Precise Measurement of Optical Reflectivity Spectra Using Defect-Free Surface of La$_{1-x}$Sr$_x$MnO$_3$: Evidence Against Extremely Small Drude Weight

K. Takenaka, K. Iida, Y. Sawaki, and S. Sugai

Department of Physics, Nagoya University, Nagoya 464-8602, Japan

Y. Moritomo and A. Nakamura

Center for Integrated Research in Science and Engineering (CIRSE), Nagoya University, Nagoya 464-8603, Japan

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Abstract

Optical reflectivity spectra of La$_{1-x}$Sr$_x$MnO$_3$ ($0 \leq x \leq 0.30$) were measured on cleavage surfaces of single crystals. The optical conductivity $\sigma(\omega)$ of ferromagnetic-metal La$_{0.70}$Sr$_{0.30}$MnO$_3$ is characterized by a Drude-like but not simple-Drude component with large spectral weight below $\sim$1.6 eV, which yields a large effective carrier number $N^*_{\text{eff}}$ consistent with the results of Hall coefficient and specific heat measurements. The present result demonstrates that the previous result of "small Drude weight" originates from the damage of the sample surface. The Sr-substitution effect on the electronic structure and the origin of the unconventional $\sigma(\omega)$ are also discussed.

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The motivation of the renewed interest in the double-exchange ferromagnetic-metal manganites has two – fundamental and practical – aspects: study on anomalous metallic phase near Mott transition and industrial application of the intriguing phenomena induced by a magnetic field such as “colossal” magnetoresistance (CMR) \([1]\). Optical reflectivity study can make an essential role in the both stages because it enables us to not only deduce dielectric function but also examine separately two key-elements of charge transport – carrier density (or Drude weight) and scattering time. The charge transport is one of the central concerns among the both fields.

The previous reflectivity studies on La\(_{1-x}A_x\)MnO\(_3\) (\(A = \text{Sr} [2], \text{Ca} [3–5]\)) have revealed the outline of the systematic change of the electronic structure with Sr(Ca)-substitution and the conspicuous transfer of spectral weight over a wide energy range of 0-3 eV accompanied by the spin polarization of conducting \(e_g\) electrons. However, a quantitative conclusion is difficult to be drawn on the far-infrared response and on the estimation of optical (dielectric) functions because the experiments were made using polycrystals or/and did not cover the sufficient energy region. Especially, the origin or truth of “small Drude weight” – pointed out by Okimoto et al. [2] but contradictory to the results of Hall coefficient [6], specific heat [7,8], and optical absorption studies [9] – is still not well-investigated.

We report the optical reflectivity spectra \(R(\omega)\) of La\(_{1-x}\)Sr\(_x\)MnO\(_3\) \((0 \leq x \leq 0.30)\) measured on the cleavage surfaces of single crystals for a wide energy range covering far-infrared(far-IR) region down to 5 meV. Our careful experiment enables us to obtain the established optical functions – optical conductivity \(\sigma(\omega)\) and Drude weight – for this prototypical double-exchange system. Especially the Drude weight estimated for \(x=0.30\) is large and consistent with the results of Hall effect and specific heat studies.

Single crystals of La\(_{1-x}\)Sr\(_x\)MnO\(_3\) were grown by a floating zone method. The details of the growth condition and characterization were described elsewhere [10]. In order to obtain defect-free surfaces we cleaved the single-crystalline rod. The typical size of the cleavage surface was 0.2 mm\(\times\)0.2 mm, which was sufficient for optical measurements when we used the microscope designed for the infrared-visible spectrometer.
Near-normal incident reflectivity measurements were made using a rapid scanning Fourier-type interferometer (0.005-2.2 eV), a grating spectrometer (1.2-6.5 eV), and a Seya-Namioka type spectrometer for vacuum-ultraviolet synchrotron radiation (4.0-40 eV) at the Institute for Molecular Science, Okazaki National Research Institutes. All the data were taken at room temperature (295 K). The experimental error of reflectivity measurement $\Delta R$ is less than 2% over the energy range covered here.

Figure 1 shows the reflectivity spectra measured on the cleavage surfaces of La$_{1-x}$Sr$_x$MnO$_3$ ($0 \leq x \leq 0.30$) single crystals on a logarithmic energy scale in the range 0.01-6.0 eV. The curves are shifted upwards as Sr-composition increases. The Curie temperature $T_C$ of the sample is measured by dc resistivity: $T_C = 235$ K ($x = 0.15$), 283 K ($0.175$), 305 K ($0.20$), and 362 K ($0.30$), yielding $T/T_C = 1.26$, 1.04, 0.967, and 0.815, respectively. The insulator-metal(I-M) phase boundary crosses room temperature (295 K) between $x = 0.175$ and 0.20 in the present case.

