Anomalous Variation of Optical Spectra with Spin Polarization in Double-Exchange Ferromagnet: $La_{1-x}Sr_xMnO_3$

Y. Okimoto,[1] T. Katsufuji,[1] T. Ishikawa,[1] A. Urushibara,[1] T. Arima,[1] and Y. Tokura[1,2]

[1]*Department of Physics, University of Tokyo, Tokyo 113, Japan*

[2]*Joint Research Center for Atom Technology (JRCAT), Tsukuba 305, Japan*

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Optical spectra and their temperature dependence have been investigated for a prototypical double-exchange ferromagnet $La_{1-x}Sr_xMnO_3$ ($x = 0.175$). The optical conductivity spectrum above T_c is characterized by interband transitions between the exchange-split bands and gradually changes into intraband excitations with decrease of temperature, accompanied by conspicuous transfer of spectral weight over a wide energy region of 0–3 eV. The results indicate a large variation of the electronic structure with the spin polarization of the conduction carriers.

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The conducting ferromagnetic states in hole-doped manganese oxides with perovskite-type structure, e.g., $La_{1-x}Ca_xMnO_3$ and $La_{1-x}Sr_xMnO_3$ [1–3], have been known to be mediated by the double-exchange mechanism [4–6]. During the recent renaissance of studies on $3d$ transition metal oxides, the electronic properties near the doping-induced insulator-metal transition in perovskite-type manganese oxides have been reconsidered and some new aspects, such as giant magnetotransport [7–13] and magnetostructural phenomena [14], have been found, which are attracting broad interest also from an applicational viewpoint. The generic features in hole-doped manganese oxides arise from the strong coupling between the correlated electrons and local spins, both of which are of $3d$ electron character. The conduction bandwidth of the $3d$ electrons is likely to be smaller than the on-site exchange energy (Hund coupling energy) in those manganese oxide perovskites, and hence the carriers in the ferromagnetic ground state are almost perfectly spin polarized, in contrast to the case of conventional itinerant ferromagnets.

In this Letter, we report on the anomalous variation of the optical conductivity spectra with temperature for a crystal of $La_{1-x}Sr_xMnO_3$ ($x = 0.175$) near the nonmetal-metal compositional phase boundary. The results indicate the unconventional features for the electronic structure and their variation with spin polarization extending over several eV; these arise from the extremely strong coupling between the $3d$ e_g conduction electrons and $3d$ t_{2g} local spins. In particular, we have demonstrated for the first time the existence of fully spin-polarized conduction bands, which are split and separated by the on-site exchange energy ($\approx$2 eV).

The parent antiferromagnetic insulator $LaMnO_3$ contains Mn^{3+} ions with $t_{2g}^3 e_g^1$ ($S = 2$) configuration. Among the four $3d$ electrons on the Mn site, the t_{2g}^3 electrons may be viewed as a local spin of $S = 3/2$, since the t_{2g} electrons show smaller hybridization than the e_g states with oxygen $2p$ states, and also their energy level is lowered by the crystal field splitting ($\geq$1 eV). $LaMnO_3$ is a correlated insulator in which one e_g electron occupies each Mn site. However, the deviation of the e_g band filling ($n = 1 - x$) from an integer value ($n = 1$) or the so-called hole doping produces a barely metallic and ferromagnetic ground state in $La_{1-x}Sr_xMnO_3$ for $x \geq 0.17$ [10,13]. The ferromagnetic state can be realized by the kinetic energy gain of the e_g holes, which is maximal for a ferromagnetic arrangement of the t_{2g} spins according to the double-exchange theory [4–6]. Thus the low-energy electronic properties of metallic $La_{1-x}Sr_xMnO_3$ may be described by the following Kondo lattice model with ferromagnetic coupling [10,15,16]:

$$H = -\sum_{i,j,\sigma} t_{i,j,\sigma}\left(c^{\dagger}_{i,j,\sigma}c_{i,j,\sigma} + \text{H.c.}\right) - J\sum_i \vec{\sigma}_i \cdot \vec{S}_i \,. \tag{1}$$

