

Optical-conductivity spectra of $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$: Filling-dependent effect of the electron correlation

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Optical-conductivity spectra have been measured on the correlated electron system $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ ($0 \leq x \leq 1$) in order to determine how the electronic structure depends on the filling of the $3d$ -electron conduction band. While metallic resistivity was observed in all samples with $x \geq 0.1$, the optical-conductivity spectra have revealed a critical change in the electronic structure: The effective carrier mass, which has been deduced by analysis of the optical-conductivity spectra and the energy-loss function, is critically enhanced as the $x = 1$ filling case (Ti $3d^1$ configuration) is approached, perhaps due to electron-correlation effects, in a manner reminiscent of the Mott-Hubbard transition.

Extensive studies on the high- T_c superconducting cuprates have led to renewed interest in strongly correlated electron systems, particularly in the drastic change in the nature of their electronic states with carrier doping. With increasing or decreasing the formal valence of copper from $2+$, the layered cuprate compounds show a crossover behavior from an antiferromagnetic insulator with localized d electrons on Cu sites to a high- T_c superconductor (or unconventional metal above T_c). Such a transitional behavior is partly due to the fact that the Coulomb correlation of $3d$ electrons loses its effect gradually with increasing departure from the half-filling case. A similar change in the electronic structure is expected to occur in a wide class of transition-metal oxides, in which electron correlations in a relatively narrow d band must be taken into account. The purpose of this paper is to report a spectroscopic investigation of the change in electronic states in titanium oxide compounds with varying formal Ti valence ($3d$ -electron configuration) from $4+ (3d^0)$ to $3+ (3d^1)$.

We study the mixed-crystal system $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ with a perovskite-like structure.^{1,2} The end compounds SrTiO_3 ($x = 0$) is a closed-shell (i.e., no d electron) oxide with cubic perovskite structure. The topmost valence and lowest unoccupied conduction bands in SrTiO_3 are of O $2p$ and Ti $3d$ character, respectively, and the band gap is ca. 3.2 eV.³ The other end compound, LaTiO_3 , is known to be barely metallic or semiconducting, showing a magnetic phase transition into the ordered Ti-spin states (weakly ferromagnetic due to the spin canting) below the critical temperature 125–149 K. The formal valence of Ti in this compound is $3+$, the number N of $3d$ electron per Ti site being exactly 1 ($3d^1$ configuration). Hereafter, let us call this situation “integer ($N = 1$) filling.” As in other $L\text{TiO}_3$ compounds (L being a rare-earth ion),⁹ LaTiO_3 shows an orthorhombically distorted perovskite structure or the so-called GdFeO_3 -type structure, in which the Ti-O-Ti angle ($\sim 157^\circ$) deviates from 180° .⁹ We have prepared a series

of solid solutions, $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$, with the aim of finely controlling the filling of the $3d$ conduction band. To see a change in the electronic structure as a function of the filling parameter $N (=x)$, we have obtained optical spectra in these mixed crystals.

The samples were melt grown by the floating-zone method in a reducing or inert atmosphere. First, we prepared sintered bars of ceramics using mixtures of appropriate quantities of La_2O_3 , Ti_2O_3 , and SrTiO_3 at 1500°C in vacuum. Then, the sintered bars were melted in Ar or Ar (93%) and H_2 (7%) atmosphere using the floating-zone furnace equipped with two halogen incandescent lamps and hemielliptic focusing mirrors. X-ray-diffraction patterns of those samples indicated that all the samples were single phase and that the diffraction peaks could be indexed with orthorhombic or cubic lattice structures. The cubic to orthorhombic structural change was observed to take place around $x \sim 0.6$ at room temperature. Upon the structural transition, however, we have observed distinct changes neither in the lattice parameters nor in electronic properties (such as resistivity,^{1,10} magnetic susceptibility,¹⁰ and optical conductivity).

It is known^{7,8} that the electronic and magnetic properties of LaTiO_3 ($x = 1$) are very sensitive to nonstoichiometry of the sample. Results of thermogravitation analysis indicate that the average valence of Ti in the presently synthesized sample was found to be ca. $3.06+$, which is slightly larger than the expected value (3.00). This is perhaps due to a small amount of La deficiency (ca. 2%) or oxygen excess (ca. 1%). We have observed an antiferromagnetic transition around 100 K in our nominally $x = 1$ sample, which is slightly lower than the previously reported values, 125 K (Refs. 4–6 and 8) or 149 K (Ref. 7), perhaps due to a larger deviation of the Ti valence from $3.00+$. Keeping in mind such a critical effect of nonstoichiometry in the $x = 1$ sample, we will denote hereafter the sample composition by the nominal one.

