Optical Reflectivity Study on Magnetoresistive Manganese Perovskites: Impurity Effect on the Ferromagnetic-Metallic and Charge-Ordered States

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Abstract

Impurity effect on manganese perovskites are investigated by the optical reflectivity measured on cleaved surfaces of the single crystals. The Al impurity affects optical conductivity $\sigma(\omega)$ of ferromagnetic-metallic $La_{1-x}Sr_xMnO_3$ over a wide energy range up to 1 eV or higher, contrary to the simple-Drude picture. The energy gap of the charge-ordered (CO) state in $Nd_{0.5}Sr_{0.5}MnO_3$ is about 0.5 eV, much larger than that suggested by the previous studies using polished surfaces. This indicates that the CO state can be easily damaged by external disorder.

Key words: manganese perovskite; CMR; optical conductivity; impurity effect

Physical properties of manganese perovskites are sensitive to impurities at the Mn site. A small amount of Cr melts the charge-ordered (CO) state [1] and a small amount of Al destroys the ferromagnetic-metallic (FM) state [2] and induces the unconventional localization state [3]. Therefore, Mn-site substitution is a promising method by which to design the properties of these materials, which have been investigated in detail due to the obvious potential for industrial applications utilizing the colossal magnetoresistance (CMR). In order to get insight more into how the electronic states vary with doping of impurities and/or randomness, we have investigated the optical spectra.

All of the single crystals were grown by a floating-zone method. Electrical resistivity $\rho(T)$ was measured using a dc four-probe method. Near-normal incident reflectivity $R(\omega)$ was measured on the cleaved surfaces using a Fourier-type interferometer (0.005−1.6 eV), a grating spectrometer (0.8−6.6 eV), and a Seya-Namioka type spectrometer for vacuum-ultraviolet synchrotron radiation (4.0−40 eV) at Okazaki National Research Institutes. Optical conductivity $\sigma(\omega)$ was deduced from $R(\omega)$ via a Kramers-Kronig transformation. The details were described elsewhere [2–5].

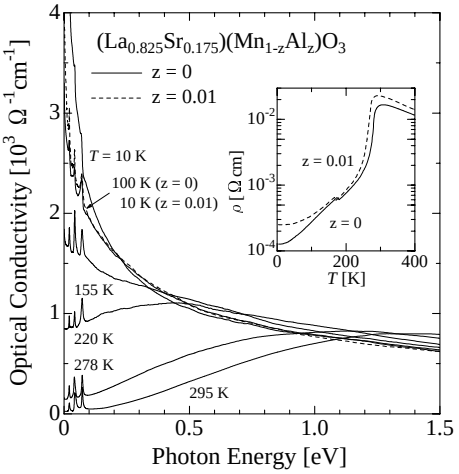

Fig. 1. Temperature-dependent optical conductivity spectra $\sigma(\omega)$ of $(La_{0.825}Sr_{0.175})(Mn_{1-z}Al_z)O_3$ for z=0 (solid line) and z=0.01 (dashed line). Inset shows the dc resistivity $\rho(T)$.

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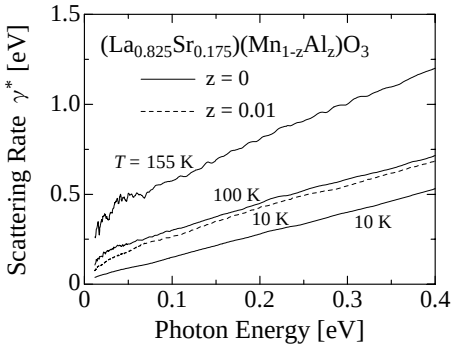

Fig. 2. Frequency-dependent (renormalized) scattering rate γ^* of $(La_{0.825}Sr_{0.175})(Mn_{1-z}Al_z)O_3$ for z=0 (solid line) and z=0.01 (dashed line).