Undoped LaMnO$_3$ is a charge-transfer(CT) insulator in the Zaanen-Sawatzky-Allen scheme [11]. The reflectivity spectrum exhibits several sharp peaks in the far-IR region due to optical phonons and two broad peaks, at about 2 eV and 5 eV, which are assigned to the CT excitations, $t_{2g}^2 e_g^1 \rightarrow t_{2g}^3 e_g^2 L$ and $t_{2g}^3 e_g^1 \rightarrow t_{2g}^4 e_g^1 L$ ($L$ denoting a ligand hole), respectively [12]. With slight substitution ($x \leq 0.10$), the lower CT peak disappears and a reflectivity edge suddenly appears at $\sim 1.6$ eV. As $x$ increases, the edge becomes sharpened, though its position does not shift appreciably, and the optical phonons are screened. For $x = 0.30$ (ferromagnetic-metal), the optical phonons almost fade away and the spectrum is characterized by a sharp edge and a large spectral weight below it.

In order to make quantitative discussion on the implications of the reflectivity data, we deduce optical conductivity $\sigma(\omega)$ (Fig. 2) from $R(\omega)$ shown in Fig. 1 via Kramers-Kronig(K-K) transformation. Since the experiment covers the region up to 40 eV which includes the contributions from almost all the valence electrons in the material, the extrapolation to higher energy region – we assumed $R \propto \omega^{-4}$ – is not the matter concerning the result in the energy region of interest. For the extrapolation to energies below 5 meV, we assumed
constant $R(\omega)$ for $x=0-0.175$. For $x=0.20$, we make a smooth extrapolation using Hagen-Rubens(H-R) formula with $\sigma(0)\sim100 \ \Omega^{-1}\text{cm}^{-1}$, which is roughly in accord with the dc value. For $x=0.30$, on the other hand, there is some room for varying extrapolated reflectivities (Fig. 3). The value of the dc resistivity for $x=0.30$ in the present experiment is $620\pm50 \ \mu\Omega\text{cm}$ at 295 K, corresponding to $\sigma(0)\sim1500-1750 \ \Omega^{-1}\text{cm}^{-1}$. In this range, a simple H-R extrapolation (dashed lines) appears not valid. However, this discrepancy can be removed by an extrapolation of Drude formula; $\epsilon(\omega) = \epsilon_\infty - \frac{4\pi\sigma(0)}{\omega(\omega\tau + i)}$ ($\epsilon_\infty$: dielectric constant in the high energy limit; $\tau$: scattering time) [13]. We assumed $\epsilon_\infty=5$ here [14]. Even in the case of the lowest $\sigma(0)$ value ($1500 \ \Omega^{-1}\text{cm}^{-1}$), we obtain rather smooth extrapolation by setting $\hbar/\tau\sim500 \ \text{cm}^{-1}$ (dashed-and-dotted line). One of the most smooth extrapolations is the case for $\sigma(0)=1700 \ \Omega^{-1}\text{cm}^{-1}$ and $\hbar/\tau=2000 \ \text{cm}^{-1}$ (solid line). Although the value of $2000 \ \Omega^{-1}\text{cm}^{-1}$ itself has less physical meaning, the smooth extrapolation of Drude formula suggests suppression of the scattering rate for $x=0.3$ at 295 K [13]. At any case, variation of the extrapolation procedures was confirmed to cause negligible difference for $\sigma(\omega)$ above 0.01 eV.

Strontium-substitution affects the optical conductivity for a wide energy range up to $\sim6 \text{ eV}$. The lower CT peak ($\sim2.4 \text{ eV}$) disappears immediately and the higher CT peak ($\sim5.2 \text{ eV}$) gradually decreases and shifts downwards as Sr-substitution proceeds. The reduced spectral weight at the two CT peaks is transferred to the lower energy region for the doped manganites. For $x=0.15-0.20$, $\sigma(\omega)$ spectrum is characterized solely by a broad peak centered at about 1 eV, which gradually develops and the peak position shifts downwards as $x$ increases; even for $x=0.20$, where the material is ferromagnetic-metallic, a Drude-like component is not observed. For $x=0.30$, the spectrum exhibits a large continuum below the edge ($\sim1.6 \text{ eV}$) centered at $\omega=0$. The transfer of the spectral weight is justified by the trend that the curves of integrated spectral weight $N_{\text{eff}}^*(\omega)$ (inset of Fig.2) given as

$$N_{\text{eff}}^*(\omega) = \frac{2m_0V}{\pi e^2} \int_0^\omega \sigma(\omega')d\omega'$$  \hspace{1cm} (1)
(\(m_0\): a bare electron mass; \(V\): the volume per Mn-atom) merge into a single line above 6 eV. Imperfect convergence is most likely due to the transfer of the spectral weight in the higher-energy region above 6 eV or/and the increasing experimental error on \(\sigma(\omega)\) with \(\omega\).