Here, the first term represents the e_g electron transfer between neighboring sites i and j, while the latter shows the ferromagnetic ($J > 0$) Kondo coupling between the conduction e_g electron spin and the localized t_{2g}^3 ($S = 3/2$) spin. The most notable feature of the present hole-doped manganese oxide is that J ($\approx$1.2 eV) [17] is much larger than $t_{i,j}$, placing the system in the strong coupling regime [10]. Thus we need to clarify the electronic features over a fairly wide energy region of the order of J as a function of the spin polarization, which can be achieved by optical spectroscopy with changing temperature from above T_c down to low temperature.

The sample investigated was a single crystal of $La_{1-x}Sr_xMnO_3$ with the composition $x = 0.175$ near the insulator-metal phase boundary. The crystal was grown by the floating zone method, the details of which are reported elsewhere [18]. The $x = 0.175$ crystal undergoes the ferromagnetic transition at $T_c = 283$ K. The temperature dependence of resistivity of the sample is shown in the inset of Fig. 1: The resistivity abruptly changes around T_c, and metallic behavior is observed below T_c. This is due to a change in mobility of the carriers (e_g holes) subject to scattering by the spin

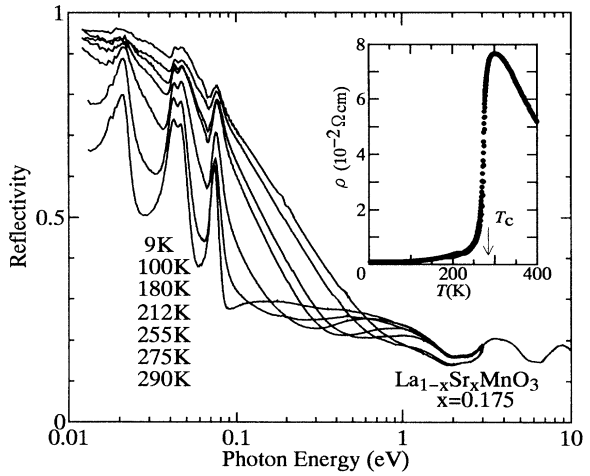

FIG. 1. Reflectivity spectra of $La_{1-x}Sr_xMnO_3$ ($x = 0.175$ and $T_c = 283$ K) at various temperatures in the photon energy range 0.01–3.0 eV and at 290 K above 3.0 eV. The inset shows the temperature dependence of resistivity for the same crystal.

fluctuation of the localized t_{2g} electrons [10,15,16]. The giant magnetoresistance of current interest observed for this compound around T_c [10] arises from the recovery of the carrier mobility due to the local spins being forcibly aligned by an external field.

Near normal incidence reflectivity was measured on the $x = 0.175$ and related crystals with a typical size of 6 mm $\phi \times 1$ mm using a Fourier transform type spectrometer for the range 0.01–0.8 eV and grating monochromators for a higher-energy region (0.6–36 eV). For the measurements above 4 eV at room temperature, we utilized synchrotron radiation at the Institute for Solid State Physics, University of Tokyo (INS-SOR). We measured reflectivity spectra between 0.01 and 3 eV with varying temperature. Optical conductivity spectra at various temperatures were obtained by Kramers-Kronig analysis of the reflectivity data from 0.01 to 3 eV at the respective temperatures and from 3 up to 36 eV at room temperature. For the analysis, we assumed the constant reflectivity below 0.01 eV and ω^{-4} extrapolation above 36 eV. Variation of the extrapolation procedures was confirmed to cause a negligible difference in the obtained conductivity spectra above 0.02 eV.