For Sr-doped samples, including low-Sr-content sam-

ples with $x = 0.98$ and 0.95 , we have not observed any magnetic phase transition at lower temperatures. For samples with $0.1 \leq x \leq 1.0$, we have observed a typically metallic behavior of the resistivity ρ , which can be approximately expressed by the relation $\rho - \rho_0 \propto T^2$, typical of metals with highly correlated electrons. (Here, ρ_0 is the residual resistivity, $10\text{--}100 \mu\Omega \text{ cm}$.) The lowest resistivity was attained in a sample with $x \sim 0.5$.

The reflectivity spectra of $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ were measured on specularly polished surfaces of melt-grown samples at room temperature ($295\text{--}300 \text{ K}$) in the photon-energy range $0.05\text{--}20 \text{ eV}$. The reflectance was obtained with use of Fourier-transform spectroscopy in the infrared region and, at higher photon energies, was measured by use of grating spectroscopy. For a light source in the vacuum ultraviolet region, we utilized synchrotron radiation at UV-SOR, Institute for Molecular Science (Okazaki). The absolute reflectivity was determined by comparison with the known reflectivity of a gold film measured with the same optical alignment. The optical conductivity spectra were obtained by Kramers-Kronig analysis of the reflectivity data.² In practice, the reflectivity data below 0.05 eV were extrapolated toward zero frequency by the Hagen-Rubens approximation [$1 - R(\omega) \propto \sqrt{\omega}$] for the metallic samples ($x \geq 0.1$). For the high-frequency extrapolation ($> 20 \text{ eV}$), we applied the Drude extrapolation $R(\omega) \propto \omega^{-4}$. Thus, calculated values of the $\omega = 0$ conductivity were in reasonable agreement with the dc conductivity data by transport measurements on the same samples within a relative error of 40%.

In Fig. 1 we show the spectra of the optical conductivity

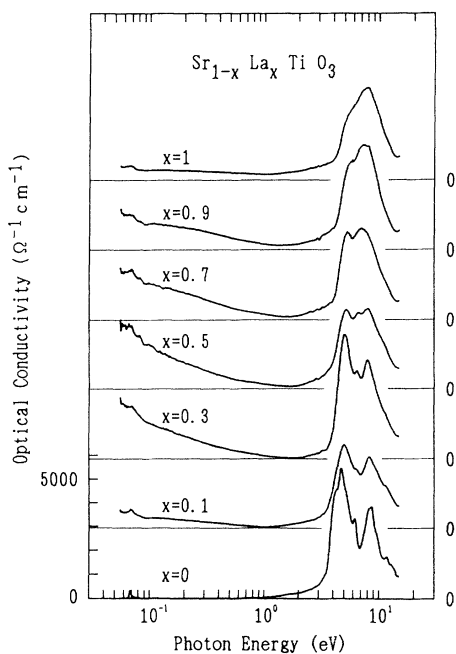


FIG. 1. Optical-conductivity spectra of $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ at room temperature. (The nominally $x = 1$ sample showed an average Ti valence of ca. $3.06+$ and suffered from a slight nonstoichiometry of the composition. See the text for details.)

ty $\sigma(\omega)$ in $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ at room temperature in a logarithmic scale of photon energy. The spectral features are composed of two parts: a Drude-like photoresponse below 1.5 eV due to the charge carriers and interband transitions observed above 3 eV . In the insulating $x = 0$ (SrTiO_3) sample, some optical phonons⁸ show up as sharp peaks in the infrared region of the $\sigma(\omega)$ spectra, which seem to persist faintly in the metallic phase with $x \geq 0.1$. The infrared spectral weight due to the charge carriers increases monotonically with x up to ca. 0.5 , reflecting the increase of carrier density. However, the spectral weight rather decreases beyond $x \sim 0.5$ in spite of an apparent increase in the number of d electrons. In particular, samples with x close to the end ($x = 1.0$) show a barely metallic photoresponse with a much reduced optical conductivity, reminiscent of the insulating sample (see, for example, the spectrum of the insulating $x = 0$ sample).

The relatively lower-lying interband transitions, which shows up in the $\sigma(\omega)$ spectra in the energy region $3\text{--}6 \text{ eV}$, are due to transitions from O $2p$ to Ti $3d$ (t_{2g} -like) states. The variation of spectral shape is ascribed to the partial filling of the $3d$ band (the final state). A detailed discussion on these high-energy excitations will be given elsewhere. Here we focus on the filling-dependent variation of the low-energy ($< 2 \text{ eV}$) spectra.

