Optical probe of anisotropic and incoherent charge dynamics in a layered ferromagnet: $La_{1.2}Sr_{1.8}Mn_2O_7$

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Highly anisotropic optical conductivity spectra and their temperature variation have been investigated for a layered ferromagnetic (T_c=121 K) crystal of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ (x=0.4). The in-plane spectra show conspicuous spectral-weight transfer over an energy region of 0–3 eV with evolution of spin polarization below T_c and in the ferromagnetic, highly conducting ground state form a prominent peak structure around 0.4 eV with minimal Drude weight. By contrast, the c-axis spectra show little change with temperature and remain insulatorlike. The results indicate highly incoherent dynamics of the fully quasi-two dimensional spin-polarized carriers. [S0163-1829(98)51714-6]

The perovskite-type manganites, $R_{1-x}A_xMnO_3$ (R and A being the rare-earth and alkaline-earth ions, respectively) have been investigated extensively since the late rediscovery of colossal magnetoresistance (CMR) phenomena.[1–4] The essential ingredient in physics of CMR is the double-exchange (DE) interaction,[5–7] that is the strong on-site (Hund's rule) coupling between the charge carriers (e_g-like state) and the local spins (t_{2g}-like state). However, the observed features not only of the CMR but even of the ferromagnetic metallic state at low temperatures cannot fully be accounted for by the DE model alone. Some additional or competing interactions/instabilities appear to be also important, such as antiferromagnetic superexchange interaction,[8,9] orbital correlation,[10] Jahn-Teller coupling,[11,12] charge-ordering instability,[13–15] and so on. The resultant, complex but intriguing phenomena would show up in a reduced bandwidth system or in a reduced electronic dimension. The layered perovskite structures (or Ruddlesden-Popper series) of the manganites, $(La,Sr)_{n+1}Mn_nO_{3n+1}$, are one such example, in which the DE interaction essentially works only within the respective Mn-O_2 layers.

In the single-layer (n=1) compound with the K_2NiF_4 structure, however, the hole doping does not produce the ferromagnetic metallic state, perhaps due to too much reduced DE interaction, but rather almost always produces the charge- and orbital-ordered state, as most stabilized around x=0.5.[16–18] By contrast, for the bilayer (n=2) compound $La_{2-2x}Sr_{1+2x}Mn_2O_7$, the highly anisotropic ferromagnetic metallic ground state is observed to show up for x=0.3–0.4.[19,20] Reflecting perhaps the reduced dimensionality, these bilayer manganites are endowed with unique features in addition to those of the anisotropic DE ferromagnet. For example, the n=2, x=0.4 crystal shows a steep (thermal activation-type) increase of the resistivity for both the in-plane and c-axis components, while retaining the appreciable anisotropy, with decrease of temperature down to the spin-ordering temperature (T_c) as reproduced in the inset of Fig. 1. However, this increase of resistivity is drastically sup-

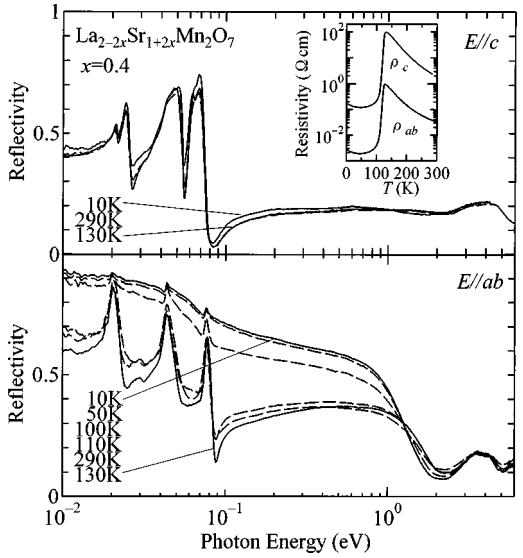

FIG. 1. Temperature dependence of $E\|ab$ (upper panel) and $E\|c$ (lower panel) reflectivity spectra for a $La_{2-2x}Sr_{1+2x}Mn_2O_7$ (x=0.4) crystal with the 3D spin-ordering temperature T_c=121 K. The inset shows the temperature dependence of in-plane(ρ_{ab}) and c-axis(ρ_c) resistivity. Solid lines show the spectra at 10 K and 130 K.

pressed by application of a magnetic field.[19] Recent neutron scattering studies have revealed the existence of short-range antiferromagnetic spin ordering above T_c (Ref. 9) as well as a sudden extension of the c-axis Mn-O bond length below T_c.[21] They both are closely correlated with the coupling of the conduction electrons with orbital or lattice degrees of freedom and responsible for occurrence of the relatively low-field CMR.[19] Although the in-plane resistivity shows slight up-turn with decreasing temperature below 30 K, the ferromagnetic state remains metallic down to the lowest temperature.[22] In this paper, we report the optical study on the anisotropic electronic structure as well as on the spin-polarization dependent charge dynamics for this $n=2$ layered manganite crystal. The results indicate an anomalously incoherent nature of the charge dynamics in the quasi-two-dimensional (quasi-2D) ferromagnetic state, suggesting the strong coupling of the spin-polarized charge carriers with orbital or phonon excitations in the ground state.