The immediate vanishing of the lower CT peak indicates that the final state of this excitation, \(e_g \uparrow\), merges into the valence band, strongly hybridized O2p−Mn\(e_g \uparrow\) orbital, and builds up one conduction band with hole-like Fermi surface. This interpretation is supported by (1) insensitiveness of reflectivity edge to the doping content and by (2) positive and weakly \(x\)-dependent Hall coefficient (carrier density \(n\) being estimated to be \(\sim 1\) hole/Mn-atom) [6].

The downward shift of the higher CT peak is explained by the change of Madelung potential in the Sr-substituted lattice [2]. However, the decrease of the intensity is hardly interpreted by the change of Madelung potential alone. It is necessary to take itinerancy of the carriers into consideration, i.e. the evolution of the spin-polarization reduces the initial states of the second CT excitation.

One of the main purposes in the present study is the estimation of the “Drude weight”. In a simple Drude model, \(N_{\text{eff}}^*(\omega_{ps}) = n(m_0/m^*)\) \((n, \omega_{ps}, \text{and } m^*\) being carrier number per Mn-atom, plasma frequency, and effective mass, respectively). \(N_{\text{eff}}^*(\omega_{ps})\) is so-called Drude weight. It is difficult, however, in the present case to estimate Drude weight because a simple Drude model seems not valid; the decay rate is too slow compared with \(\propto \omega^{-2}\) and hence the spectral weight at the mid- and near-IR regions is too large to be interpreted within the Drude model. Consequently, there is some arbitrariness in the choice of \(\omega_{ps}\) and/or a possibility that estimated Drude weight contains both coherent and incoherent parts. However, the present result clearly demonstrates at least the following fact: for \(x=0.30\) Drude weight is much larger than that of the previous work [2]. For example, we assume \(\omega_{ps}=1.6\) eV (reflectivity edge), then \(N_{\text{eff}}^*(\omega_{ps})=0.346\). Using \(n\sim 1\) per Mn-atom estimated from Hall effect study [3], mass-enhancement \(m^*/m_0\) is estimated to be 2.9, which is consistent with the result of specific heat measurement [4,8]. The present result clearly denies the previous picture that the optical response is characterized by such small Drude weight that we cannot attribute it to the mass-enhancement. Although the unconventional nature of \(\sigma(\omega)\) indicates that
even for \( x=0.30 \) the common mechanism is persistently working which yields the incoherent broad peak for the compositions near I-M transition, such mechanism is considered to be weakened as \( x \) increases.

The above mechanism is hardly produced solely by the double-exchange interaction \([16]\). The most plausible candidate of the additional physics is Jahn-Teller instability. The model incorporating both double-exchange and dynamical Jahn-Teller couplings \([17]\) predicts that the carriers are localized as polarons at \( T>T_C \) or where electron-phonon coupling constant \( \lambda \) is large, but restore gradually the metallic behavior as \( T \) or \( \lambda \) decreases. In this scenario, the broad peak observed for \( x=0.15-0.20 \) is interpreted due to the small polarons. The formation of the polarons is supported also by the optical \([18]\) and x-ray \([19]\) absorption studies. It is difficult, however, to make a quantitative comparison between the experimental results and the theoretical predictions. This is because the nominal concentration \( x \) does not correspond to the carrier density (or doping level) \( n \) straightforward. Moreover, the Sr-substitution is considered to increase the band-width \( W \) or/and weaken the Jahn-Teller instability. In fact, the decrease of \( x \) in the actual spectra \( \sigma(\omega) \) seems to correspond to the decrease of \( \lambda \) rather than the decrease of \( n \) in the calculated spectra, though the calculated spectra reproduce the actual spectra as a whole (Fig. 7 of Ref. \([17]\)).