We show in Fig. 2 the $\sigma(\omega)$ spectra below 2 eV in a magnified scale together with the similarly deduced spectra of the energy-loss function, $\text{Im}(-1/\epsilon)$ (shown by dashed lines). The peaks of the energy-loss function represent the $k \sim 0$ plasmon excitations and approximately correspond to the plasma edges in the reflectance spec-

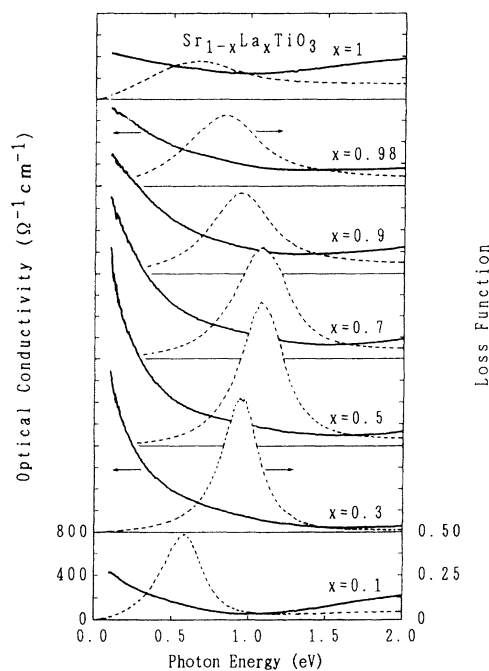


FIG. 2. Low-energy spectra of optical conductivity $\sigma(\omega)$ (solid lines) and energy-loss function $\text{Im}(-1/\epsilon)$ (dashed lines) in $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$.

tra.² In accord with the observed variation of the infrared spectral weight, the peak of the energy-loss function increases with x in the region $0 < x < 0.6$, but rather decreases in approaching the end ($x = 1$) and also shows an appreciable broadening of the profile. According to conventional Drude model, the plasmon peak energy ($\hbar\omega_p'$) is related to the ratio of electron density (n) to the effective mass (m^*); $\omega_p'^2 = 4\pi ne^2/m^*\epsilon_\infty$. [The high-frequency dielectric constant ϵ_∞ (~ 4) is nearly independent of x judging from the ϵ_1 data at the photon energy (around 2.5 eV) well above the plasma edge but below the interband transition region.] The results shown in Fig. 2 indicate that the value of n/m^* is anomalously suppressed as $N = 1$ filling is approached. On the basis of these optical spectra, the $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ compound seems to undergo a continuous phase change to a barely metallic or insulating state with x approaching the $N = 1$ filling ($x = 1$). Our interpretation for this transitional behavior is, as will be argued in the following, that the effective d -electron mass m^* near the Fermi level is critically enhanced as the end point $x = 1$ is approached because of the increasing importance of electron correlations (or so-called Hubbard U term).

To analyze the variation of the low-energy spectra with filling, we have adopted the extended Drude model,¹¹ in which the frequency dependence of the effective electron mass m^* and scattering rate γ^* is taken into account. m^* and γ^* can be deduced from the complex dielectric constants by the relations

$$m^* = 4\pi e^2 n \gamma^* / \epsilon_2 \omega (\omega^2 + \gamma^{*2})$$

and

$$\gamma^* = \omega \epsilon_2 / (\epsilon_\infty - \epsilon_1).$$

Here, the electron density n can be taken to be x/v_c , where v_c is the unit-cell volume (including one Ti site) with the pseudocubic setting. In other words, we start with the weak-correlation limit or a simple-band model that the d -electron conduction band is simply filled by the chemical doping procedure, but allowed a frequency (energy) variation in m^* and γ^* . The results for m^* are shown in Fig. 3 for a series of compounds.

As seen in Fig. 3, m^* is almost frequency independent for $x \leq 0.3$, representing the fact that the reflectivity spectra and conductivity spectra are well fitted by the conventional Drude model. The value of m^*/m_0 (m_0 being the bare electron mass) is ~ 2 , which is consistent with the value predicted by the band calculation for SrTiO_3 .¹² With increasing x above 0.3, however, the enhancement of m^* value as well as its frequency dependence gradually becomes more prominent. In particular, the m^* value in the compounds with x close to 1 is significantly enhanced at lowering frequency (photon energy).