Crystals of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x=0.4$) were grown by the floating zone method. We confirmed by inductively coupled plasma atomic emission spectroscopy that the sample stoichiometry coincides with the prescribed one. The details of the crystal growth and the structural characterization have been reported in literature.[19,20] Near-normal-incidence reflectivity spectra were measured on the ab (for $E\|ab$) and ac (for $E\|c$) face of the $x=0.4$ (and $x=0.3$) single crystals with a typical size of $6\times6\times2$ mm^3. The specular ab face was freshly prepared by cleaving the crystal boule, while the ac face was polished with alumina powder to a mirrorlike surface. We used Fourier spectroscopy for the photon energy range of 0.01–0.8 eV and grating spectroscopy for 0.6–36 eV. For the higher-energy (>6 eV) measurements at room temperature, the synchrotron radiation at INS-SOR, Institute for Solid State Physics, University of Tokyo, was utilized as a polarized light source. The temperature dependence of the polarized reflectivity spectra was measured for 0.01-6 eV and the room-temperature data above 6 eV were connected to perform the Kramers-Kronig analysis and deduce the optical-conductivity spectra at respective temperatures. For the analysis, we assumed the constant reflectivity or Hagen-Rubens relation below 0.01 eV and ω^{-4} extrapolation above 36 eV. Variation of the extrapolation procedures was confirmed to cause negligible difference for the calculated conductivity spectra above 0.02 eV.

We show in Fig. 1 temperature (T) dependence of reflectivity spectra for the respective polarizations, $E\|ab$ and $E\|c$. Spiky structures in the far-infrared region ($\hbar\omega<0.07$ eV) are due to optical-phonon modes. All the infrared-active modes expected from the factor group analysis are observed for $E\|c$ spectra. In the T range from 290 K down to 130 K, the $E\|ab$ reflectivity below 0.3 eV once decreases as a whole, while the $E\|c$ reflectivity in the same region shows minimal change or rather slightly decreases. As T is decreased below T_c(=121 K), the $E\|ab$ spectra show a drastic change on a large energy scale up to 3 eV. By contrast, the $E\|c$ spectra show little change even below T_c, except for the change in phonon mode structures, which may be related to the aforementioned change of the Mn-O bond length along the c axis.[21] Thus the $E\|c$ spectrum behaves like an insulating one over the whole T region.

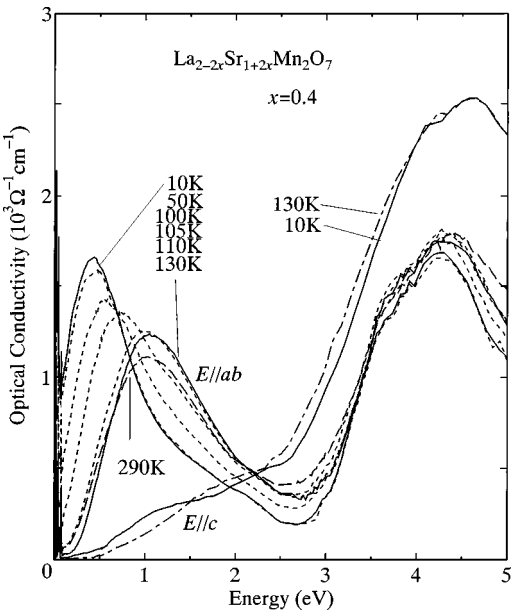

FIG. 2. Temperature dependence of $E\|ab$ and $E\|c$ optical-conductivity spectra for a $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x=0.4$) crystal with the 3D spin-ordering temperature $T_c=121$ K. Solid lines represent the spectra at 10 and 130 K.

Figure 2 shows the T dependence of the optical-conductivity spectra for $E\|ab$ and $E\|c$ which were deduced by Kramers-Kronig analysis of the reflectivity data. At a glance, one may notice a conspicuous T-dependent change for the in-plane ($E\|ab$) spectra up to 3 eV. By contrast, the $E\|c$ spectra shows a minimal T-dependent change, except for slight accumulation of the spectral weight below 1.5 eV with decreasing T below T_c. Both the $E\|ab$ and $E\|c$ spectra show an onset around 3 eV, peaking at 4 eV. This peak can be assigned to the charge-transfer type transition between the O2p and Mn t_{2g}-like (down-spin) states.[23,24] The spectra below 3 eV are dominated by the intra- and interband transitions relevant to O2p and Mn e_g-like states. The in-plane conductivity spectrum shows a broad peak around 1 eV above T_c, forming the pseudogap ($\approx$0.2 eV) structure. As T decreases from 290 K to just above T_c, the 1 eV-peak height increases and the gap feature becomes clearer, although the overall feature is rather unchanged. Thus the optical-conductivity spectra confirms the insulating behavior above T_c.

