Optical study of the doping effect in the metallic oxide (Nd,Sr)CoO$_3$

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The metallic oxide (Nd,Sr)CoO$_3$ can be a good reference for high-T_c cuprates in the sense that it shows a metal-insulator transition and has holes as carriers. The reflectivity spectra of (Nd,Sr)CoO$_3$ were measured in the range from 0.03 to 3 eV, and the optical conductivity was obtained from them through the Kramers-Kronig relation. The conductivity spectra for doped samples have a broad absorption around 0.3 eV, and the 0.3-eV absorption gradually grows with further doping. Peculiar features of high-T_c cuprates are discussed by comparing them with (Nd,Sr)CoO$_3$.

Doped carriers play an important role in high-T_c cuprates because many kinds of physical properties, e.g., superconducting transition temperature, strongly depend on the carrier concentration.[1,2] Recently, a set of single-crystal samples of high-T_c cuprates with various amount of dopants has been prepared and the doping effect in the optical properties has been investigated.[3-6] It was found in (La,Sr)$_2$CuO$_4$,[3] (Nd,Ce)$_2$CuO$_4$,[3] and Bi$_2$Sr$_2$(Ca,L)Cu$_2$O$_{8+\delta}$ (L=Y and Nd) (Ref. 6) that the optical conductivity for lightly doped semiconducting samples has a broad peak in the midinfrared (ir) region. The peak shifts of 0 eV for further doping and cannot be clearly seen for superconducting samples. The spectra for superconducting samples have been explained so far by the Drude excitation, i.e., the plasma oscillation of the valence electrons (not doped carriers) with large effective mass due to the strong electron-electron correlation.[5,7] This explanation is, however, inappropriate for lightly doped samples, and an improved model, which should cover the optical properties and the doping mechanism in the whole range of carrier concentration, is needed. Although many models have been proposed to explain the doping mechanism in high-T_c cuprates,[6-11] it is difficult to choose a correct answer at present. This is partially because information on optical properties of general metallic oxides is not enough. It might be necessary for understanding the nature of high-T_c cuprates to compare them with other conducting oxides. We therefore measured and analyzed the optical reflectivity of (L,Sr)CoO$_3$ (L =La and Nd) which has long been known as a metallic oxide.[12]

There are some common features between high-T_c cuprates and (L,Sr)CoO$_3$. First of all, both of them show a metal-insulator transition by doping. Secondly, the Seebeck coefficient of (La,Sr)CoO$_3$ shows a positive sign[13] and the doped carriers in (L,Sr)CoO$_3$ are regarded as holes, as in high-T_c cuprates except for (Nd,Ce)$_2$CuO$_4$. Furthermore, Bocquet *et al.* have suggested that, from the x-ray photoemission spectroscopy measurement, the doped carriers in (La,Sr)CoO$_3$ have O 2p character, like the "p hole" in high-T_c cuprates.[14] Thus, conducting (L,Sr)CoO$_3$ can be a good reference for high-T_c cuprates. There is one more advantage of the study of (L,Sr)CoO$_3$. The crystal structure of this material is cubic perovskite (LaCoO$_3$ shows a slightly rhombohedral distortion), and

so a dielectric tensor reduces to a scalar function, where little harm will be caused by using polycrystalline samples instead of single crystals.

In this work, we present measurements and an analysis of the optical reflectivity of polycrystalline (Nd,Sr)CoO$_3$ from the infrared to the visible region. The measured spectra were transformed into the optical conductivity through the Kramers-Kronig (KK) relation. The doping mechanism and the metal-insulator transition are discussed from the obtained conductivity, and compared with those of high-T_c superconductors.

