

# Variation of optical gaps in perovskite-type 3d transition-metal oxides

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(Received 16 September 1993)

The optical study of trivalent 3d transition-metal-oxide compounds ( $RM\text{O}_3$ ) with the perovskite-like structure has revealed the variation of their electronic structure with the 3d element ( $M$ ) as well as the A-site rare-earth element ( $R$ ). The crossover of the gap nature from the Mott type to charge-transfer (CT) type with increasing atomic number of  $M$  is observed to occur around  $M = \text{Cr}$ . The variation of Mott and CT gaps with  $M$  species is quantitatively consistent with the tendency expected from an ionic model. However, for the low-energy electronic structures for the narrow-gap (or metallic) compounds ( $M = \text{Ti, Co, Ni}$ ), the effects of the  $M$ -3d-O-2p hybridization must be included.

Strong on-site Coulomb repulsion between 3d electrons often causes an integer-filled 3d-electron ( $3d^N$ ) system to be insulating. Zaanen, Sawatzky, and Allen (ZSA) have pointed out that insulating 3d-electron systems can be classified into two categories.<sup>1</sup> One is the Mott insulator, where the charge gap is determined by the Hubbard splitting ( $U$ ) of the  $d$  band. The other is the so-called charge transfer (CT) insulator, the charge gap of which is typically an energy difference ( $\Delta$ ) between filled  $p$  bands of ligand anions and unoccupied upper Hubbard 3d band. More recently, Torrance *et al.*<sup>2</sup> pointed out that an ionic model can be used to estimate the energies  $U$  and  $\Delta$  quantitatively, which depend on the Madelung and the atomic ionization potentials. Using these estimates, one can account for the optical gaps of closed shell oxides as well as the differences between metallic and insulating transition-metal oxides within the ZSA framework.

In this paper, we report a systematic experimental study of the variation of optical charge gap in perovskite-type  $\text{LaMO}_3$  and  $\text{YMO}_3$  with trivalent 3d transition element ( $M$ ). This family of rare-earth ( $R$ )- $M$  oxides ( $RM\text{O}_3$ ) with the perovskitelike structure is one of the most suitable systems to investigate the systematic variation of the electronic structure with  $M$  species: The perovskite compound with  $R = \text{La}$  can be synthesized for all the 3d transition elements ( $M = \text{Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu}$ ). The fundamental data for the structural and conductivity properties have been also reported. The optical spectroscopy can give much quantitative information about the electronic structures and their variation in the series of  $RM\text{O}_3$  compounds.

Another advantage of targeting the perovskite system is that by changing the  $R$  species we can investigate how the O-2p- $M$ -3d transfer energy  $t_{pd}$  modifies the electronic structure of the system. The  $t_{pd}$  value depends strongly on the  $M$ -O- $M$  bond angle, which is closely related to the ionic size of  $R$ . When the ionic size of  $R$  (and hence the tolerance factor of the perovskite-type structure) is small, the  $M$ -O- $M$  bond bends and deviates from  $180^\circ$  of the ideal perovskite

structure, and  $t_{pd}$  decreases.<sup>3,4</sup> We should note that the effective one-electron bandwidth of the 3d states is also governed by the  $t_{pd}$  interaction via the second order process ( $\sim t_{pd}^2/\Delta$ ). We compare optical spectra of  $\text{YMO}_3$  with those of  $\text{LaMO}_3$  to probe the effect of the electron transfer interaction.

Dense polycrystalline samples of  $\text{LaTiO}_3$ ,  $\text{YTiO}_3$ ,  $\text{YVO}_3$ ,  $\text{YCrO}_3$ ,  $\text{LaMnO}_3$ ,  $\text{LaFeO}_3$ ,  $\text{YFeO}_3$ , and  $\text{LaCoO}_3$  were melt-grown using a floating zone (FZ) furnace equipped with two halogen incandescent lamps in an adequate atmosphere. Since the melting temperature of  $\text{LaScO}_3$ ,  $\text{LaVO}_3$ , and  $\text{LaCrO}_3$  is too high to be melted by the FZ furnace, we used a tri-arc melting furnace. We also prepared highly dense samples of  $\text{YCoO}_3$ ,  $\text{LaNiO}_3$ ,  $\text{YNiO}_3$ , and  $\text{LaCuO}_3$  by the high-pressure (5 GPa) synthesis technique using  $\text{KClO}_3$  as an oxygen buffer, since strongly oxygenating atmosphere is necessary for their syntheses.<sup>5-7</sup> All the details of the sample preparation will be published elsewhere. The obtained samples were characterized by measurements of x-ray diffraction and temperature dependence of magnetization.

