Spectral Weight Transfer of the Optical Conductivity in Doped Mott Insulators

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Optical spectra have been systematically investigated for $R_{1-x}Ca_xTiO_3$ with various rare earth ions R (= La, Pr, Nd, Sm, and Y) as a typical three-dimensional correlated electron system, in which both the electon-correlation strength (U/W) and the band filling (n) can be varied. With a decrease of n from 1, the spectrum of the Mott-gap excitation collapses and the Drude part evolves. We found that the rate of the Drude-part evolution with the nominal hole-doping level δ ($= 1 - n$) is critically enhanced as U/W approaches the critical value $(U/W)_c$ for the bandwidth-controlled Mott transition.

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The electron-correlation effect and resultant electron localization (Mott insulator) have long been an important subject of condensed matter physics [1]. In the 1970s, V_2O_3 and related compounds were extensively studied [2] as a typical system for the Mott transition, i.e., the transition from a metallic state to a Mott insulator under variation of the strength of the electron correlation (U/W, where U is the on-site Coulomb repulsion energy and W the one-electron bandwidth of the conduction band). The discovery of high-T_c cuprate superconductors has revived interest in this problem [3,4], as well as provided a new viewpoint on the problem of the metal-insulator transition that is a filling-controlled Mott transition rather than the conventional bandwidth-controlled Mott transition. The end compound of the cuprates is a Mott insulator with one hole per Cu site, but it becomes metallic with hole or electron doping, i.e., under variation of band filling (n). Associated with this phase change, the collapse of the correlation gap of the insulating phase and the evolution of an in-gap state were observed, for example, in the spectra of optical conductivity [5], electron energy loss [6], and x-ray absorption [7]. Recent experimental investigations [8–12] have indicated that such a change of electronic structure with n is a generic feature of $3d$-transition-metal oxides with strong electron correlation. Several theoretical studies on this problem [13–16] have also been made with variation of two parameters, i.e., band filling n and strength of electron correlation U/W. In this Letter, we describe the systematic experimental investigation by means of optical spectroscopy of the change of electronic structure in doped Mott insulators under variation of n and U/W for the perovskite-type titanate oxides.

The perovskite-type $R_{1-x}Ca_xTiO_3$ (R = rare earth) that we have chosen here is a unique three-dimensional system suitable for such a systematic investigation [8–11]. The end compound ($RTiO_3$) of this family is a Mott insulator with one electron per Ti site ($3d^1$), and a change of the species of R (a change of the ionic radius) induces a change of the Ti-O-Ti bond angle, which leads to a change of the transfer energy of electrons between adjacent Ti sites [10,11]. In other words, we can control the magnitude of W by changing R. Also, we can control the number of electrons per Ti site (n) from 1 ($RTiO_3$) to 0 by substituting Ca^{+2} (or Sr^{+2}) for R^{3+}, which leads to the transition of the system to a metallic phase [9]. Accordingly, a systematic change of R (i.e., U/W) and Ca concentration (i.e., n) enables us to investigate the electronic structure in the two-dimensional parameter space (U/W and n). Here, we quantitatively discuss the change of electronic structure under variation of the two parameters, based on the optical spectra of this system. The result indicates that the rate of electronic-structural change with nominal hole doping ($\delta = 1 - n$) is strongly dependent on the value of U/W for the parent Mott insulators, and is critically enhanced as U/W approaches the critical value for the bandwidth-controlled Mott transition.

Samples of $R_{1-x}Ca_xTiO_3$ were prepared with R = La, Pr, Nd, Sm, and Y, and with various Ca concentrations, by the floating zone method similar to previous works [9]. The band filling (n), i.e., the nominal number of d electrons per Ti site, which would relate to the Ca concentration x as $n = 1 - x$ in the ideal case, is affected by slight oxygen off-stoichiometry; thus we determined the accurate value of n from a thermogravimetric analysis of the Ti valence. For the estimate of the strength of electron correlation (U/W), we have taken the following procedure. We made a tight-binding calculation of the band dispersion using Harrison's parametrization [17] for the Ti $3d$ level and the oxygen $2p$ level, taking account of the Ti-O-Ti bond angle (θ, which was determined by neutron scattering measurements for the end compounds [18]), and obtained the one-electron bandwidth of the conduction band (W). Within the range of the bond angle of the present compounds, the calculated W value is 2.04–2.45 eV (~20% change) and is approximately a linear function of $\cos\theta$. We assumed that θ is constant against a small increase of x ($0 \leq x \leq 0.3$) for each series of $R_{1-x}Ca_xTiO_3$, and hence that W is independent of n. Concerning U, we assumed that U is constant [19] against the variation of R and x. Therefore, the strength of electron correlation in these compounds is given by the calculated value of W^{-1}.