In the inset of Fig. 3 is plotted a variation of the m^* values estimated at 0.1 eV (with closed circles) by this extended Drude model. For comparison, we have also plotted (with open squares) the m^* values, which are deduced from the peak position ($\hbar\omega_p'$) of the energy-loss function (plasmon excitation), assuming the above-mentioned rela-

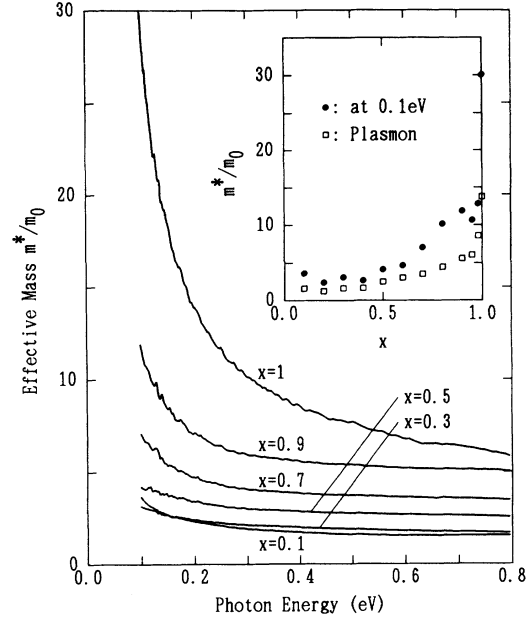


FIG. 3. Energy dependence of carrier mass (m^*) in $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$. Inset shows the x dependence of m^* values estimated at 0.1 eV (closed circles) by the extended Drude analysis and deduced from the plasmon peak energy (open squares) based on the conventional Drude analysis. (See the text for details.)

tion based on the conventional Drude model. The latter value for m^* corresponds to the high-energy mass, e.g., at 0.5–1.0 eV, based on the extended Drude model (Fig. 3). Both the low-energy (0.1 eV) and high-energy (plasmon energy) masses are observed to increase for $x > 0.5$ and critically enhanced as $N = 1$ filling is approached. Clearly, the effect is more conspicuous for the low-energy mass.

To understand the origin of enhancement of m^* , it is useful to note electronic properties in the other $L\text{TiO}_3$ crystals (L representing a trivalent rare-earth ion). LaTiO_3 and CeTiO_3 have been known to be barely metallic around room temperature, but the resistivity in $L\text{TiO}_3$ with a smaller L^{3+} ion shows a thermally activated behavior. Typically, YTiO_3 is an insulator with a localized half spin on each Ti site and undergoes a ferromagnetic phase transition at ca. 30 K. Recent optical¹⁰ and photoemission¹⁴ measurements have indicated the existence of a fairly large d -band gap (> 0.5 eV) and no Drude-like ir photo-response. Depending on the radius of L^{3+} ions or equivalently on the tolerance factor, the Ti-O-Ti angles in the orthorhombic $L\text{TiO}_3$ crystal deviate from 180° ; for example, they are 157° and 158° for LaTiO_3 and 140° and 144° for YTiO_3 .⁹ Such an orthorhombic distortion may result in a reduction of the hopping interaction or one-electron bandwidth W of d electrons and hence in a variation of effective electron correlations as scaled with W/U in the simple Hubbard model.¹³

Keeping in mind such systematic behavior of $L\text{TiO}_3$ systems, we may consider some possible origins of the barely metallic behavior in $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ systems in the vicinity of $x = 1$. The following two features should be

included: (1) x -dependent change of lattice distortion, which may cause a reduction of the one-electron band width W with x , and (2) change of the band filling, which should cause a drastic change in the electronic structure in the case of strong correlation (small W/U). The former alone might cause a carrier localization (small-polaron effect) due to electron-lattice interactions, without invoking the electron correlation U . However, such a scenario can account neither for the filling-dependent behavior of the whole conductivity spectra over a fairly wide energy region (Fig. 2) nor for the fairly large charge gap and magnetically ordered phase observed in other $LTiO_3$ compounds, e.g., in $YTiO_3$ crystal.^{4,10,14} A more plausible explanation can be given based on the filling-dependent effect of the d -electron correlation. At $N=1$ filling, the Coulomb repulsion interaction U may cause an

enhancement of the electron mass.¹³ However, the effect of electron correlations depends not only on the W/U value at integer ($N=1$) filling but also on the filling itself. Our interpretation for the transitional behavior for m^* is that $Sr_{1-x}La_xTiO_3$ verges on being a Mott-Hubbard insulator as x approaches $N=1$ filling, in which case the correlation energy U works most effectively. Such a critically filling-dependent enhancement of m^* has been predicted by recent theoretical investigations of the Hubbard model.^{15,16}

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