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Systematic trends in the electronic structure parameters of the $4d$ transition-metal oxides $\mathrm{Sr}M\mathrm{O}_3$ ($M=\mathrm{Zr}$, Mo, Ru, and Rh)

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We investigated the electronic structures of the perovskite-type $4d$ transition-metal oxides $\mathrm{Sr}M\mathrm{O}_3$ ($M=\mathrm{Zr}$, Mo, Ru, and Rh) using their optical conductivity spectra $\sigma(\omega)$. The interband transitions in $\sigma(\omega)$ are assigned, and some important electronic structure parameters, such as charge-transfer energy Δ_{pd}, and crystal-field splitting $10Dq$, are estimated. It is observed that Δ_{pd} and $10Dq$ decrease systematically with increasing the atomic number of the $4d$ transition metal. Compared with the case of $3d$ oxides, the magnitudes of Δ_{pd} and $10Dq$ are larger. These behaviors can be explained by the more extended nature of the orbitals in the $4d$ oxides.

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Recently, attention to $4d$ transition-metal oxides (TMO) has increased because numerous intriguing properties, such as superconductivity,[1] non-Fermi liquid behavior,[2] pseudogap formation,[3] and metal-insulator transitions,[4,5] have been observed in ruthenates and molybdates. The $4d$ TMO are characterized by more extended orbitals than those of $3d$ TMO. So, it has been generally believed that electrons in the extended $4d$ orbitals feel rather weak on-site Coulomb repulsion energy and exchange energy J, and that the $4d$ orbitals hybridize more strongly with neighboring orbitals, e.g., O $2p$ orbitals, than $3d$ orbitals. However, these qualitative ideas are not sufficient to understand the intriguing physical phenomena observed in some 4 d TMO. Unfortunately, there have been few quantitative studies about the electronic structures of $4d$ TMO, except ruthenates.[4,6] Quantitative information on physical parameters related to the electronic structures of TMO will serve as a starting viewpoint in investigating various $4d$ TMO with a potential to discover other new intriguing phenomena. They will also allow us to make comparisons with the $3d$ TMO cases, which can provide us with a better understanding on the strongly correlated electron systems.

Optical spectroscopy is known to be a powerful tool to analyze electronic structures of TMO by probing joint density of states between unoccupied and occupied states. In this paper, we report a systematic investigation on electronic structures of perovskite-type $4d$ $\mathrm{Sr}M\mathrm{O}_3$ ($M=\mathrm{Zr}$, Mo, Ru, and Rh) by measuring their optical conductivity spectra $\sigma(\omega)$. From these series with the same crystal structure and valency state M^{4+}, one can investigate how their electronic structures vary with M. Based on proper electronic structures, the interband transitions observed in their $\sigma(\omega)$ are assigned. From this, we estimate important physical parameters, such as charge transfer energy Δ_{pd} and crystal field splitting energy $10Dq$, which show systematic trends with M. Compared with the $3d$ cases, it is found that the magnitudes of Δ_{pd} and $10Dq$ are larger. These behaviors can be understood in terms of the more extended characters of the $4d$ orbitals.

Polycrystalline SrZrO_3, SrMoO_3, and SrRhO_3 were prepared using the solid state reaction technique. Especially for SrMoO_3 and SrRhO_3, a high pressure (~6 GPa) of sintering technique was used.[7,8] This technique is highly effective to prepare metastable samples with Mo^{4+} or Rh^{4+} ions. From x-ray diffraction measurements, it was confirmed that all the samples are single phases. From dc resistivity and magnetization measurements, it was also found that their electric and magnetic properties are consistent with the previous reports.[7,9]

Near normal incident reflectivity spectra $R(\omega)$ were measured in a wide photon energy region of 5 meV–30 eV. The Kramers-Kronig (KK) analysis was used to calculate $\sigma(\omega)$ from the measured $R(\omega)$. All of our $4d$ oxides have the slightly distorted perovskite structure and their optical constants should be nearly isotropic, so the KK analysis could be applied to our polycrystalline samples without much problem.[10] For the analysis, the reflectivity below 5 meV was extrapolated with a constant value for the insulating SrZrO_3 sample, and with the Hagen-Rubens relation for the other metallic samples. For a high frequency region, the reflectivity value at 30 eV was used for reflectivities up to 40 eV, above which ω^{-4} dependence was assumed.[11]