We show in Fig. 1 reflectivity spectra of $La_{1-x}Sr_xMnO_3$ ($x = 0.175$) taken at various temperatures. Corresponding to the changes of the electrical conduction (see the inset), the reflectivity spectrum below 3 eV shows a large variation with temperature. The reflectivity spectrum above and near T_c shows up as typical of a nonmetal with sharp far-infrared features due to the optical phonons at 0.02, 0.04, and 0.08 eV. As the temperature decreases, the lower energy reflectivity is gradually increased and then the spectrum turns into the metallic reflectance band at low temperatures. The phonon structures are observed to fade away with decreasing temperature due to the dielectric screening effect.

Spectra of the optical conductivity $\sigma(\omega)$ are shown in Fig. 2 together with the inset for magnification in the far-infrared region; they were obtained by the aforementioned Kramers-Kronig analysis. It is clearly discernible that the temperature-dependent change in the spectra extends beyond 2 eV, indicating that the energy scale of the quantity (say, the exchange energy J) responsible for the change in the electronic structure is quite large. The spectrum at 290 K ($>T_c$) with no spin polarization shows gaplike features. The gap region appears to be gradually filled in with decrease of temperature or with increase of the spin polarization. Such spectral weight in the low-energy region, say, 0–1 eV, appears to be transferred from the higher-lying energy region (1–3 eV). Remarkably, the temperature-dependent spectral change persists down to the lowest temperature with no sign of saturation. Such a conspicuous temperature dependence of $\sigma(\omega)$ over a wide energy region, as it were a sort of thermochromism, is quite unusual as compared with other strongly correlated electron systems near the metal-insulator phase boundary.

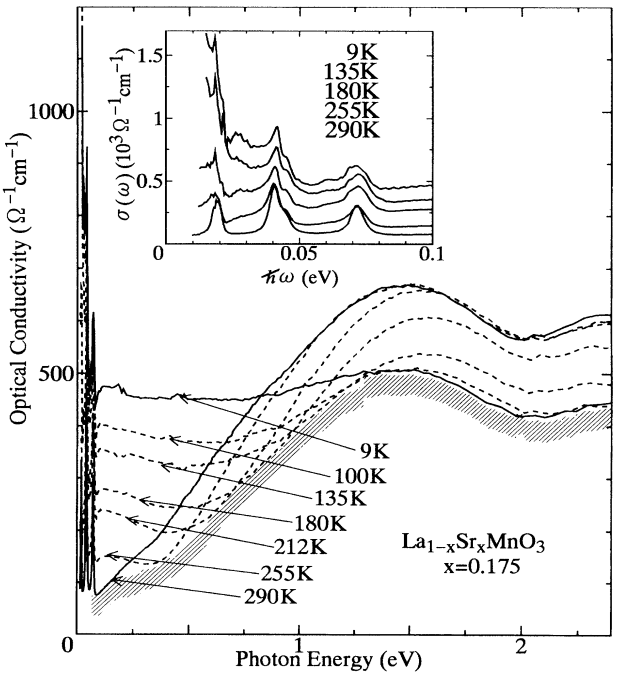

FIG. 2. Optical conductivity spectra of $La_{1-x}Sr_xMnO_3$ ($x = 0.175$ and $T_c = 238$ K) at various temperatures. The hatched curve represents the temperature-independent part of the spectra deduced from the envelope of the respective curves. The inset shows a magnification of the far-infrared part.

To analyze quantitatively the spectral weight transfer with the spin polarization, let us sort the spectral structure into temperature-dependent and -independent parts: A number of spectral curves at various temperatures shown in Fig. 2 appear to draw an envelopelike trace (the hatched curve in the figure) setting the lower bound of the optical conductivity at each photon energy, and hence the temperature-independent part. Such a spectral part arises perhaps from the interband transitions between the O $2p$ and Mn $3d$ bands. Thus we can deduce the temperature-dependent spectral part by subtracting the temperature-independent part (the hatched curve) from each spectrum. The result is shown in Fig. 3 (excluding the far-infrared phonon region to avoid complexity) together with the schematics for the change of the electronic structure (inset). As clearly seen in this figure, the gaplike transition on the higher-energy side is gradually shifted to higher energy and decreases in intensity with decrease of temperature, while the spectral weight of the lower-lying band increases.