The resistivity measurement and thermogravimetric analysis (TGA) were also done for some of them, since the electrical properties have been reported to be often sensitive to nonstoichiometry.<sup>8,9</sup> For example, electrical and magnetic properties of  $\text{LaTiO}_3$  are known to be most sensitive to offstoichiometry.<sup>8</sup> The presently prepared sample shows semiconductive resistivity ( $0.5 \Omega \text{ cm}$  at 300 K) and undergoes weak ferromagnetic transition at 138 K, which suggests minimal oxygen nonstoichiometry. The oxygen nonstoichiometry was also estimated to be less than 0.01 from TGA. A slight deviation of the band filling due to offstoichiometry does not change a major frame of electronic structure like charge gap, but may induce the subgap levels in some cases. These may be responsible for the tailing of the optical gap transitions and the in-gap absorption.

The optical reflectivity spectrum was measured on a surface of the sample polished with alumina powder. We used a Fourier-transform-type interferometer and a grat-

ing type monochromator for the photon energy of 0.015–0.8 eV and of the 0.6–36 eV, respectively. For the measurement above 6 eV, we utilized synchrotron radiation at INS-SOR, Institute for Solid State Physics, University of Tokyo. The incident angle was less than  $15^\circ$  to be regarded as the normal incident reflection within a relative experimental accuracy of reflectivity of  $\sim 5\%$ . The optical conductivity spectrum was calculated from the reflectivity spectrum using the Kramers-Kronig relation. For the Kramers-Kronig analysis, we assumed the constant reflectivity below 0.015 eV for all the samples except for the metallic (LaNiO<sub>3</sub> and LaCuO<sub>3</sub>) samples, in which we applied the Hagen-Rubens type extrapolation. For the higher-energy reflectivity above 36 eV, the  $\omega^{-4}$  type extrapolation was used for all the spectra.

Spectra of optical conductivity  $\sigma(\omega)$  in LaMO<sub>3</sub> are shown Fig. 1. Except for metallic LaNiO<sub>3</sub> and LaCuO<sub>3</sub>, the spectra show a gap feature. An optical gap can be observed as a gradual onset of the spectral intensity rather than a peak structure as observed in the parent compounds of the high- $T_c$  cuprates like La<sub>2</sub>CuO<sub>4</sub>,<sup>10</sup> perhaps due to the three-dimensional electronic feature in the RMO<sub>3</sub> system. As the optical gap energy ( $E_{\text{gap}}$ ), we have taken the photon energy at which the spectral intensity shows a sharp rise, as determined by the crossing point of the base line and the dashed line in Fig. 1. The values of  $E_{\text{gap}}$  thus obtained including those of the YMO<sub>3</sub> series are plotted against the  $M$  species in Fig. 2. The Mott and CT gap are shown by filled and open symbols, while the circles and squares indicate the gap in the La and Y derivatives, respectively. It is seen from this plot that the crossover between the Mott and CT regime occurs near  $M=\text{Cr}$  in the RMO<sub>3</sub> system, while it occurs at higher atomic number, i.e., around  $M=\text{Mn}$ , in the monoxide (MO) system.<sup>11</sup> This is likely because the higher valence of  $M$  in perovskites reduces  $\Delta$ .

Let us survey the optical gap features in the La deriva-

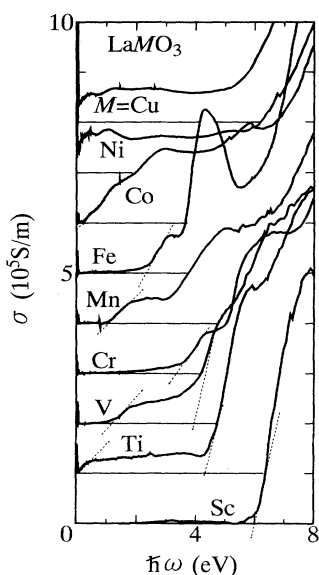


FIG. 1. Spectra of optical conductivity in (a) LaMO<sub>3</sub> and (b) YMO<sub>3</sub>.

