Temperature evolution of the 1.5-eV absorption band in doped manganites: Formation of Jahn-Teller clusters

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A systematic investigation of the absorption spectra of thin films of doped manganites has revealed an anomalous temperature variation of the $\sim$1.5-eV absorption band. On approaching the insulator-metal transition temperature T_C from the high-temperature side, the band increases in intensity and then merges into the Drude-like band in the ferromagnetic metallic state. We have interpreted the temperature variation in terms of formation and disappearance of Jahn-Teller clusters. [S0163-1829(98)02943-9]

The doped manganites $R_{1-x}Sr_xMnO_3$, where R is a rare-earth metal, show colossal magnetoresistive properties near above the insulator-metal transition temperature T_C, and are attracting current interest from a technological point of view. Its generic behaviors of paramagnetic-to-ferromagnetic transition are understood within the framework of the double-exchange theory,[1] which includes only the transfer integral t of the e_g electrons and on-site exchange interaction (Hund's-rule coupling J_H) between the itinerant e_g electrons and localized t_{2g} spins ($S=3/2$). To explain the ''colossal'' value of the magnetoresistance for the system with small one-electron bandwidth W, however, we need an additional mechanism for carrier localization above T_C as well as the magnetic-field release of the localization.

The most probable mechanism to supplement the double-exchange model is the strong electron-lattice interaction due to the Jahn-Teller (JT) instability[2] inherent to the constituent Mn^{3+} ions with four $3d$ electrons. In fact, several optical data[3,4] suggest formation of small polarons (or JT polarons) in the paramagnetic insulating state above T_C. According to their scenario, the insulator-metal transition can be viewed as transformation of small polarons into bare electrons (or large polarons) due to the enhanced transfer integral t in the perfectly spin-polarized ferromagnetic state. Here, we should be careful of the concept of ''small polarons'' because doped manganites is a dense carrier system. In such a system, correlation among the JT polarons becomes significant. In some case, the correlated polarons spontaneously gather to form a cluster state, analogously to the case of the cooperatively JT distorted charge-ordered state of $La_{0.5}Ca_{0.5}MnO_3$.[5] Recently, Mori *et al.*[6] have performed low-temperature electron-diffraction measurements for $La_{1-x}Ca_xMnO_3(x=1/2, 2/3$ and $3/4)$, and have found stripe patterns that are ascribed to two heavily JT distorted diagonal $Mn^{3+}O_6$ pairs. This observation suggests that such a cooperatively JT distorted structure is stable in doped manganites.

In this paper, we have systematically investigated temperature evolution of absorption spectra in thin films of the doped manganites $R_{0.6}Sr_{0.4}MnO_3$. With changing the averaged ionic radius $\langle r_A \rangle$ of the perovskite A site, we can control the W value; the ferromagnetic metallic phase is suppressed with reducing $\langle r_A \rangle$ and disappears below $\langle r_A \rangle \approx 1.32$ Å ($R=Sm$).[7] We have found that the spectral evolution of the $\sim$1.5-eV band shows a close resemblance with that of the prototypical charge-ordered compound $Pr_{0.6}Ca_{0.4}MnO_3$.[8] This suggests formation of the cluster state of the JT polarons, or the short-range charge-ordered state, in the paramagnetic insulating state.