It would be helpful to check the electronic structures of the $4d$ $\mathrm{Sr}M\mathrm{O}_3$ compounds, where M is either Zr, Mo, Ru, or Rh.[12] SrZrO_3 is known to be a $4d^0$ insulator with a bandgap between the occupied O $2p$ and the unoccupied Zr $4d\,t_{2g}$ bands.[13] The e_g band has a higher energy level by $10Dq$ than the t_{2g} band. Usually, the Sr $4d$ band is located at a higher energy level than M $4d$ bands.[6] As the atomic number of M increases from Zr, the extra $4d$ electrons start to fill the t_{2g} band partially without any significant change in the overall band structure. SrMoO_3, a $4d^2$ system, is known to be a Pauli paramagnetic band metal.[9] On the other hand, when the number of the extra $4d$ electrons is more than three, the electron occupancy in the $4d$-orbitals will be determined by the spin configuration. Because SrRuO_3, a d^4 ferromagnetic metal,[14] and SrRhO_3, a d^5 paramagnetic metal,[7] have the

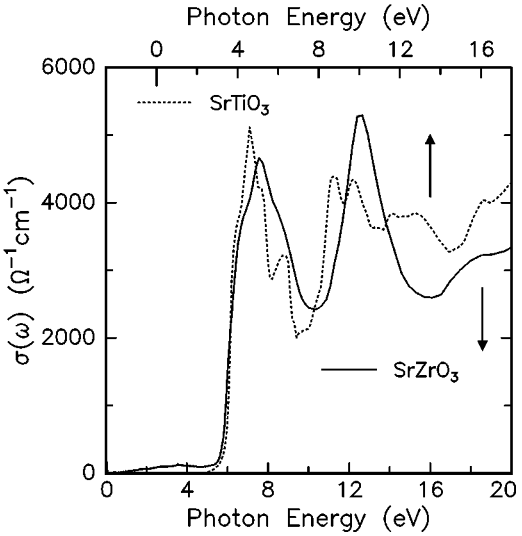

FIG. 1. Room temperature $\sigma(\omega)$ of $4d^0$ $\mathrm{SrZrO_3}$ (the solid line) up to 20 eV. The $\sigma(\omega)$ of $3d^0$ $\mathrm{SrTiO_3}$ (the dotted line), quoted from Ref. 15, is also displayed with a 2.5 eV shift to higher energy for comparison with $\mathrm{SrZrO_3}$.

low-spin configurations, all the $4d$ electrons fill only the t_{2g} band. It should be noted that the e_g bands remain empty in all the $\mathrm{Sr}M\mathrm{O_3}$ compounds.

According to the Fermi golden rule, the p-d transitions, such as O $2p \rightarrow M$ $4d\,t_{2g}$, M $4d\,e_g$, and Sr $4d$, should be distinct in $\sigma(\omega)$ of the $4d$ $\mathrm{Sr}M\mathrm{O_3}$ systems. From the interband transitions, we can estimate some electronic structure parameters; Δ_{pd} from the O $2p \rightarrow M$ $4d\,t_{2g}$ transition, and $10Dq$ from the energy difference between O $2p \rightarrow M$ $4d$ t_{2g} and M $4de_g$ transitions.

Figure 1 shows $\sigma(\omega)$ of $\mathrm{SrZrO_3}$ up to 20 eV. It is clearly shown that this insulating d^0 compound has a large optical gap of $\sim$5.6 eV, consistent with the previous report.[13] This value is larger by $\sim$2 eV than that of a $3d^0$ insulator $\mathrm{SrTiO_3}$, i.e., 3.4 eV. Distinct interband transitions are observed around 8 and 12 eV. To our knowledge, there has been no band calculation reported on this compound, so we assigned the interband transitions by referring to the band structure of $\mathrm{SrTiO_3}$. The dotted line in Fig. 1 represents $\sigma(\omega)$ of $\mathrm{SrTiO_3}$.[15] Its overall features are very similar to that of $\mathrm{SrZrO_3}$, but with $\sim$2.5 eV shift to lower energy. van Benthem *et al.* assigned the peaks around 5 and 9 eV of $\mathrm{SrTiO_3}$ as O $2p \rightarrow$Ti $3d\,t_{2g}$ and O $2p \rightarrow$Ti $3d\,e_g$ transitions, respectively.[16] (They also claimed that the higher frequency peak should come from O $2p \rightarrow$Ti $3d\,e_g$ and/or Sr $4d$.) Similarly, we can assign the peaks around 8 and 13 eV in $\mathrm{SrZrO_3}$ as O $2p \rightarrow$Zr $4d\,t_{2g}$ and O $2p \rightarrow$Zr $4d\,e_g$ transitions, respectively. By using the positions of the strong peaks, we can approximately estimate that $\Delta_{pd} \sim 8$ eV and $10Dq$ $\sim$5 eV in $\mathrm{SrZrO_3}$, which are larger than the values for $\mathrm{SrTiO_3}$ (i.e., $\Delta_{pd} \sim 5$ eV and $10Dq \sim 4$ eV).