We measured the reflectivity from 0.06 to 40 eV at room temperature. We used a microscope spectrometer in the infrared region, with which we can obtain a more accurate value of reflectivity than by the usual method. We estimated that the accuracy of the absolute value is within 3% below 3 eV. Optical conductivity spectra $\sigma(\omega)$ were obtained by Kramers-Kronig transformations, with constant-reflectivity extrapolation for $\hbar\omega < 0.06$ eV and $R = \omega^{-1/4}$ extrapolation for $\hbar\omega > 40$ eV. We also used the same procedure for the reflectivity spectra shifted by 3% from the original data to check the uncertainties of the derived $\sigma(\omega)$. According to this procedure, a 3% error of the reflectivity yields only the same order of error of $\sigma(\omega)$, which ensures that we can make a quantitative discussion about the obtained $\sigma(\omega)$ spectra. We also measured the reflectivity spectra for two different samples of $YTiO_3$ to check the reproducibility, and found that the difference of the derived $\sigma(\omega)$ is within ~10%.

Figure 1 shows $\sigma(\omega)$ spectra for several species of R and various Ca concentrations. Here, δ $(= 1 - n)$ stands for the nominal number of holes per Ti site. We show the bandwidth of each RTiO$_3$ normalized to that of $LaTiO_3$ $(\tilde{W} = W_R/W_{\mathrm{La}})$ in the figure. The open circles show the magnitude of dc conductivity at room temperature obtained by the conventional four-probe method, which appears to agree with the value of $\sigma(\omega \to 0$ eV). In the case of $R =$ Nd ($Nd_{1-x}Ca_xTiO_3$), for example, $\sigma(\omega)$ at $\delta = 0$ $(n = 1)$ shows negligible spectral weight below 0.8 eV but steeply increases above 0.8 eV. Previous works [9,11,20] assigned the spectral weight above 0.8 eV (up to 4 eV) to a Mott-gap excitation (from the lower Hubbard band to the upper Hubbard band composed of Ti $3d$ states). In the study of the Mott-gap structure for V_2O_3 [4], the energy gap 2Δ was determined by fitting the spectra with the form $\sigma = \sigma_0(E - 2\Delta)^{3/2}$. However, such $E^{3/2}$ dependence was not clearly observed in the spectra for the titanates. Thus we estimated the energy gap 2Δ by extrapolating the steeply increasing part of $\sigma(\omega)$ to zero (dashed lines). The residual spectral weight inside the gap may be assigned to the remnant due to a very slight deviation of δ from zero. Comparing the values of 2Δ thus estimated with various R, one finds that 2Δ increases with U/W (*vide infra*).