Thin films of doped manganites $R_{0.6}Sr_{0.4}MnO_3$ with thickness of $\sim$100 nm were fabricated using a vacuum pulsed-laser deposition apparatus. Calcined powder was pressed into a pellet with a size of 20 mm$\phi \times$5 mm and sintered at 1300 °C for 48 h. An excimer laser beam of 248 nm with a repetition rate of $\approx$5 Hz and pulse energy of $\approx$180 mJ was focused onto the target in the vacuum chamber. The compound was deposited onto a MgO (100) substrate that was heated at 850–950 °C in an atmosphere of $\approx$300 mTorr oxygen. The fabricated films were annealed in 760 Torr oxygen atmosphere for 1 h, and then slowly cooled down. The MgO substrate is transparent in a wide energy region of 0.1–5.0 eV, and is suitable for the optical measurements. X-ray diffraction measurements revealed that the obtained films were (110)-oriented in the pseudocubic setting. Thickness of the films was determined by a scanning electron microscope. Critical temperature T_C for the insulator-metal transition was determined from the inflection point of the M-T curve. Absorption coefficient $\alpha(\omega)$ was determined from transmission spectra using the standard formula neglecting a multireflection effect, since the optical density of our films is larger than 0.7 in the spectral region investigated. Reflectance correction is not performed, since the reflectivity is low and nearly constant $(1-R \sim 0.85)$ in the spectral
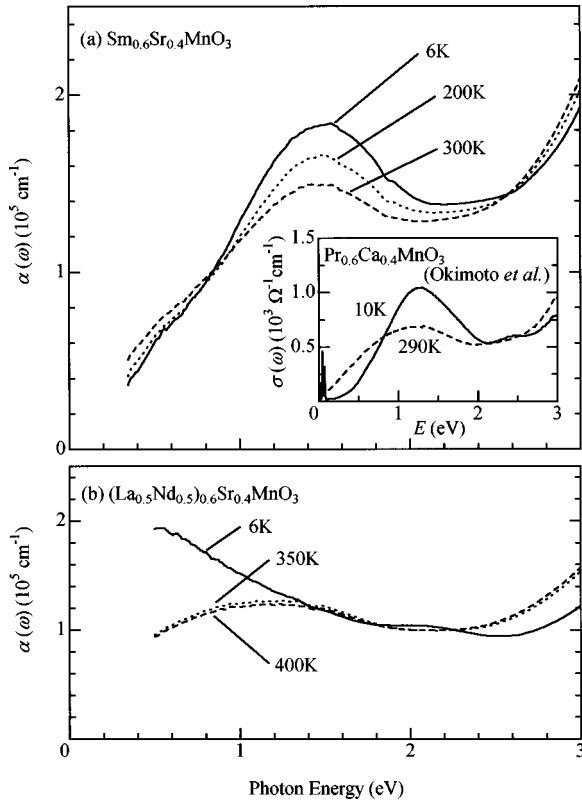
FIG. 1. Temperature dependence of absorption spectrum $\alpha(\omega)$ for (a) $Sm_{0.6}Sr_{0.4}MnO_3$ and (b) $(La_{0.5}Nd_{0.5})_{0.6}Sr_{0.4}MnO_3$. Inset shows optical conductivity $\sigma(\omega)$ for $Pr_{0.6}Ca_{0.4}MnO_3$ single crystal (cited from Ref. 8).

FIG. 2. Differential absorption spectra $\Delta\alpha(T)$ for (a) $Sm_{0.6}Sr_{0.4}MnO_3$ (insulator), (b) $(Nd_{0.25}Sm_{0.75})_{0.6}Sr_{0.4}MnO_3$ ($T_C = 90$ K), and (c) $(Nd_{0.5}Sm_{0.5})_{0.6}Sr_{0.4}MnO_3$ ($T_C = 175$ K). Solid and broken curves are for above and below T_C.

region investigated (0.4 – 5.0 eV). Resistivity of the films was measured by a conventional four-probe method. The ρ-T curves for $R = $ Sm, $Nd_{0.25}Sm_{0.75}$, and $Nd_{0.5}Sm_{0.5}$ are of activation-type above T_C with activation energy E_a of ~ 0.2 eV. The ρ value steeply decreases below Curie temperature T_C, showing an insulator-metal behavior.