Polycrystalline samples were prepared by the usual sintering method.[13,14] The mixture of Nd$_2$O$_3$ (99.9%), SrCO$_3$ (99.9%) and CoO (99.9%) in an appropriate ratio was presintered at 950 °C in air for 5 or 6 days with several regrindings. The powders were then pressed into pellets and sintered at 1400 °C in air for 6 h. The pellets were well sintered and their density was about 85–90 % of the bulk density. In order to compensate the deficient oxygen in the samples, pellets were annealed at 350–400 °C for 48 h in the oxygen flow. The dc-resistivity measurement revealed that the Sr substitution for Nd lowers the resistivity, and the heavily doped (30 or 40 at. % Sr-substituted) samples become metallic. The 273-K resistivity of the 40 at. % Sr-substituted sample is less than 1 mΩ cm, which is rather small for ceramics. It should be noted that the 273-K resistivity of the 5 at. % Sr-substituted sample is about 100 times smaller than that of insulating NdCoO$_3$.

The optical reflectivity in the range from 0.03 to 3 eV was measured with a rapid-scanning Michelson interferometer. All the measurements were performed at room temperature. The magnitude of the reflectivity was determined by using silver as a reference. The samples were polished using Al$_2$O$_3$ powders down to 0.3-μm grain size. In order to check the smoothness of the polished surface of the sample, we measured the reflectivity of the polycrystalline LaCoO$_3$. It was then compared with the spectrum of single crystal,[15] and any serious differences could not be found between them, including the magnitude of reflectivity. Since the differences of reflectivity between polycrystalline and single-crystal samples can be assumed to be much smaller in cubic (Nd,Sr)CoO$_3$ than in rhombohedrally distored (La,Sr)CoO$_3$, we think that the spectra of the polycrystalline samples reflect the bulk
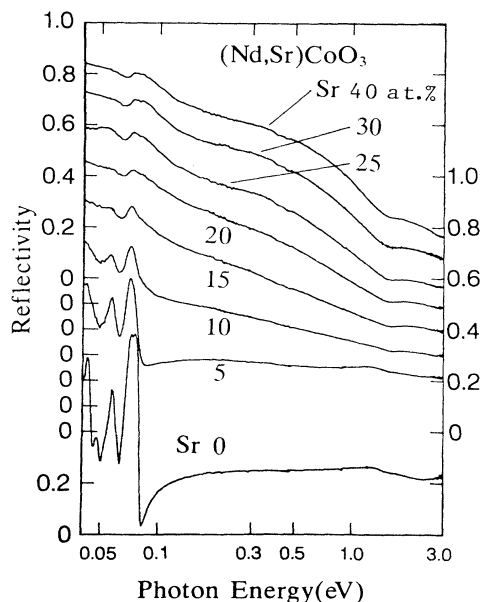
FIG. 1. The reflectivity spectra of (Nd,Sr)CoO$_3$.

FIG. 2. The conductivity spectra of (Nd,Sr)CoO$_3$ obtained from the reflectivity through the KK relation.

nature of (Nd,Sr)CoO$_3$.

The reflectivity spectra are shown in Fig. 1. A systematic change with doping is seen in the spectra, and the doping effect in the reflectivity of (Nd,Sr)CoO$_3$ has some features common to that of the high-T_c cuprates as follows: (i) the reflectivity of doped samples rises up toward 0 eV, and the magnitude in lower energy increases with doping, (ii) the reflectivity edges of all doped samples are about 1.5 eV and almost independent of the Sr content, and (iii) the high-energy reflectivity above the edge decreases with doping, which corresponds to the decrease of the oscillator strength of the charge-transfer (CT) excitation in the high-T_c cuprates.[3,6] The last one is not clearly seen in Fig. 1, but we measured high-energy reflectivity in some samples up to 40 eV, and observed the decrease of the reflectivity around 2–3 eV with doping.