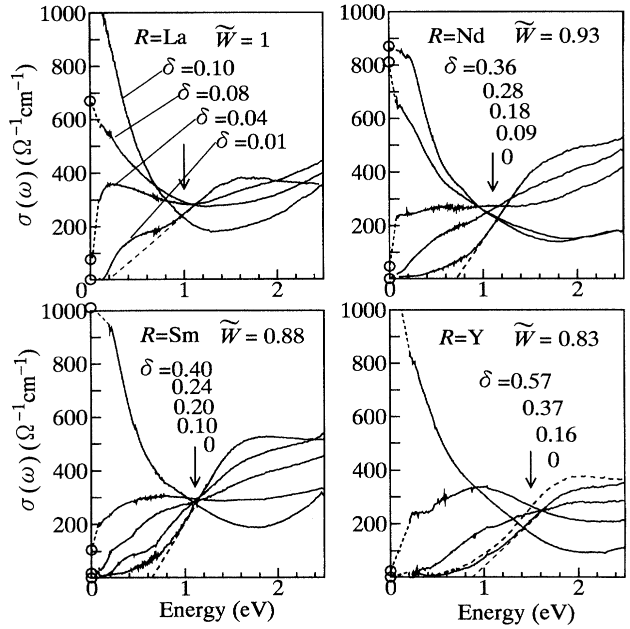

FIG. 1. Optical conductivity spectra for $R_{1-x}Ca_xTiO_3$ with $R =$ La, Nd, Sm, and Y. δ is nominal hole concentration, i.e., $\delta = 1 - n$ where n is the number of d electrons per Ti site. Spectra for two different samples of $YTiO_3$ $(\delta = 0)$ are shown by solid and dashed lines. $\tilde{W} = W_R/W_{\mathrm{La}}$ is the one-electron bandwidth of each RTiO$_3$ normalized to that of $LaTiO_3$, obtained by a tight-binding calculation. Open circles indicate the measured dc conductivity and are connected by a dotted straight line with experimental spectra. Dashed straight lines indicate the energy gap for $\delta = 0$, and arrows show the isosbetic points as cutoff energies (ω_c) for the calculation of the effective number of electrons.

In the spectra for $Nd_{1-x}Ca_xTiO_3$, the spectral weight of the Mott-gap excitation is reduced with an increase of δ, while that inside the gap increases. An interesting problem is whether the spectrum evolving inside the gap can be divided into two parts, i.e., a coherent-state part (Drude absorption peak) and an incoherent-state part, the latter of which comes from incoherent motion of the doped carriers caused by the electron-correlation effect [5,21]. However, the randomness effect often leads to electron localization (Anderson localization) and may shift the Drude absorption peak at $\omega \sim 0$ to higher energy. In fact, $\sigma(\omega = 0)$ for $Nd_{1-x}Ca_xTiO_3$ with $\delta = 0.09$ is approximately zero, in spite of the existence of the spectral weight inside the Mott gap, which means that this compound should be interpreted as an Anderson insulator. In such a case, the spectrum at $\omega > 0$ caused by the incoherent motion of the carriers and that caused by the randomness effect are difficult to distinguish experimentally. In addition, finite temperature increases the scattering rate of carriers, which makes the Drude absorption peak larger in width and merged into the incoherent-state part. Therefore, we do not discuss separately the coherent- and incoherent-state parts, and define the "Drude part" as the sum of these two parts, which shows up as the inner-gap absorption in the $\sigma(\omega)$ spectrum.

It is remarkable in Fig. 1 that, though $\sigma(\omega)$ changes with an increase of δ in a similar way irrespective of the species of R, the evolution rate of the Drude part with δ is dependent on the magnitude of $\tilde{W}$. Namely, the rate of the Drude-part evolution decreases with a decrease of $\tilde{W}$. To make a quantitative discussion of this point, we define the effective number of electrons as

$$N_{\mathrm{eff}}(\omega) = \frac{2m_0}{\pi e^2 N} \int_0^{\omega} \sigma(\omega')\, d\omega', \tag{1}$$

where m_0 is the free electron mass and N the number of Ti atoms per unit volume. We found that $N_{\mathrm{eff}}(\omega)$ is nearly independent of δ with $\omega = 2.5$ eV, which includes spectral weights both for the Drude part and for the Mott-gap excitation. In other words, the sum of the spectral weight of these two parts is nearly conserved under a variation of δ, but the spectral weight is transferred from the Mott-gap-excitation part to the Drude part across the isosbetic point (~1.1 eV for $Nd_{1-x}Ca_xTiO_3$). Thus, the value defined as

$$N_D = N_{\mathrm{eff}}(\omega_c)_\delta - N_{\mathrm{eff}}(\omega_c)_{\delta=0}, \qquad (2)$$

where ω_c stands for the isosbetic point, is the low-energy spectral weight transferred from the higher-energy region with doping. Numerical studies [13,15] have indicated that the Mott-gap-excitation spectrum does not discernibly shift in energy with doping but is suppressed in intensity, whereas the spectrum spread over inside the gap evolves. It is therefore expected that the N_D value refers to the Drude part (the sum of the normal Drude absorption part plus the in-gap-state part). We adopted ω_c (isosbetic point) of 1.0, 1.1, 1.1, 1.1, and 1.5 eV for R = La, Pr, Nd, Sm, and Y, respectively. Such an increase of the isosbetic point energy with a decrease of $\tilde{W}$ reflects the increase of the energy gap 2Δ with $\delta = 0$.