Figure 2 shows $\sigma(\omega)$ of the $\mathrm{Sr}M\mathrm{O_3}$ series, with $M=$Zr, Mo, Ru, and Rh, up to 12 eV. The $\sigma(\omega)$ of $\mathrm{SrRuO_3}$ is quoted from our previous paper.[4] For other metallic compounds except the insulating $\mathrm{SrZrO_3}$, $\sigma(\omega)$ below 1.0 eV have zero-frequency spectral weights, which decrease with the increasing atomic number of M. The coherent peak of $\mathrm{SrMoO_3}$ can be fitted by the Drude model with a plasma frequency of $\sim$2.8 eV and a scattering rate of $\sim$0.3 eV. For other metallic $\mathrm{SrRuO_3}$ and $\mathrm{SrRhO_3}$, the low frequency $\sigma(\omega)$ decreases more slowly than $1/\omega^2$, which is a prediction of the Drude model. This strong incoherent character in the midinfrared region, which has often been observed in many correlated metals, indicates that the electron correlation could play important roles in these $4d$ oxides.[2]

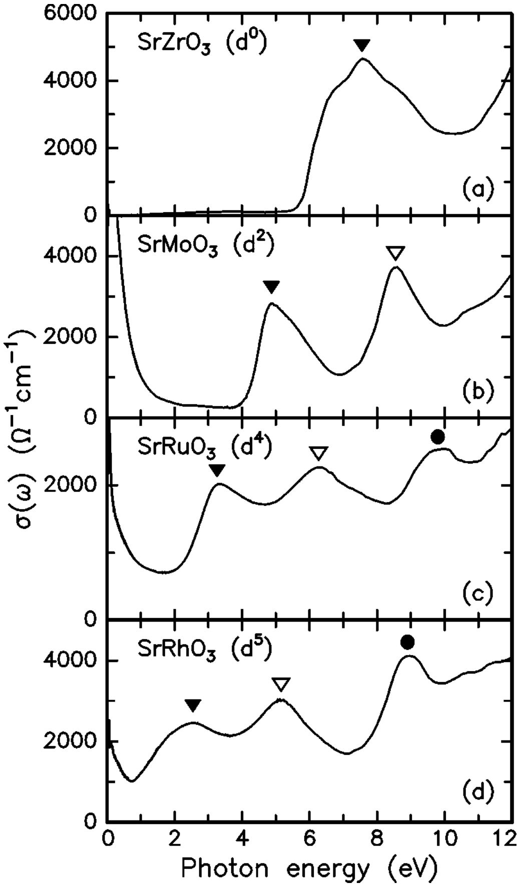

FIG. 2. Room temperature $\sigma(\omega)$ of the $4d$ $\mathrm{Sr}M\mathrm{O_3}$ series. (a) $\mathrm{SrZrO_3}$ (d^0), (b) $\mathrm{SrMoO_3}$ (d^2), (c) $\mathrm{SrRuO_3}$ (d^4), and (d) $\mathrm{SrRhO_3}$ (d^5) up to 12 eV. The solid triangles, the open triangles, and the solid circles represent positions of O $2p \rightarrow M$ $4d$ t_{2g}, O $2p \rightarrow M$ $4d$ e_g, and O $2p \rightarrow$Sr $4d$ transitions, respectively.

The observed peaks of the $\mathrm{Sr}M\mathrm{O_3}$ compounds can be assigned according to their electronic structures. The assignments for the $\mathrm{SrZrO_3}$ peaks were already given. For $\mathrm{SrMoO_3}$, 5.0 and 8.5 eV peaks are observed clearly, as shown in Fig. 2(b). These two peaks can be assigned as O $2p \rightarrow$Mo $4d\,t_{2g}$ and O $2p \rightarrow$Mo $4d\,e_g$ transitions, respectively. For $\mathrm{SrRuO_3}$, the 3.0, 6.0, and 10 eV peaks shown in Fig. 2(c) can be assigned as O $2p \rightarrow$Ru $4d\,t_{2g}$, O $2p \rightarrow$Ru $4d\,e_g$, and O $2p \rightarrow$Sr $4d$ transitions, respectively.[4] The interband transitions in $\mathrm{SrRhO_3}$ can be assigned similarly with the case of $\mathrm{SrRuO_3}$. So, the 2.6, 5.2, and 9.0 eV peaks in $\mathrm{SrRhO_3}$ can be assigned as O $2p \rightarrow$Rh $4d\,t_{2g}$, O $2p \rightarrow$Rh $4d\,e_g$, and O $2p \rightarrow$Sr $4d$ transitions, respectively.