The measured reflectivity spectra were transformed into the optical conductivity through the KK relation. Each spectrum was extrapolated by using Hagen-Rubens fit in the lower-energy region and by using the relation $R(\omega) \propto \omega^{-4}$ in the higher-energy region. The obtained optical conductivity is shown in Fig. 2 The spectrum for NdCoO$_3$ has no significant structures below 1 eV except for phonons. This is consistent with the fact that NdCoO$_3$ is insulating. When Sr is substituted for Nd, the spectra show a broad absorption in the mid-ir region, which is responsible for the mid-ir reflectivity. As the carriers are doped more, the broad absorption gradually grows up with its center fixed around 0.3 eV. It is noteworthy that the broad absorption is observed even in completely metallic samples.

Above the mid-ir absorption, it can be clearly seen that the conductivity above 1 eV decreases with doping, showing that the Sr substitution affects the higher-energy exci-
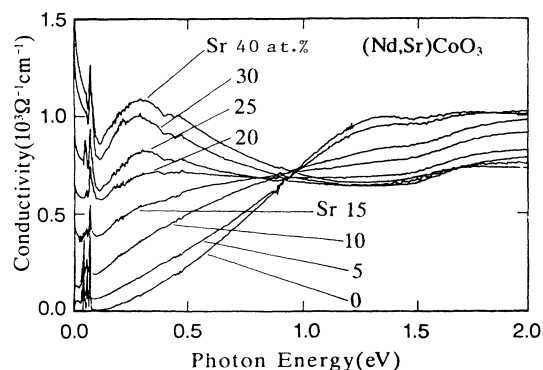
tations. The increase of the 0.3-eV absorption accompanied with the decrease of the higher-energy conductivity makes the conductivity around 1.0 eV approximately constant for all the samples. Below the mid-ir absorption, a finite background with sharp peaks of phonons is seen in the spectra for conducting samples. The conductivity near 0 eV increases with increasing carrier concentration, which we assigned to the plasma excitation of doped holes. This "plasma excitation" has a different meaning from that usually used in the optical spectra of high-T_c oxides. For example, in Refs. 5 and 7, the spectra in the range below the reflectivity edge (~ 1 eV) were assigned to the plasma excitation of the valence electrons with large effective mass. On the contrary, the present plasma excitation comes from the doped holes and is responsible for the far-ir spectra. This excitation is most clearly seen in 30 or 40 at. % Sr-substituted samples, where the conductivity makes a maximum at 0 eV and shows a broad slope below 0.1 eV. The highest-energy phonon can be observed in the spectra even for metallic samples, whereas phonons are screened in the spectra of doped samples of high-T_c cuprates. This may come from the fact that the far-ir Drude excitation is well separated from the mid-ir excitation and it cannot fully screen the highest-energy phonon.

As is already described, a similar mid-ir absorption has been found in lightly doped high-T_c cuprates.[3,6] There are, however, two significant differences between (Nd,Sr)CoO$_3$ and high-T_c cuprates. First, the energy of the mid-ir peak is almost independent of doping and stays constant near 0.3 eV in (Nd,Sr)CoO$_3$, while it drastically shifts to 0 eV with doping in Bi$_2$Sr$_2$(Ca,L)Cu$_2$O$_{8+\delta}$ and other high-T_c cuprates. Secondly, the mid-ir absorption gradually increases with doping and is roughly scaled to the Sr content, while it rapidly increases in Bi-based cuprates as soon as the carriers are doped in the system and does not clearly increase any more for further doping. We studied the doping effects in two-dimensional Co oxides, Bi$_2$M$_3$Co$_2$O$_{9+\delta}$ (M = Ca, Sr, and Ba), and found that they are similar to those of (Nd,Sr)CoO$_3$.[16] Then we think that the above two features essentially arise from the difference between Co^{3+} and Cu^{2+} states, not from that of the dimensionality of the system.
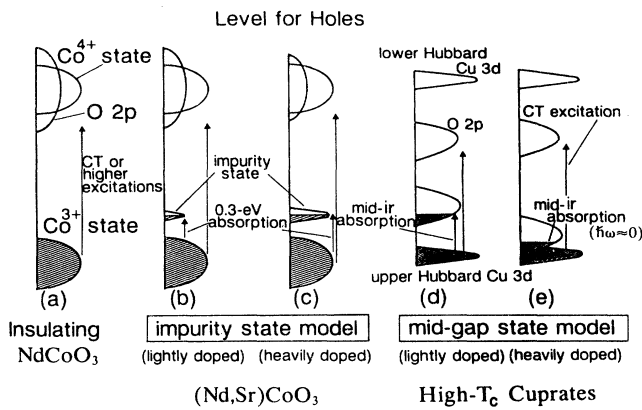
FIG. 3. A model of the electronic states for (Nd,Sr)CoO$_3$ is proposed [(a)–(c)], and the corresponding model for high-T_c cuprates proposed in Ref. 6 is shown for comparison [(d) and (e)]. Note that the energy level is described for holes.