We plot N_D, which is normalized to N_{D0}, that is, the value of N_D for $U = 0$ and $\delta = 0$ ($n = 1$) [22], as a function of δ in Fig. 2. The linear increase of N_D with δ is similar to the result for cuprates and other 3d transition-metal oxides [5,9–12] and is consistent with several theoretical studies [13,14,16] based on the Hubbard Hamiltonian. The solid lines are the result of least-squares fitting by the function

$$N_D/N_{D0} = C\delta. \qquad (3)$$

As can be seen in Fig. 2, the slope of the line, i.e., the C value, decreases with a decrease of $\tilde{W}$. To check the possible dependence of N_D and C on the adopted value of ω_c, we also calculated N_D for $Nd_{1-x}Ca_xTiO_3$ with $\omega_c = 0.8$ eV (open squares and the dashed line) instead of 1.1 eV, and found that the variation of C originating from the different ω_c values is not so large as to affect the discussion below.

Figure 3 shows the $\tilde{W}^{-1}$ (strength of electron correlation) dependence of C^{-1} (lower panel), where C is the rate of the Drude-part evolution with δ defined in Eq. (3), together with the value of $2\Delta/W$ (the energy gap normalized to the bandwidth; upper panel). We also plot the activation energy ($2\Delta_{\mathrm{act}}$) determined by resistivity measurements of $R\mathrm{TiO_3}$ [$\rho(T) = \rho_0 \exp(\Delta_{\mathrm{act}}/k_BT)$] in the upper panel of the figure. 2Δ and $2\Delta_{\mathrm{act}}$ have nearly the same dependence on $\tilde{W}^{-1}$, i.e., a linear decrease with a decrease of $\tilde{W}^{-1}$ [23]. Several optical studies of other compounds, e.g., $La_xY_{1-x}TiO_3$ [11] and V_2O_3 [4], demonstrated qualitatively a similar $\tilde{W}^{-1}$ dependence of 2Δ. The extrapolation of the data points of $2\Delta_{\mathrm{act}}/W$ by a linear function (solid line) crosses the $2\Delta = 0$ line (abscissa) at a finite value of $\tilde{W}$ (~0.97). It seems reasonable to consider that this value corresponds to the critical value of the bandwidth-controlled Mott transition [$(U/W)_c$] at which the charge gap closes and the system becomes metallic for $n = 1$. Note that recent calculations of the Hubbard model at infinite dimensions [24] confirmed a metal-insulator transition for $n = 1$ with a finite value

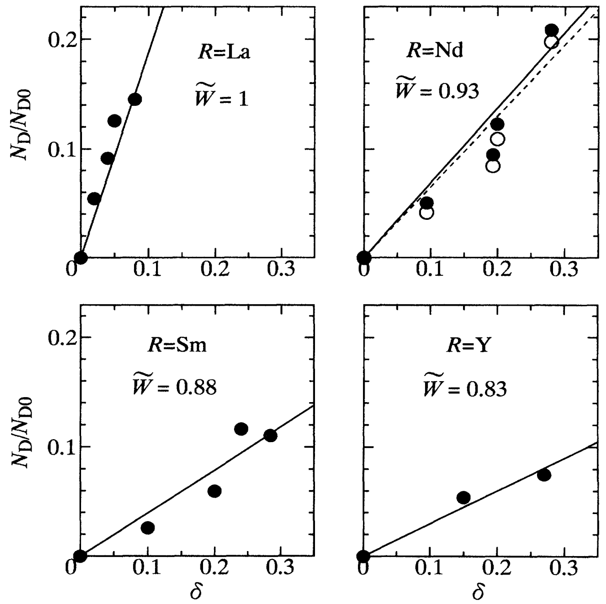

FIG. 2. Effective number of electrons of the Drude part (N_D) normalized to that for $U = 0$ and $\delta = 0$ (N_{D0}) as a function of δ for $R_{1-x}Ca_xTiO_3$ with R = La, Nd, Sm, and Y. Straight lines are the result of least-squares fitting by the function $N_D/N_{D0} = C\delta$. For $Nd_{1-x}Ca_xTiO_3$, two different cutoff energies ω_c are adopted; closed circles and a solid line are for $\omega_c = 1.1$ eV (isosbetic point), and open circles and a dashed line are for $\omega_c = 0.8$ eV.