With decreasing T below T_c a large spectral change occurs in the $E\|ab$ spectra over an energy range of 0–3 eV. Importantly, the transferred spectral weight does not form the Drude-like coherent peak centered at $\omega=0$, while peaking around 0.4 eV. This signals unconventional charge dynamics in the metallic state of this layered manganite, as discussed later using the magnified low-energy spectra (see Fig. 4). Here, let us first argue the overall spectral-weight transfer as observed. To estimate the transferred spectral weight, we have calculated the effective number of electrons ($N_{\rm eff}$), which is defined as

$$N_{\rm eff}(\omega)=\frac{2m}{\pi e^2 N}\int_0^{\omega}\sigma(\omega')d\omega'. \qquad (1)$$

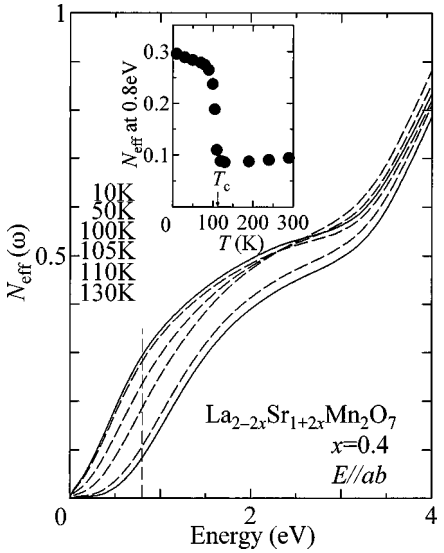

FIG. 3. Temperature variation of spectra of the effective number of electrons $N_{\rm eff}(\omega)$, which were deduced by integrating the observed $\sigma(\omega)$. The inset shows the temperature dependence of $N_{\rm eff}$ at 0.8 eV as a measure of the kinetic energy of the conduction electrons (see the text).

Here, N represents the number of Mn atoms per unit volume. The $N_{\rm eff}$ spectra at various temperatures are shown in Fig. 3. Taking account of the increasing experimental error in $\sigma(\omega)$ with ω, we may view that the $N_{\rm eff}(\omega)$ curves tend to merge into a nearly single line above 3 eV. In other words, the T-dependent distribution of the spectral weight ($N_{\rm eff}\approx 0.5$) occurs nearly below 3 eV, which is relevant to the doped holes or the band-filling e_g-like electrons. The inset of Fig. 3 shows the T dependence of $N_{\rm eff}$ at $\omega_c = 0.8$ eV, an appropriate cutoff energy for the estimate of the transferred low-energy spectral weight. Between 290 K and 120 K $N_{\rm eff}(\omega_c)$ is nearly constant. Once the compound undergoes the 3D spin ordering transition, $N_{\rm eff}(\omega_c)$ show a conspicuous increase in accord with the occurrence of the metallic conduction.

Similar spectral change with temperature or with evolution of the ferromagnetic magnetization was also observed for the underdoped pseudocubic perovskite manganite crystals such as barely metallic $La_{1-x}Sr_xMnO_3$ around $x=0.2$ (Refs. 25 and 26) and insulating (semiconducting) $Nd_{1-x}Sr_xMnO_3$ ($x=0.3$).[27] Such a large spectral change as observed in the perovskite manganites has been argued in various contexts: (1) the T-dependent change of the density of state for the spin polarized e_g-state conduction bands with a large exchange splitting exceeding the band width,[25,26,28–30] (2) the Jahn-Teller polaron band with T-dependent *effective* coupling strength,[11,27] and (3) the T-dependent change of the interband transitions between the different-orbital branches at nonspecific k points.[31,32] All the respective scenarios may be relevant, more or less, to the observed features, perhaps depending on the energy region. For example, the spectral change extending up to as large an energy scale as 3 eV cannot be accounted for by (2) or (3), but should be interpreted in terms of the electronic-structural change on an energy scale of Hund's-rule coupling as in (1). Namely, the model considers the conduction-band split by the Hund's-rule coupling energy ($\approx$2 eV), that is in fact demonstrated by the LDA+U calculation on this compound.[33] In the case of zero net magnetization above T_c, the lower-lying up-spin and down-spin bands are equally occupied, while in the ferromagnetic ground state with full spin polarization the partially occupied up-spin band and the totally unoccupied down-spin band are separated by the exchange splitting. The presently observed spectral weight transfer with onset of the ferromagnetic magnetization can partly be assigned to the change in the character of the conduction-electron related transitions, namely from the interband transition between the exchange-split conduction bands to the intraband excitation within the up-spin band, as in the case of $La_{1-x}Sr_xMnO_3$.[25,26]