These two types of transitions, between which the spectral intensity is exchanged depending on the spin polarization, can be interpreted as follows. The strong ferromagnetic coupling energy ($3/2J \approx 2$ eV) between the e_g charge carriers and t_{2g} local spins exceeds perhaps the one-electron bandwidth of the e_g band [19], and hence the e_g band should be split into two bands by the order of J as pictorially shown in the inset of Fig. 3 [16]. Optical transitions are then allowed only between the lower and upper up-spin bands or otherwise between the lower and upper down-spin bands. When $T > T_c$, the occupations of the up-spin and down-spin lower bands are equal and the optical gap transitions have contributions from both the interband transitions. The observed higher-lying gap transitions at relatively high temperatures in Fig. 3 are assigned to such interband transitions between the J-split bands. In the case that $J > W$, as in the present manganese oxide, such an interband transition bears close analogy to the Hubbard gap (U gap) transition in the Mott insulator ($U > W$).

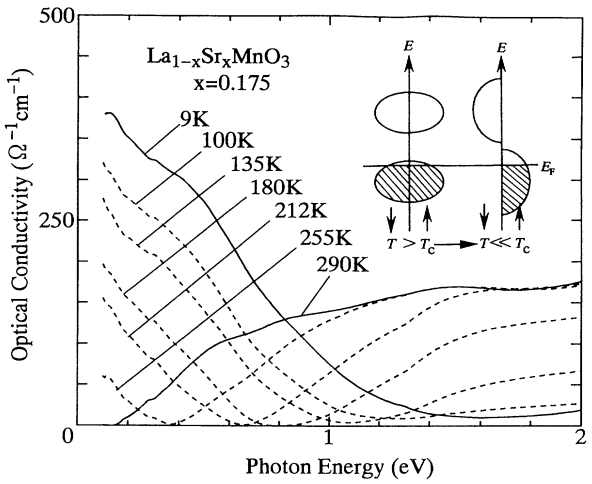

FIG. 3. Reduced optical conductivity spectra of $La_{1-x}Sr_xMnO_3$ ($x = 0.175$ and $T_c = 283$ K) which are obtained by subtracting the temperature independent part (the hatched curve in Fig. 2) from the respective spectra. The far-infrared region dominated by the phonon features is omitted to avoid complexity. The inset depicts the schematic electronic structures for the exchange-split bands with up spins (↑) and down spins (↓) and their change with the magnetization (spin polarization).

When the temperature is decreased below T_c, the density of states for the lower (upper) up-spin band increases (decreases) and vice versa for the down-spin bands. Therefore the interband transition across the J gap should decrease in intensity. In contrast, the intraband excitation within the lower up-spin band becomes dominant, which corresponds to the growth of the lower-lying Drude-like band at low temperatures (Fig. 3). At intermediate temperatures, say, 50–250 K, the two optical bands corresponding to the intraband and interband excitations for the J-split bands are clearly observed to coexist while changing relative intensities with temperature (Fig. 3). One may consider again the analogy to the case where the doped Mott-Hubbard insulator shows increased spectral weight for the inner-gap excitation with increase of the one-electron bandwidth W or nominal hole concentration [20]. Complete transfer of the spectral weight from the J-gap transitions to the intraband excitations at the lowest temperature as observed in Fig. 3 indicates the nearly complete spin polarization of the conduction carriers in the e_g band. This is a consequence of the strong coupling ($J > W$) situation in the present system, and in fact the saturated magnetization at $T \ll T_c$ is about $4\mu_B$, in accord with the classical value expected for the e_g electron fully spin polarized by the t_{2g} local spin ($S = 3/2$) [10].