Figure 1 shows $\sigma(\omega)$ of Al-doped $La_{0.825}Sr_{0.175}MnO_3$ and the inset shows the $\rho(T)$ data. The $\sigma(\omega)$ spectra of the Al-free crystal is characterized by the coherent-to-incoherent crossover [5]. $\sigma(\omega)$ exhibits a slowly decaying quasi-Drude peak only below a certain temperature $T^* \simeq 200$ K, which is lower than Curie temperature T_C=283 K. Above T^* $\sigma(\omega)$ is characterized by a finite-energy peak regardless of metallic $\rho(T)$. $\sigma(\omega)$ of the Al 1%-doped crystal at 10 K almost coincides with that of the Al-free crystal at 100 K over the entire ω range relevant to the charge dynamics (up to 1 eV or higher).

These characteristics are more clearly described by the extended-Drude analysis. The quasi-Drude response below T^* can be numerically expressed by a monotonic ω-linear dependence of scattering rate γ^* over a wide energy range up to 0.4 eV (Fig. 2). The Al doping does not alter this characteristic behavior; γ^* of the Al 1%-doped crystal at 10 K coincides with γ^* of the Al-free crystal at 100 K. The dc conductivity $\sigma_{dc} = \rho^{-1}$ of the Al 1%-doped crystal at 10 K is almost identical to that of the Al-free crystal at 100 K. For the manganites, the overall feature of the charge dynamics up to 1 eV or higher seems to be dominated by σ_{dc} unless the doped Al destroys the metallic state [3]. The above features are incompatible with the simple-Drude response, which predicts that impurity effect is limited below a low-energy region. The one-component model seems to offer a more useful description of the charge dynamics in the manganites.

Then we discuss the effect of the randomness on the optical spectra of the CO state. Figure 3 shows $R(\omega)$ (top panel) and $\sigma(\omega)$ (bottom panel) of $Nd_{0.5}Sr_{0.5}MnO_3$ at 10 K obtained on cleaved (solid line) and polished (dashed line) surfaces. Below 160 K the charges and orbitals are ordered with the CE-type antiferromagnetic spin structure in $Nd_{0.5}Sr_{0.5}MnO_3$ [4,6]. Not only for the FM phase [7] but also for the CO phase, the optical spectra are susceptible to the surface deterioration; the charge gap estimated from

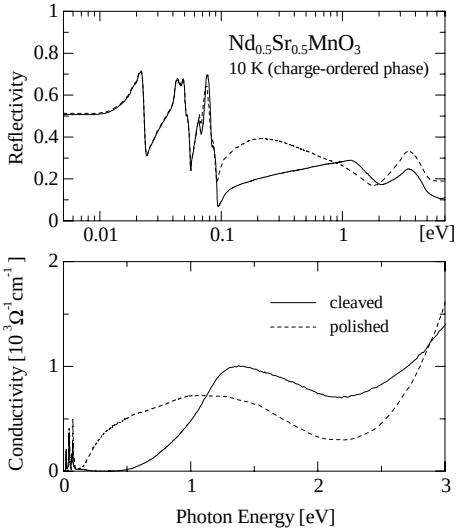

Fig. 3. Optical reflectivity (top panel) and conductivity (bottom panel) spectra of $Nd_{0.5}Sr_{0.5}MnO_3$ at 10 K obtained on cleaved (solid line) and polished (dashed line) surfaces.

$\sigma(\omega)$ obtained on the polished surface (0.1 eV) becomes much smaller than that estimated from $\sigma(\omega)$ obtained on the cleaved surface (0.5 eV). The CE-type CO state can be easily destructed by extrinsic disorder. The gap value 0.5 eV is comparable with that estimated from the data obtained on the cleaved surface of $La_{0.5}Sr_{1.5}MnO_4$ [8], which undergoes the same CE-type charge ordering at low temperatures. The rather small value ($\leq$0.1 eV) reported previously [9] originates from the surface deterioration. The intrinsic gap value of the CE-type CO state is about 0.5 eV.

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