be introduced either in e_g ($3d_{x^2-y^2}$ and $3d_{3z^2-r^2}$) and/or their bonding counterparts O $2p_\sigma$ orbital, or in t_{2g} ($3d_{xy}$, $3d_{yz}$, $3d_{zx}$) and/or O $2p_\pi$ orbitals. The orbital $3d_{3z^2-r^2}$ is the most unlikely candidate, since the out-of-plane CT excitation is stable against hole doping and the low-energy absorption induced by hole doping is polarized in the NiO_2 plane. The cluster calculation to reproduce the photoemission spectra concludes that the doped holes in La-Sr-Ni-O have O $2p$ character with appreciable contribution from Ni 3d.¹⁰ The result of the photoemission experiment further suggests, though not conclusively, that the holes might have O $2p_\pi$ and/or Ni $3d_{xy}$ symmetry. One may expect that the holes with xy symmetry less affect the CT excitation than those with x^2-y^2 symmetry, since the orbitals with xy symmetry are not directly involved in the CT excitation. Holes with xy symmetry would ferromagnetically couple to the Ni spins

of $S=1$. As Ni spins are antiferromagnetically coupled to each other, holes with xy symmetry are expected to reduce this antiferromagnetic correlation less effectively than those with x^2-y^2 symmetry. Furthermore, the quantum spin fluctuation in the NiO_2 plane ($S=1$) is much weaker than in the CuO_2 plane ($S=\frac{1}{2}$). So hopping of the xy -symmetry hole to the neighboring site is energetically unfavorable because of the ferromagnetic coupling with the Ni spin. This would explain the absence of the Drude-type absorption in the spectra of La-Sr-Ni-O unlike that in La-Sr-Cu-O.

Of particular interest is the spectrum of the metallic phase of La-Sr-Ni-O, which was reported for $x > 1.0$. In view of the results that the peaks of the infrared absorptions do not shift in energy, and Drude-type absorption does not develop up to $x=0.5$, it might be speculated that additional holes might occupy different states which favor the itinerant motions in the NiO_2 plane or drastically alter the electronic structure, in such a way that, the $S=\frac{1}{2}$ low-spin state might be stable for $x > 1.0$.¹⁵

In summary, we have studied the optical spectrum of the $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ system from $x=0$ to 0.50 in the semi-conducting compositional range. The results are com-

pared with the result of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. It is found that La_2NiO_4 can be classified to the CT-type insulator with the in-plane CT energy gap of about 4 eV. The doping induces the absorptions in the ir region as observed in La-Sr-Cu-O. However, La-Sr-Ni-O has two strong and broad absorptions in the midinfrared and near-infrared regions which do not shift with an increase of dopant concentration. A Drude-type absorption does not develop up to $x=0.5$ unlike that in La-Sr-Cu-O. The different behavior of doped holes would come from the different symmetry of doped holes and from the weaker quantum spin fluctuation of $S=1$ Ni spin state.

The authors would like to thank T. Arima and Y. Tokura of the University of Tokyo for the help with the optical measurement. We also acknowledge discussions with A. Fujimori of the University of Tokyo on the results of photoemission spectroscopy. We are also grateful to the staff of Professor Kitazawa's laboratory for the use of the floating zone furnace and for the EPMA measurement. This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Area from the Ministry of Education, Science and Culture of Japan.

*Present address: Central Research Laboratory, Hitachi Ltd., Kokubunji, Tokyo 185, Japan.

¹H. Takagi, T. Ido, S. Ishibashi, M. Uota, S. Uchida, and Y. Tokura, *Phys. Rev. B* **40**, 2254 (1989).

²Y. Takeda, R. Kanno, M. Sakano, O. Yamamoto, M. Takano, Y. Bando, H. Akinaga, K. Takita, and J. B. Goodenough, *Mater. Res. Bull.* **25**, 293 (1990).

³J. Gopalkrishnan, G. Colsmann, and B. Reter, *J. Solid State Chem.* **22**, 145 (1977).

⁴R. J. Cava, B. Batlogg, T. T. Palstra, J. J. Krajewski, W. F. Peck, Jr., A. P. Ramirez, and L. W. Rupp, Jr., *Phys. Rev. B* **43**, 1229 (1991).

⁵G. Aeppli and D. J. Buttrey, *Phys. Rev. Lett.* **61**, 203 (1988).

⁶Xiang-Xin Bi, P. C. Ekulund, E. McRae, Ji-Guang Zhang, P. Metcalf, J. Spalek, and J. M. Honig, *Phys. Rev. B* **42**, 4756 (1990); the values of the optical conductivity obtained by these authors are smaller by a factor of about 10 at all frequencies than those presented here, which might have arisen from using an incorrect coefficient on the calculation of the optical conductivity.

⁷S. Uchida, T. Ido, H. Takagi, T. Arima, Y. Tokura, and S. Ta-

jima, *Phys. Rev. B* **43**, 7942 (1991).

⁸D. E. Rice, M. K. Crawford, D. J. Buttrey, and W. E. Farneth, *Phys. Rev. B* **42**, 8787 (1990).

⁹S. Tajima, H. Ishii, T. Nakahashi, T. Takagi, S. Uchida, M. Seki, S. Suga, Y. Hidaka, M. Suzuki, T. Murakami, K. Oka, and H. Unoki, *J. Opt. Soc. Am. B* **6**, 475 (1989).

¹⁰H. Eisaki, S. Uchida, T. Mizokawa, H. Namatame, A. Fujimori, J. van Elp, P. Kuiper, G. A. Sawatzky, S. Hosoya, and H. Katayama-Yoshida (unpublished).

¹¹R. Newman and R. M. Chrenko, *Phys. Rev.* **114**, 1507 (1959); R. J. Powell and W. E. Spicer, *Phys. Rev. B* **2**, 2182 (1970).

¹²Joseph Orenstein, G. A. Thomas, A. J. Millis, S. L. Cooper, D. H. Rapkine, T. Timusk, L. F. Schneemeyer, and J. V. Waszczak, *Phys. Rev. B* **42**, 6342 (1990).

¹³I. Terasaki, T. Nakahashi, S. Takebayashi, A. Maeda, and K. Uchinokura, *Physica C* **165**, 152 (1990).

¹⁴S. Uchida, H. Takagi, and Y. Tokura, *Physica C* **162-164**, 1677 (1989).

¹⁵M. Kato, Y. Maeno, and T. Fujita, *Physica C* **176**, 533 (1991).