The weight of the Drude-like part represents the kinetic energy of the e_g carriers. To estimate the transferred weight, we have calculated the effective number of electrons ($\tilde{N}_{\rm eff}$) which is defined as

$$\tilde{N}_{\rm eff}(\omega_c) = \frac{2m}{\pi e^2 N} \int_0^{\omega_c} \tilde{\sigma}(\omega) d\omega \,. \qquad (2)$$

Here, N represents the number of formula units (i.e., Mn atoms) per unit volume. The cutoff energy $\hbar\omega_c$ adopted for the estimate is the energy at which the reduced optical conductivity spectrum $\tilde{\sigma}(\omega)$ (Fig. 3) shows a minimum as a boundary between the interband and intraband excitations. Figure 4 shows the temperature dependence of $\tilde{N}_{\rm eff}$ for $La_{1-x}Sr_xMnO_3$ (for $x = 0.175$). $\tilde{N}_{\rm eff}$ shows the onset at T_c and keeps increasing with decreasing temperature, as already noticed in the conspicuous change of the optical conductivity spectrum (Figs. 2 and 3), even at low temperatures. For reference, we have also plotted the temperature dependence of the normalized ferromagnetic

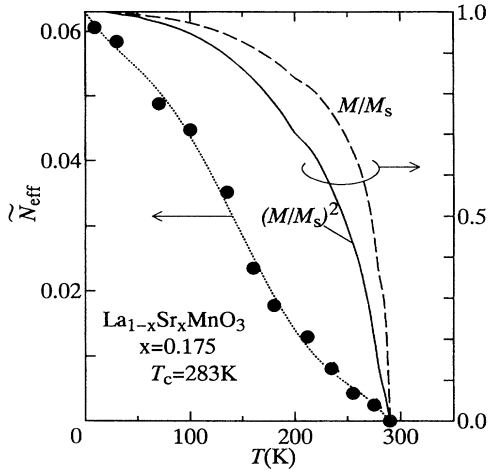

FIG. 4. Temperature dependence of the effective number of electrons ($\tilde{N}_{\rm eff}$), which is deduced from the optical conductivity spectra for the intraband excitations (Drude-like band). The dotted line is merely a guide to the eye. The dashed and solid lines show the temperature dependence of the normalized ferromagnetic magnetization M/M_s and its square $(M/M_s)^2$, M_s being the saturated magnetization ($4\mu_B$) at the lowest temperature.

magnetization M/M_s as well as of its square $(M/M_s)^2$ (M_s being the saturated moment at the lowest temperature), which were estimated at 0.5 T to avoid the complexity arising from the nonremanent behavior of the present system [10]. According to the mean-field type interpretation [16], the value of M/M_s indicates the spin polarization of the lower J-split band, and hence its square $(M/M_s)^2$ may represent the variation of the spectral weight of the intraband excitations within the lower J-split band. However, the observed temperature dependence of $\tilde{N}_{\rm eff}$ for the Drude-like (or intraband) excitations differs greatly from that of $(M/M_s)^2$: $\tilde{N}_{\rm eff}$ still varies conspicuously in the low-temperature region where the magnetization M is almost saturated. The quantum fluctuation of the local spin is likely to affect the dynamics of the charge carriers at low temperatures via mutual strong coupling, yet this unexpectedly large discrepancy is left to be quantitatively elucidated.

In summary, we have observed conspicuous variation of the optical conductivity spectrum with temperature (9–300 K) for a single crystal of $La_{1-x}Sr_xMnO_3$ ($x = 0.175$), which undergoes the ferromagnetic transition at 283 K. A large spectral weight transfer with spin polarization is observed from the interband transitions between the exchange-split lower and upper bands to the Drude-like intraband excitations within the lower up-spin band. This is the first observation of a fully spin-polarized (exchange-split) conduction band in metallic ferromagnets. The observed change in the optical spectra with temperature over a wide energy region (0–3 eV) arises from the novel electronic situation of the hole-doped manganese oxides; i.e., the coupling energy ($3/2J \approx 2$ eV) between the conduction carriers and local spins at every Mn site exceeds the one-electron bandwidth of the conduction band. A similar spectral change (as it were magnetochromism) would be expected even at a fixed temperature under an external magnetic field of the order of 10 T.

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