tives. The spectrum in LaScO<sub>3</sub>, which is a band insulator with the 3d<sup>0</sup> configuration, is shown in the bottom of Fig. 1(a). The band gap can be clearly observed around 6 eV, which is formed between the O 2p valence band and the Sc 3d conduction band and hence corresponds to the CT gap (i.e., 2p-3d gap) of the other LaMO<sub>3</sub> compounds. The Mott gap excitation can be observed when the 3d band starts to be filled. In the spectra in LaTiO<sub>3</sub> (3d<sup>1</sup>) and LaVO<sub>3</sub> (3d<sup>2</sup>), we observe a weak optical transition in the low photon energy region below 2 eV as well as an intense one which lies above 4 eV. The former can be assigned to the Mott gap transition, while the latter to the CT gap transition, on the basis of their energy and spectral intensities. (The oscillator strength of the Mott gap transition should be smaller than that of the CT gap transition, because the former is a fourth-order process in  $t_{pd}/U$  or  $t_{pd}/\Delta$  based on the simplest perturbation calculation, while the latter is only second-order.) The observed Mott gap in LaVO<sub>3</sub> is larger than in LaTiO<sub>3</sub>, which is consistent with the general tendency that the electron correlation becomes stronger as the atomic number of  $M$  increases. By contrast, the CT gap energy gradually decreases in going from  $M=\text{Sc}$  to  $M=\text{V}$ . The CT excitation appears to be composed of at least two structures separated by  $\sim 1$  eV, which is perhaps the ligand field splitting of the 3d level.

An optical gap in LaCrO<sub>3</sub> is clearly observed at around 4 eV. It is characterized with enough intensity to be regarded as the CT gap. A clear splitting of the optical band can be found as in the titanate and the vanadate, but for its origin we have to consider the effect of the Hund coupling in addition to the simple ligand field effect: The possible final states of the CT transitions in LaCrO<sub>3</sub> are  $3d_{e\uparrow}^3 3d_{\gamma\uparrow}\bar{L}$ ,  $3d_{e\uparrow}^3 3d_{e\downarrow}\bar{L}$ , and  $3d_{e\uparrow}^3 3d_{\gamma\downarrow}\bar{L}$  ( $\bar{L}$  represents the ligand hole). Among them, the lowest CT excitation is perhaps the transition,  $3d_{e\uparrow}^3 \rightarrow 3d_{e\uparrow}^3 3d_{\gamma\uparrow}\bar{L}$ , reflecting the strong Hund coupling. Incidentally, the excitation corresponding to the Mott gap in LaCrO<sub>3</sub> is overlapped by the stronger CT excitation and becomes indiscernible.

The minimum optical gap in LaMnO<sub>3</sub> is rather small and its oscillator strength is relatively weak as seen in Fig. 1(a), but it should be assigned to the CT gap from the reason mentioned later. (Note that the oscillator strength of the CT transition gradually decreases as the 3d-electron number increases, since unoccupied 3d states decreases.) The spectrum in LaFeO<sub>3</sub> resembles that of LaMnO<sub>3</sub> except for an increase in the gap energy. LaCoO<sub>3</sub> is found to be a narrow gap compound with  $E_{\text{gap}} < 1$  eV.

The spectra of LaNiO<sub>3</sub> and LaCuO<sub>3</sub> are quite similar to each other: There is no more charge gap, which is consistent with their metallic dc conductivity. However, the spectral shape is quite different from the typical Drude type: There is some remnant structure in the CT excitation region below 2 eV, which is linked to the higher-lying excitation around 6 eV probably related to O-2p-La-5d excitations.

We can find a general tendency of the CT gap against the  $M$  species in Fig. 2: The  $\Delta$  value decreases as the atomic number of  $M$  increases. The tendency seems

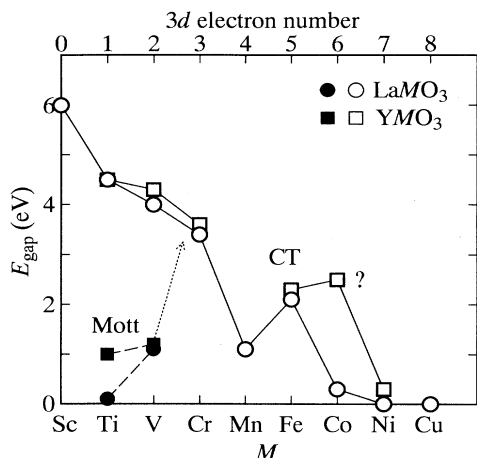


FIG. 2. Optical gap plotted against the 3d transition-metal element. Solid circles: Mott gap in  $\text{LaMO}_3$ . Solid squares: Mott gap in  $\text{YMO}_3$ . Open circles: CT gap in  $\text{LaMO}_3$ . Open squares: CT gap in  $\text{YMO}_3$ .