In a previous paper, we studied the conductivity spectra of high-T_c Bi-based cuprates by dividing them into three parts,[6] i.e., the CT excitation, the mid-ir excitation, and the far-ir plasma oscillation of the doped holes. We fitted the conductivity with two Lorentz oscillators and a Drude term which represent the above three, and proposed a model of the electronic states of high-T_c cuprates from the obtained fitting parameters. In the present case, it is difficult to fit the spectra with Lorentz oscillators and Drude terms because of serious overlap of higher-energy excitations. Nonetheless, we emphasize that the spectra are well understood in the same manner as in the case of high-T_c oxides; that is, it is useful to divide them into three contributions, the mid-ir absorption and the excitations above and below it. Then we propose a model of the electronic states of (Nd,Sr)CoO$_3$, as we did in a previous study.

A possible model of the electronic states in (Nd,Sr)CoO$_3$ is deduced from the obtained conductivity spectra, as shown in Figs. 3(a)–3(c). Note that the diagrams are described by the level for holes in order to emphasize that the doped carriers are holes. Since information on the electronic states of Co oxides is insufficient, we state the following assumptions: (i) The electronic states responsible for the measured spectra are predominantly composed of Co $3d$ and O $2p$ bands. (ii) The complexity of Co^{3+} states, where the high- and low-spin states are almost degenerate, is ignored for simplicity. (iii) The energy to add an extra hole on Co^{3+} states (i.e., Co^{4+} states) is comparable with that to do the same on O^{2-} states. According to this model, the mid-ir absorption is assigned to the excitation between the $3d$ bands for Co^{3+} states and additional states formed by doping as shown in Figs. 3(b) and 3(c). As the carrier concentration increases [Fig. 3(c)], the additional states grow up roughly in proportion to the Sr content with their energy level almost fixed. The decrease of the conductivity above 1 eV is explained as follows: the excitations above 1 eV are partially deprived of the oscillator strength by those associated with the additional states in order to keep the sum

rules of optical transition. Since the properties of the additional states on doping is similar to those of the impurity band in heavily doped semiconductors, the proposed model can be called the "impurity-state model." It has long been suggested that the doped holes in (La,Sr)CoO$_3$ move among the impurity states formed by the substituted Sr,[12,14] but no direct proof for the impurity states has been reported. Then the present study may be the first observation of the impurity states with various amount of dopants.