It is interesting to observe systematic trends in the inter-

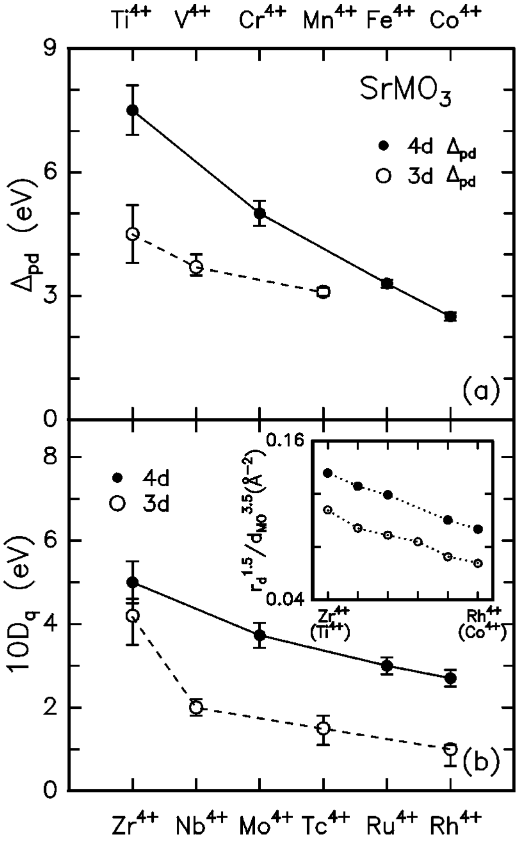

FIG. 3. (a) Charge transfer energy Δ_{pd} and (b) crystal field splitting energy $10Dq$ in $4d$ SrMO$_3$ with M=Zr, Mo, Ru, and Rh (solid symbols) and $3d$ SrM'O$_3$ with M'=Ti (Ref. 16), V (Ref. 21) Mn (Refs. 22,23), and Co (Ref. 24) (open symbols). We included only the optical results, except for the $10Dq$ value of SrCoO$_3$. In the inset of Fig. 3(b), the values of $d_r^{1.5}/d_{M\text{-O}}^{3.5}$ are estimated for the $3d$ and the $4d$ oxides. The values of d_r are used from Ref. 18. [We also estimated d_r from the ionic size of M^{4+} (M'^{4+}). The results show a similar trend, except the case of SrFeO$_3$.] The $d_{M\text{-O}}$ values of the $3d$ compounds are from Ref. 17. For the $4d$ oxides, because detailed structural analyses have not been done, we used the values of $d_{M\text{-O}}$ as half of the pseudocubic lattice constants, which were obtained from our x-ray diffraction measurements. The pseudocubic lattice constants a of SrZrO$_3$, SrMoO$_3$, SrRuO$_3$, and SrRhO$_3$ are 4.11, 3.97, 3.94, and 3.92 Å, respectively. The a value of 4.02 Å is used for SrNbO$_3$ [H. Hannerz *et al.*, J. Solid State Chem. **147**, 421 (1999)].

band transitions of the SrMO$_3$ series. As the atomic number of M increases, the O $2p \rightarrow M$ $4d$ transitions shift to the lower energy side. In addition, the peak interval between the O $2p \rightarrow M$ $4d$ t_{2g} and the O $2p \rightarrow M$ $4d$ e_g transitions decreases. As mentioned earlier, these interesting trends in peak positions should be originated from systematic changes of Δ_{pd} and $10Dq$.

Figure 3(a) shows a systematic trend in the Δ_{pd} values. As the atomic number increases, Δ_{pd} decreases. According to the work of Torrance *et al.* on the ionic model,[17] the change of Δ_{pd} with the atomic number is attributed mainly to the change in electronegativity (or ionization energy) of the transition metal; as the electronegativity becomes larger, Δ_{pd} decreases. So, the decrease of Δ_{pd} in $4d$ SrMO$_3$ can be explained by the increase of electronegativity with increasing the atomic number.