Another candidate is the orbital degree of freedom. One of the theories with emphasis on it is the “orbital liquid theory” \([20]\), where the isospin is introduced to describe the orbital degree of freedom. The charge dynamics is characterized by a crossover around \( \Omega \) corresponding to the tunneling frequency in the vibronic state of the isospin coupled with the Jahn-Teller distortion: the orbital fluctuation behaves like a quasi-static disorder for \( \omega>\Omega \) and like an averaged potential during a lot of tunneling processes for \( \omega<\Omega \) and hence yields the incoherent and coherent responses, respectively. The Fermi-liquid picture incorporating the orbital degree of freedom is also proposed \([21]\) and it predicts that the orbital dependence of transfer integral produces the interband transition within \( e_g \) orbitals. At any case, however, these theories should predict the more detailed \( x \)-dependence of \( \sigma(\omega) \) in order to clarify the effect of the orbital degree of freedom on the charge dynamics.
Finally we show that the discrepancy to the previous result originates from the damages of the sample surface introduced by polishing. In Fig. 4 are shown the reflectivity spectra measured on the cleavage surface (solid line) as well as that measured on the surface polished by lapping films with diamond powder of diameter 0.5 (dashed line) or 0.3 (dashed-and-dotted line) $\mu$m. It is found that polishing distorts drastically $R(\omega)$ for ferromagnetic metal La$_{0.70}$Sr$_{0.30}$MnO$_3$ [Fig. 4(b)] whereas it alters little for undoped LaMnO$_3$ [Fig. 4(a)]. The previous data by Okimoto et al. [2] resembles closely the spectrum measured on the surface polished by 0.3 $\mu$m-diamond film. The damage of the surface probably localizes the carriers. However, as the wavelength of the incident light becomes longer, light reaches the inner, not damaged part, and hence $R(\omega)$ recovers the true spectrum, which is consistent with that the discrepancy almost disappears below 0.03 eV. “Small Drude weight” originates from the above restoration process [inset of Fig. 4(b)] [22].

In summary, we have established the optical response of the prototypical double-exchange system La$_{1-x}$Sr$_x$MnO$_3$ by the precise measurement of optical reflectivity spectra using the cleavage surfaces. For the compositions near the insulator-metal transition, $\sigma(\omega)$ is characterized solely by an incoherent broad peak at about 1 eV. However, the anomaly weakens as Sr-substitution proceeds and $\sigma(\omega)$ of ferromagnetic-metal La$_{0.70}$Sr$_{0.30}$MnO$_3$ exhibits a pronounced Drude-like, but not simple-Drude, component, which yields the large Drude weight consistent with the results of Hall effect and specific heat studies. The present result demonstrates that polish of the sample surface damages optical spectra of the doped manganites, suggesting that the charge dynamics of the conducting electrons in the manganites are extremely sensitive to the static imperfections.

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* Electronic address: k46291a@mucc.cc.nagoya-u.ac.jp

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FIGURES

FIG. 1. Optical reflectivity spectra measured on the cleavage surface of La$_{1-x}$Sr$_x$MnO$_3$ ($0 \leq x \leq 0.30$). All data were taken at room temperature (295 K). The curves are shifted upwards with Sr-composition increases.

FIG. 2. Optical conductivity spectra of La$_{1-x}$Sr$_x$MnO$_3$ deduced from the reflectivity spectra measured on the cleavage surfaces (shown in Fig. 1) via Kramers-Kronig transformation: $x=0$ (dashed-and-double-dotted line), 0.10 (long-dashed line), 0.15 (dotted line), 0.175 (dashed-and-dotted line), 0.20 (short-dashed line), and 0.30 (solid line). Inset: Effective carrier number per Mn-atom $N_{\text{eff}}^*(\omega)$ defined as the integration of $\sigma(\omega)$. $T_C=235$ K ($x=0.15$), 283 K ($0.175$), 305 K ($0.20$), and 362 K ($0.30$). The insulator-metal phase boundary crosses room temperature (295 K) between $x=0.175$ and 0.20.

FIG. 3. Magnified reflectivity spectra of La$_{0.70}$Sr$_{0.30}$MnO$_3$ in the far-infrared region (0-0.02 eV). Solid circle represents the actual data measured on the cleavage surface. Extrapolated reflectivities using Drude or Hagen-Rubens (dashed lines) formula are also shown. The variable parameters at the Drude-extrapolation are as follows: $\sigma(0)=1700 \ \Omega^{-1}\text{cm}^{-1}$, $\hbar/\tau=2000 \ \text{cm}^{-1}$ (solid line) and $\sigma(0)=1500 \ \Omega^{-1}\text{cm}^{-1}$, $\hbar/\tau=500 \ \text{cm}^{-1}$ (dashed-and-dotted line). $\epsilon_\infty$ is fixed at 5. The former is one of the most smooth extrapolation here.

FIG. 4. Optical reflectivity spectra measured on the cleavage (solid line) and polished surfaces: (a) LaMnO$_3$ and (b) La$_{0.70}$Sr$_{0.30}$MnO$_3$. We polished the surfaces using lapping films with diamond powder of diameter 0.5 (dashed line) or 0.3 (dashed-and-dotted line) $\mu$m. Inset: Optical conductivity spectra deduced from the Kramers-Kronig transformation of the reflectivity spectra shown in Fig. 4(b).