to be quite reasonable because the 3d level becomes more stable as the positive charge of the atomic nucleus increases.<sup>1</sup> One can notice some discrepancy from the general tendency: For example, the CT gap in the Mn oxides is much smaller than in the Fe oxides. The most important factor for the discrepancy would be the stability of the  $3d^N$  configuration via exchange interaction. Such an exchange term is reflected in the experimental value of the ionization potential for an isolated ion. (The only exception is the cobaltate. It has been reported that the cobalt ion takes the low spin state  $3d_{e\downarrow}^3 3d_{e\uparrow}^1$  configuration in the compound,<sup>12</sup> while the atomic ionization potential must be the value for the high spin state  $3d_{\uparrow}^5 3d_{\downarrow}^1$ . The spin configuration correction and the ligand field correction for the cobaltates may be as large as  $\sim -0.4$  eV.)

Figure 3 is a comparison between the calculation using the ionic model<sup>2</sup> and the present optical investigation. The calculated values for  $U$  and  $\Delta$  on the horizontal axis are

$$U = I_4(M) - I_3(M) - e^2/d_{M-M},$$

$$\Delta = e(V_M^O - V_M^M) + A(\text{O}^-) - I_3(M) - e^2/d_{M-O},$$

which are calculated using the third [ $I_3(M)$ ] and fourth [ $I_4(M)$ ] atomic ionization potentials, the second electronic affinity of oxygen [ $A(\text{O}^-)$ ], and unscreened electrostatic potential [Madelung potential ( $V_M^i$  for  $i$  site)] on the point charge approximation. Here, the excited electron and hole in the final state of the optical transition are assumed to be located on neighboring sites. Because of the lack of a complete data set for the crystal structure of  $\text{YMO}_3$ , we assume the same calculated results for the La and Y compounds. The difference in the lattice parameters for the both compounds is too small to cause an appreciable difference in the Madelung potential. (For example, the calculated values for  $\text{RNiO}_3$  are 10.64 eV for  $R=\text{La}$  and 10.72 eV for  $R=\text{Y}$ .)

Figure 3 shows a good correlation between the experiment and the ionic model: The straight line in the figure

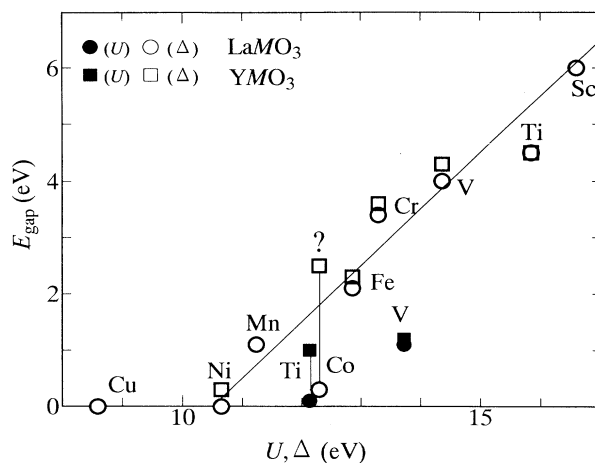


FIG. 3. The measured value of optical gap plotted against the calculated value based on the simple ionic model. Solid circles: Mott gap in  $\text{LaMO}_3$ . Solid squares: Mott gap in  $\text{YMO}_3$ . Open circles: CT gap in  $\text{LaMO}_3$ . Open squares: CT gap in  $\text{YMO}_3$ .

shows the slope of 1, on which most of the experimental data fall within the errors of  $\pm 0.5$  eV. This agreement supports the assignment given above for the Mott or CT nature of the optical peaks in Fig. 1. (Similarly good agreement was found<sup>2</sup> for the optical gaps of 13 closed shell oxides, with a slope of 1 and an intercept of 10 eV.) Since the electrostatic potential terms including the electron-hole binding energies ( $e^2/d_{M-O}$  and  $e^2/d_{M-M}$ ) change little with the  $M$  species, the ionization potential in the 3d elements seems to be the most important factor to determine the gap variation.