Let us compare the electronic states of (Nd,Sr)CoO$_3$ with those of Bi$_2$Sr$_2$(Ca,L)Cu$_2$O$_{8+\delta}$. From the viewpoint of the optical study, these two materials have a common structure associated with the mid-ir absorption. We previously proposed the "midgap-state model," a possible model for the electronic states of the high-T_c cuprates,[6] which is shown in Figs. 3(d) and 3(e) for comparison. The midgap states, which correspond to the impurity states in (Nd,Sr)CoO$_3$, shift to the upper Hubbard band of Cu $3d$ with doping, and the energy difference between them is approximately zero for superconducting samples [Fig. 3(e)]. In the real-space picture, a localized hole on Cu^{2+} begins to transfer to neighboring oxygens with doping, and it becomes itinerant in the heavily doped samples reflecting that the transfer energy from Cu^{2+} to O^{2-} goes to zero. In other words, the magnetic properties associated with localized holes on Cu^{2+} are drastically changed or destroyed with doping. The above consideration is consistent with the fact that the heavily doped (La,Sr)$_2$CuO$_4$ shows Fermi-liquid–like properties, e.g., a weak temperature dependence of paramagnetism and negative Hall coefficient.[1] On the contrary, the impurity states in (Nd,Sr)CoO$_3$ keep the 0.3-eV gap from Co^{3+} states for all the measured carrier concentration. Therefore, the magnetic properties for the localized Co^{3+} are essentially unchanged, even if they are modified by the interaction with doped holes. In fact, conducting (La,Sr)CoO$_3$ shows ferromagnetism,[17] and the Seebeck coefficient does not show a negative sign up to 30 at. % Sr substitution.[18]

The above two models also explain the different behaviors of metal-insulator transitions of the two systems. A small amount of doping [3 at. % Sr substitution for La in (La,Sr)$_2$CuO$_4$] makes the material metallic or superconducting in high-T_c cuprates, whereas the heavy doping, 30 at. % Sr substitution for Nd, is needed to produce metallic samples in Co oxides. In high-T_c cuprates, the energy of the mid-ir excitation goes to zero in superconducting samples and the doped holes can migrate both on Cu^{2+} and O^{2-}. This means that Cu $3d$ and O $2p$, which should be hybridized in band theories but are prevented by the electron-electron correlation, get hybridized when the doped holes disturb the antiferromagnetic order. Then the doped states of superconducting samples are, in a sense, regarded as the "hybridized" states of Cu $3d$ and O $2p$, although this "hybridization" does not come from a first-principles band picture, but comes from newly formed states of the doped CT insulator. On the other hand, Co $3d$ and O $2p$ are essentially separated in energy and are not hybridized. Resonant photoemission of LaCoO$_3$ shows that the central energy of O $2p$ bands is 3

eV lower than that of Co $3d$ bands, while a clear energy difference between O $2p$ and Cu $3d$ bands is not observed in high-T_c cuprates.[19] The doped carriers cannot cause the hybridization between Co $3d$ and O $2p$ bands, even if they perturb the magnetic order of Co^{3+}. This is consistent with the observation that the mid-ir absorption stays at finite energy with doping. Therefore, the system cannot be metallic until the impurity bands grow sufficiently and prevent the carriers from localizing at the disorders introduced by the Sr substitution for Nd.

As is discussed above, the electronic and magnetic properties and metal-insulator transition of high-T_c cuprates and metallic Co oxides are qualitatively explained by the presented models—the impurity-state model and midgap-state model. Taking into account the difference of the two models, we think that the characteristic feature of the high-T_c cuprates is the energy shift of the midgap states or the mid-ir absorption, while the formation of the mid-ir absorption by doping is common to conducting $3d$ transition-metal oxides irrespective of superconducting or nonsuperconducting oxides.

In summary, the optical reflectivity spectra of polycrystalline $(Nd,Sr)CoO_3$ with various Sr contents were measured in the range from 0.03 to 3 eV. The conductivity spectra obtained from the measured reflectivity through the Kramers-Kronig relation show a broad peak around 0.3 eV for all the doped samples, which is responsible for the midinfrared reflectivity. It grows up roughly in proportion to the Sr content and is accompanied by the decrease of the conductivity above 1 eV. The spectra are well explained by the introduction of the impurity states formed with the Sr substitution for Nd. By the comparison between $(Nd,Sr)CoO_3$ and $Bi_2Sr_2(Ca,L)Cu_2O_{8+\delta}$, it was found that the peculiar feature of the high-T_c cuprates is the energy shift of the mid-ir absorption to 0 eV, and that the formation of the mid-ir absorption with the decrease of higher-energy conductivity is common to conducting $3d$ transition-metal oxides.

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