Figure 3(b) shows a systematic trend in the $10Dq$ values. The $10Dq$ value decreases with increasing the atomic number. It is generally accepted that, as the overlap (or covalency) between the O $2p$ and the d orbitals becomes stronger, $10Dq$ becomes larger.[13] So, the decrease of $10Dq$ in the $4d$ SrMO$_3$ series can be understood as shrinking of the d orbitals, and resultant weakening of the covalency between the M $4d$ and the O $2p$ orbitals. To obtain a better understanding, we estimated the covalency strength as the p-d matrix element with the σbonding $V_{pd\sigma} \propto d_r^{1.5}/d_{M\text{-O}}^{3.5}$, suggested by Harrison.[18,19] Here, d_r and $d_{M\text{-O}}$ are the radial size of the d-orbital[18] and the distance between the M and the O ions, respectively. As shown in the inset of Fig. 3(b), the value of $d_r^{1.5}/d_{M\text{-O}}^{3.5}$ in the $4d$ compounds decreases with increasing the atomic number, consistent with the decrease of $10Dq$. This suggests that the p-d covalency should play an important role in determining the $10Dq$ value.[20]

For quantitative comparisons, we also display the reported values of Δ_{pd} and $10Dq$ for some $3d$ SrM'O$_3$ (M'=Ti, V, Mn, and Co), as the open circles in Fig. 3.[16,21–24] Most of the results were determined from $\sigma(\omega)$ in the way as described earlier in this paper. Similar to the case of the $4d$ TMO, the Δ_{pd} value of $3d$ SrM'O$_3$ in Fig. 3(a) decreases as the atomic number of M' increases. [While there are no optical reports on metallic SrFeO$_3$ and SrCoO$_3$, photoelectron spectroscopy results claimed that their Δ_{pd} values be nearly zero.[24,25]] On the other hand, the magnitudes of Δ_{pd} in $4d$ SrMO$_3$ are larger by 1–3 eV than those of $3d$ SrM'O$_3$ with the same electron occupancy in d orbitals. Because the systematic change of Δ_{pd} is attributed to the change in electronegativity, the larger Δ_{pd} values in $4d$ SrMO$_3$ can be explained by the smaller electronegativity for $4d$ transition metals, which originates from the more extended character of the $4d$ orbitals.[26]

The general trend of $10Dq$ in the $3d$ series is also similar to that in the $4d$ series, as shown in Fig. 3(b). It should be noted that the $10Dq$ of $4d$ SrMO$_3$ is larger by 1–2 eV than that of $3d$ SrM'O$_3$. This behavior is consistent with the larger values of $d_r^{1.5}/d_{M\text{-O}}^{3.5}$ in $4d$ SrMO$_3$ than those in $3d$ SrM'O$_3$, as shown in the inset of Fig. 3(b). It is evident that the more extended $4d$ orbitals should induce stronger p-d covalency, which causes the larger $10Dq$ values.

While the high-spin configuration is more prevalent in $3d$ TMO, the low-spin configuration can be more easily found in $4d$ SrMO$_3$. This behavior should be closely related to the relatively larger $10Dq$ values in the $4d$ SrMO$_3$ series. For $3d$ Mn oxides, their values of $10Dq$ and a Hund coupling energy J_H ($\sim 3J$) are estimated to be 1.1–1.8 eV (Ref. 23) and ~ 3 eV,[22] respectively, which indicates that the Mn oxides should have the high-spin configuration, where $10Dq < J_H$. On the other hand, the values of $10Dq$ and J_H in $4d$ Ru-oxides can be estimated to be 3 eV and 1.5–1.8 eV,[6] respectively, which indicates that the Ru oxides should have a low-spin configuration, where $10Dq > J_H$. Although there is no report on J_H of SrRhO$_3$, the large $10Dq$ value of ~ 2.6 eV supports that this compound should also have the low-spin configuration.

In summary, we reported systematic investigations on physical parameters, such as charge transfer energy Δ_{pd} and crystal-field splitting energy $10Dq$, of the perovskite type of $4d$ SrMO$_3$ (M=Zr, Mo, Ru, and Rh) using optical conductivity analyses. While the systematic changes of these parameters with the transition metal atomic number are similar to the case of $3d$ transition metal oxides, their magnitudes are different; the Δ_{pd} and the $10Dq$ values are relatively larger. These behaviors can be explained by the more extended character of $4d$ orbitals, which can be a main factor to distinguish physical properties of the $4d$ compounds from those of the $3d$ ones.

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