Figure 1(a) shows absorption spectrum $\alpha(\omega)$ for $Sm_{0.6}Sr_{0.4}MnO_3$, whose resistivity is typical of an insulator. $\alpha(\omega)$ spectrum shows strong temperature dependence; the spectral weight below ~ 0.9 eV transfer around ~ 1.5 eV with decreasing temperature. Such a spectral evolution has a close resemblance with that of $Pr_{0.6}Ca_{0.4}MnO_3$, which shows the charge-ordering transition at $T_{CO} = 220$ K.[9] The inset of Fig. 1(a) shows optical conductivity $\sigma(\omega)$ spectra[8] (electronic field E parallel to the b axis) for $Pr_{0.6}Ca_{0.4}MnO_3$: solid and broken spectra stand for below and above T_{CO}, respectively. In the low-temperature charge-ordered state, the nominally Mn^{3+} and Mn^{4+} species alternate within the ab plane in the pseudocubic setting. Then, the moved spectral weight around 1.3 eV corresponds to transition of an e_g electron from the JT-distorted $Mn^{3+}O_6$ site to the undistorted $Mn^{4+}O_6$ site. The same charge-ordering pattern is commonly observed in doped manganites with commensurate hole concentration ($x = 1/2$), e.g., $Nd_{0.5}Sr_{0.5}MnO_3$,[10] $(La,Nd)_{0.5}Sr_{0.5}MnO_3$[11] and $(Nd,Sm)_{0.5}Sr_{0.5}MnO_3$.[12]

In the lower panel of Fig. 1, we show $\alpha(\omega)$ spectra for ferromagnetic $(La_{0.5}Nd_{0.5})_{0.6}Sr_{0.4}MnO_3$ ($T_C = 315$ K) with large W. With decreasing temperature below T_C, spectral weight above ~ 2.2 eV transfers to the lower-energy region
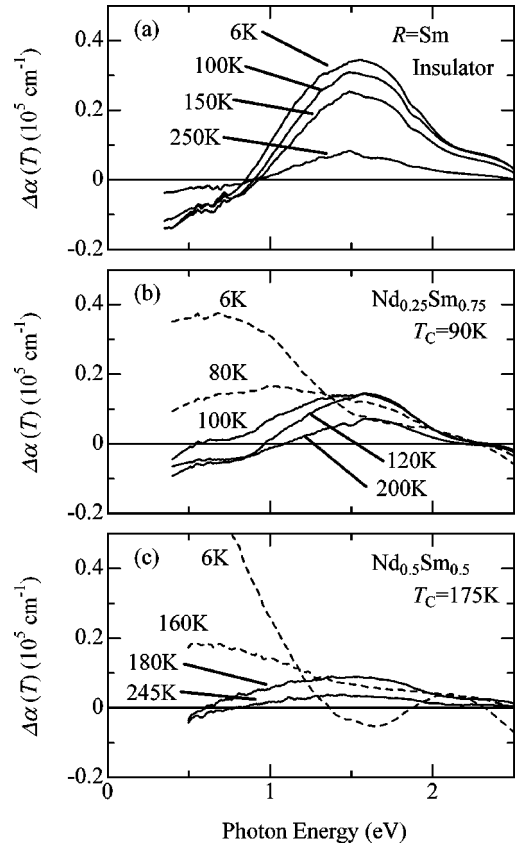
below ~ 1.4 eV. The higher-lying component is assigned to the interband transition between the exchange-split bands,[7] while the lower-lying component is to the intraband transition (so-called Drude-band). The temperature dependence of the interband transition is well reproduced by that of $1 - (M/M_s)^2$, where M and M_s are the induced and saturated magnetizations, respectively, as expected from a mean-field-type interpretation.

To analyze the spectral behavior in more detail, we define differential absorption spectrum $\Delta\alpha(T)$ as