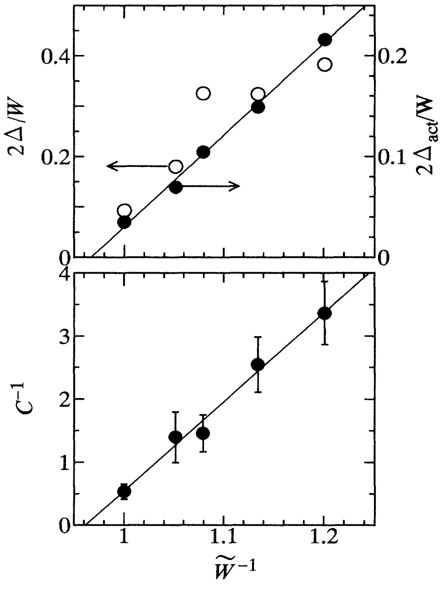

FIG. 3. Upper panel: $\tilde{W}^{-1}$ dependence of 2Δ (an energy gap obtained by optical conductivity spectra) and $2\Delta_{\mathrm{act}}$ (twice the activation energy obtained by the temperature dependence of resistivity) normalized to the bandwidth (W). The solid line is the result of least-squares fitting of the data of $2\Delta_{\mathrm{act}}/W$ by a linear function. Lower panel: $\tilde{W}^{-1}$ dependence of C^{-1}, where C is the rate of the Drude-part evolution with δ defined in Eq. (3). The solid line is the result of least-squares fitting by a linear function.

of U/W, and quantitatively explained the U/W dependence of the magnitude of the Mott gap in V_2O_3, i.e., $2\Delta \propto (U/W) - (U/W)_c$ [4].

On the other hand, the lower panel of Fig. 3 indicates that C^{-1} also decreases linearly with a decrease of $\tilde{W}^{-1}$. The solid line in the lower panel is the result of a least-squares fitting with a linear function. It is noteworthy that the value of $\tilde{W}^{-1}$ at which C^{-1} becomes zero is nearly the same as the value at which 2Δ becomes zero. This means that the rate of the Drude-part evolution with δ is critically (divergently) enhanced as the strength of electron correlation (U/W) approaches the critical value of the bandwidth-controlled Mott transition $(U/W)_c$, following the relation

$$C \propto [(U/W) - (U/W)_c]^{-1}. \tag{4}$$

According to a calculation for a one-dimensional Hubbard system using the Bethe ansatz for the large U limit [14], N_D increases linearly with $\delta = 1 - n$ for the small δ limit, and the coefficient C is such that

$$C = \frac{\pi}{2}\left(1 + 2(\ln 2)\frac{W}{U}\right), \tag{5}$$

where $W = 4t$ in one-dimensional systems. However, this functional form shows no critical behavior at finite values of U/W, in contrast to the case of the present compounds. A calculation for a two-dimensional Hubbard system using the exact diagonalization method [13] indicates that the U/W dependence of C is qualitatively the same as that in one dimension. The difference between our experimental result and the calculations in lower dimensions apparently comes from the difference of the magnitude of $(U/W)_c$ (critical value for the bandwidth-controlled Mott transition); $(U/W)_c$ is zero for one- or two-dimensional systems (i.e., the ground state is always an insulator for $n = 1$ with nonzero U/W), while it is likely a finite value for the present compounds, that is, for a three-dimensional system.

In summary, we investigated the optical spectra for $R_{1-x}Ca_xTiO_3$, varying the strength of electron correlation (U/W) as well as the band filling $n = 1 - \delta$. With a decrease of n from 1 (an increase of δ from 0), the spectral weight of the Mott-gap excitation is reduced and that of the (quasi) Drude part increases linearly. We found that the rate of the Drude-part evolution with δ is critically enhanced as U/W approaches the critical value of the bandwidth-controlled Mott transition for $n = 1$ $[(U/W)_c]$, in the manner of $[U/W - (U/W)_c]^{-1}$.

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[22] This value was estimated as follows: We obtained N_D of $La_{1-x}Sr_xTiO_3$ over the whole filling range from the $\sigma(\omega)$ spectra reported in Ref. [9], and found that N_D for $x > 0.5$ (i.e., $n < 0.5$) linearly increases with n (not $\delta = 1 - n$). Such a relation for low band filling is in accordance with the result of numerical studies (Ref. [13]); namely, N_D linearly increases with n for $n < 0.4$, and the magnitude is nearly U independent. Thus, we made a linear extrapolation for the points of $n < 0.5$ to $n = 1$ ($\delta = 0$) in the n vs N_D plot, and obtained the value N_{D0} for $La_{1-x}Sr_xTiO_3$ as the $n = 1$ ($\delta = 0$) intersection ($\sim$0.45). The value of N_{D0} for another R was determined by the relation $N_{D0,R} = N_{D0,\mathrm{La}}\tilde{W}$ ($\tilde{W} = W_R/W_{\mathrm{La}}$).

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