The overall feature of the T-dependent change of the in-plane low-energy conductivity spectrum can thus be explained similarly to the case of the 3D analog, $La_{1-x}Sr_xMnO_3$, yet some distinct features can be noticed for this quasi-2D ferromagnet in addition to the inherent anisotropic behavior. The spectral weight is rapidly accumulated with decrease of T, but forms the broad peak around 0.4 eV. The formation of such a midinfrared peak implies the small-polaronic conduction in this system. According to a conventional small-polaron model,[34] the peak energy of the $\sigma(\omega)$ corresponds approximately to twice the polaron binding energy. In fact, the 290 K (or higher-temperature) in-plane spectrum can be crudely fitted with a set of polaron parameters (binding energy $E_b = 0.535$ eV, hopping energy $J = 0.59$ eV). However, such a calculation completely fails to reproduce the shape of the lower-temperature $\sigma(\omega)$ spectrum that shows a subsisting low-energy (down to $\omega=0$ eV) tail as well as a pronounced peak structure around 0.4 eV. As a more suitable model, we may consider the dynamical mean-field calculation (infinite-dimensional approach) on the dynamic Jahn-Teller effect [the above scenario (2)] by Millis *et al.*[11] In fact, the calculated Jahn-Teller polaron spectra with the electron-phonon coupling strength $\lambda\approx 1.08$ (Ref. 11) can qualitatively reproduce the observed temperature-dependent feature that the 1 eV peak around and above T_c is gradually shifted to a lower energy (down to 0.4 eV) with increasing spectral weight. (In this calculation, J_H is assumed infinite, so that the higher-energy scale structure than the Jahn-Teller coupling energy ($\approx$1 eV) cannot be dis-

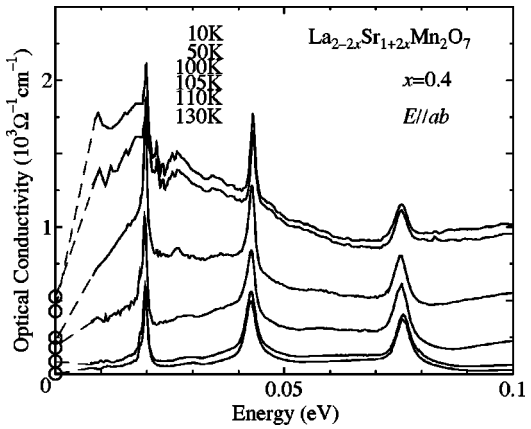

FIG. 4. Temperature dependence of magnified $E\|ab$ optical-conductivity spectra in the low-energy region (0–0.1 eV). Open circles represent the value of dc conductivity at respective temperatures. The dashed lines are merely guides to the eyes.

cussed.) To be more quantitative about the singular shape of the low-temperature $\sigma(\omega)$ for the *metallic* ground state, however, the consideration of the collective nature of the dynamic Jahn-Teller distortion or the short-range orbital ordering would be necessary for this quasi-2D system beyond the infinite-dimensional approach.[11]

The optical-conductivity spectra magnified in the low-energy (0–0.1 eV) region and the comparison with the dc conductivity are shown in Fig. 4 for temperatures below T_c. Four peaks are due to the optical-phonon modes as mentioned before and do not change essentially as T decreases, indicating that the tetragonal lattice symmetry is preserved below T_c. The zero-frequency extrapolation of the optical conductivity is roughly in accord with, but apparently higher than, the dc value based on the resistivity measurement. At low temperatures, e.g., 50 K and 10 K, the Drude-like increase of $\sigma(\omega)$ is barely observed below 0.05 eV, but the $\sigma(\omega)$ seems to fall again below 0.02 eV towards the dc value. The localization effect, as evidenced by the logarithmic T dependence of the in-plane resistivity below 20 K (see the inset of Fig. 1), may be partly responsible for this further suppression of the Drude peak.

Thus in the present quasimetallic layered manganites ($x=0.4$) the carrier motion is diffuse down to near zero frequency even in the fully spin-polarized ground state. Namely, the strong scattering of the spin-polarized carriers by bosonic excitations such as phonons and orbital excitations gives rise to a broad midinfrared peak around 0.4 eV in the optical-conductivity spectra, while the lower-energy spectral weight (Drude weight) is extremely small. The orbital fluctuations originating from the pseudodegeneracy of the e_g-like state or the associated dynamical Jahn-Teller distortion forming the polaronic carriers is likely responsible for the diffuse charge transport and incoherent low-energy spectral feature as revealed in this study.

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