$$\Delta\alpha(T) = \alpha(T) - \alpha(T_{max}), \qquad (1)$$

where T_{max} is 300 K. In Fig. 2 are shown the differential absorption spectra $\Delta\alpha(T)$ for (a) $R = Sm$ (insulator), (b) $Nd_{0.25}Sm_{0.75}$ ($T_C = 90$ K), and (c) $Nd_{0.5}Sm_{0.5}$ ($T_C = 175$ K): solid and broken curves stand for above and below T_C. In the case of $R = $ Sm [Fig.2(a)], the ~ 1.5-eV absorption band grows as temperature decreases. Overall spectral evolution in the insulating state ($\geqslant T_C$; solid curve) is similar for $R = Nd_{0.25}Sm_{0.75}$ [Fig. 2(b)] and $Nd_{0.5}Sm_{0.5}$ [Fig. 2(c)]. With further decreasing temperature below T_C, however, the ~ 1.5-eV band merges into the Drude-like component (see broken curves in Fig. 2). These have been interpreted in terms of crossover from JT polarons to large polarons due to the enhanced W in the perfectly spin-polarized ferromagnetic state.[4] In Fig. 3 we plotted the spectral weight S:
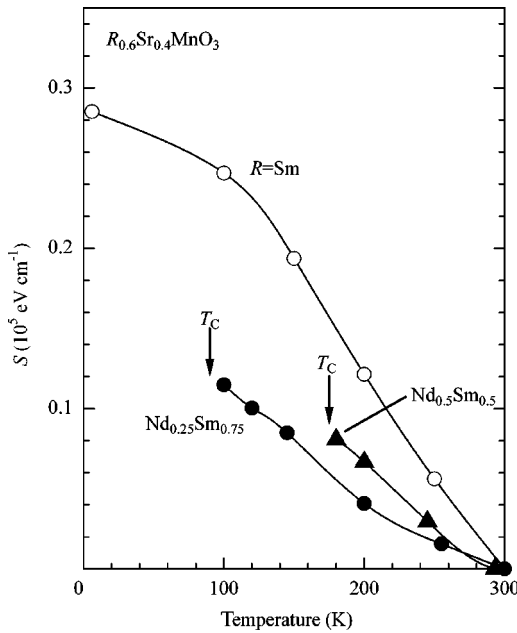
FIG. 3. Spectral weight S of the ~ 1.5-eV band against temperature. Downward arrows represent the insulator-metal transition temperature T_C.

$$S \equiv \int_{1.0\,\mathrm{eV}}^{2.2\,\mathrm{eV}} \Delta\alpha(\omega)\,d\omega. \qquad (2)$$

In all cases, S steeply increases on approaching T_C from the high-temperature side, and then disappears below T_C. If the absorption band were due to excitation of *isolated* small polarons,[13] growth of the band means increase in number of small polarons. This is rather curious because the estimated polaron binding energy $[E_p \approx 0.8$ eV (Ref. 4)$]$ is much higher than the energy scale of temperature. In addition, activation energy E_a (~ 0.2 eV) for resistivity is smaller than the E_p value. These contradictions imply that polaron correlation plays a significant role in temperature evolution of the absorption band. The close resemblance of the spectral evolution (see Fig. 1) suggests that the *cluster* state of JT polarons is realized in the insulating state.

The most plausible local structure of the cluster state is the cooperatively JT distorted state observed in the low-temperature phase of $La_{1/2}Ca_{1/2}MnO_3$.[14] In this structure, the gain in lowering the elastic energy overwhelms the cost of Coulomb energy. Nearly free electrons outside of the cluster can mediate the charge transport, but are amenable to the scattering at the cluster boundaries causing the insulating behavior. These electrons are captured at the cluster boundaries as temperature decreases. Then, the clusters increase in size, causing growth of the ~ 1.5-eV band as observed (see Fig. 3). Application of an external magnetic field (or further cooling) enhances the t value via alignment of the local spins, and hence, erases the clusters to achieve the ferromagnetic metallic state. This is the scenario of the field- and temperature-induced insulator-metal transitions.

In summary, we have systematically investigated the absorption spectra of doped manganites, and have revealed an anomalous temperature dependence of the ~ 1.5-eV band. The observation suggests formation of a JT cluster in the insulating state within the undistorted matrix. We believe that formation of the cluster is the origin of the colossal magnetoresistance as well as the insulator-metal behavior of doped manganites. Electron diffraction and Raman-scattering measurements are now in progress to get direct evidence of the cluster formation in the paramagnetic insulating state.

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[14] S. Mori, N. Yamamoto, and Y. Moritomo (unpublished) have performed electron diffraction measurements for $Sm_{0.6}Sr_{0.4}MnO_3$, and observed $(1/2,0,0)$ diffused scattering at 125 K. The position is the same as that in the cooperatively JT distorted state of $La_{1/2}Ca_{1/2}MnO_3$. This observation strongly suggests formation of JT clusters in the paramagnetic insulating state.