The calculated values are all about 10.5 eV higher than the experimental results. The most important factor for such a constant deviation is supposedly the electron transfer energy and the resultant covalency. The hybridization between the  $M$  3d and O 2p weakens the localized nature of 3d electrons, and hence reduces electron correlations. As a result, the effective  $U$  and  $\Delta$  values should be reduced. (The  $U$  and  $\Delta$  values are also reduced by the polarization of the constituent ions.<sup>13</sup>) The  $p$ - $d$  mixing also plays a role in increasing the bandwidths of  $d$  and  $p$  bands, though it may be not always related to the gap narrowing effect. However, the effect of covalency appears to be well corrected by subtracting the constant term ( $\sim 10.5$  eV) from the calculated value irrespective of the  $M$  species as shown in Fig. 3. The simple ionic model seems to be a very good starting point to understand the magnitude and nature of the charge gap of an oxide compound and hence whether the compound is metallic or insulating.

If we look closely at the data in Fig. 3, we can clearly see the deviation from the model. One of the most important effects which are not involved in the ionic model is the ligand field splitting of the  $M$  3d states. The splitting ( $10Dq$ ) can be estimated to be about 1 eV from the splitting of the CT excitation in the spectrum of  $\text{LaVO}_3$  shown in Fig. 1. The ligand field correction is as follows:

$+6Dq$  for the  $\Delta$  values in  $M=\text{Cr, Mn, and Ni}$ , and  $-4Dq$  for the  $\Delta$  values in  $M=\text{Sc, Ti, V, and Fe}$ . The corrections can obviously improve the agreement between the calculated and the measured values.

Another important effect is the  $d$ - $p$  mixing in narrow gap compounds. Figure 4 shows the conductivity spectra for La and Y derivatives of the niccolate, cobaltate, and titanate with relatively small or zero charge gaps. For all cases, the Y derivative has a smaller  $3d$ - $2p$  transfer energy because of its larger lattice distortion.  $RTiO_3$  are the Mott insulators on the verge of the phase boundary with a low- $U$  metal. The difference between the spectrum of  $LaTiO_3$  and that of  $YTiO_3$  can be interpreted in terms of the rigid shift of the Mott gap induced by the change in the  $3d$ -band width.

In contrast, the spectra of  $RCoO_3$  and  $RNiO_3$  show a drastic change with the substitution of the  $R$  ion. It can be found that the gap collapsing is accompanied by the transfer of spectral weight from the higher energy region above the gap, rather than the gap shift as in the case of the titanates. It is also to be noted that the spectrum of the metallic  $LaNiO_3$  (and also  $LaCuO_3$ ), which is reminiscent of the remnant CT gap excitations, differs significantly from the conventional Drude-type profile. This means that the charge degrees of freedom of the lower Hubbard band ( $3d$  state) are not completely released even in the metallic state. Such a CT insulator-metal transition with increasing the  $d$ - $p$  mixing may show qualitatively different aspects from the conventional Mott transition, and will deserve further study.

In summary, optical spectra of the perovskite-type oxides  $RMoO_3$  with the trivalent  $3d$  transition element  $M$  have been systematically investigated. The variety of the optical gap with the  $M$  species can be well comprehended in terms of the simple ionic model based on the atomic ionization potential and Madelung-type electrostatic en-

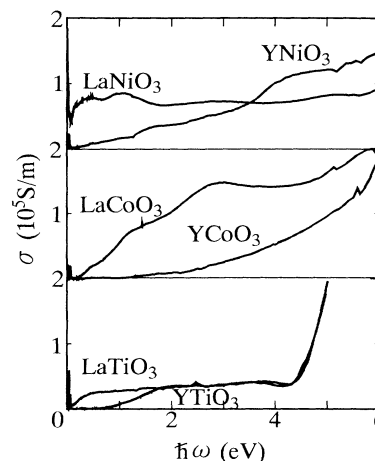


FIG. 4. Comparison between the spectra of optical conductivity in  $LaMO_3$  and  $YMO_3$  for  $M=\text{Ti, Co, and Ni}$ .

ergy. Assuming a constant shift of the gap of  $\sim 10.5$  eV, the observed gap agrees well with the calculated value on the model. The transfer energy seems to play a crucial role in determining the electronic structure in the narrow gap compounds, such as the Ti, Co, and Ni compounds.

The authors are grateful to J. Akimitsu, K. Tomimoto, M. Uoshima, T. Yagi, T. Uchida, T. Hishinuma, N. Mōri, F. Inaba, Y. Taguchi, Y. Okada, K. Tamasaku, S. Uchida, and M. Fujisawa for their help in sample preparations and optical measurements. They also thank A. Fujimori for enlightening discussion. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan.

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