Systematic trends in the electronic structure parameters of 4d transition metal oxides SrMO$_3$ ($M =$ Zr, Mo, Ru, and Rh)

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

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I. INTRODUCTION

There have been lots of investigations on 3d transition metal oxides (TMO), including cuprates and manganites, because they show a variety of interesting electric and magnetic properties. These behaviors are closely related to the strong electron-electron (el-el) correlation, which originates from the localized 3d-orbitals. On the other hand, 4d TMO have attracted relatively less attention because it was thought that the el-el correlation effects should be small and insignificant due to their more extended d-orbitals. However, numerous intriguing properties, such as superconductivity, non-Fermi liquid behavior, pseudogap formation, and metal-insulator transitions, have been observed recently in the 4d TMO, especially ruthenates and molybdates. These observations have stimulated new attention to the 4d TMO. Because 4d TMO are characterized by more extended orbitals than 3d TMO, it has been generally believed that electrons in the extended 4d-orbitals feel rather weak on-site Coulomb repulsion energy $U$ and exchange energy $J$, and the 4d-orbitals hybridize more strongly with neighboring orbitals, e.g., O 2$p$-orbitals, than 3d-orbitals. Additional interactions, such as spin-orbit coupling, also become significant. However, these qualitative ideas are not sufficient to understand the intriguing physical phenomena observed in some 4d TMO. In 3d TMO, systematic investigations on $U$ and charge transfer energy $\Delta_{pd}$ provide a basis to elucidate origins of numerous intriguing properties. Unfortunately, there have been few quantitative studies about the electronic structures of 4d TMO, except ruthenates, which makes it difficult to understand their physical properties in more depth. 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. And, they will also allow us to make comparisons with the 3d TMO cases, which can provide us a better understanding of physics of both TMO.

Optical spectroscopy is known to be a powerful tool to analyze the electronic structures of TMO by probing the joint density of states between unoccupied and occupied states. In this paper, we report a systematic investigation on the electronic structures of the perovskite-type 4d SrMO$_3$ ($M =$ Zr, Mo, Ru, and Rh) by measuring their optical conductivity spectra $\sigma(\omega)$. From these series with the same structure and valency state $M^{4+}$, one can investigate how the electronic structures change with $M$. As far as we know, our study is the first systematic effort to investigate wide range optical properties of the 4d SrMO$_3$ series. Based on proper electronic structure diagrams, the interband transitions observed in their $\sigma(\omega)$ are assigned properly. From this, we estimate im-
portant physical parameters, such as $\Delta_{p_d}$, $U$, and crystal field splitting energy $10D_q$, which show systematic trends with $M$. Compared with the 3$d$ cases, the magnitudes of $\Delta_{p_d}$ and $10D_q$ are larger and those of $U$ are smaller in the $4d$ $SrMO_3$ compounds. These behaviors can be understood as the more extended character of the 4$d$-orbitals than the 3$d$-ones. From our observations, it is found that these 4$d$ oxides belong to the Mott-Hubbard regime.

II. EXPERIMENTAL TECHNIQUES

Polycrystalline $SrZrO_3$, $SrMoO_3$, and $SrRhO_3$ were prepared using the solid state reaction technique. For the $SrZrO_3$ sample, $SrCO_3$ and $ZrO_2$ were used as raw materials. After calcining and grinding repeatedly, the resultant powders were pressed into a pellet under 200 MPa using cold isostatic pressing. The $SrZrO_3$ pellet was sintered at 1700 °C for 5 hours. For the $SrMoO_3$ sample, the fine and pure $SrO_2$, $MoO_3$, and $Mo$ powders were mixed with a composition of $SrMoO_3$. The mixture of approximately 0.2 g was placed into a gold capsule and then compressed at 6 GPa in a high-pressure apparatus. The sample was heated at 1300 °C for 1 hour and quenched to room temperature at the elevated pressure. For the $SrRhO_3$ sample, a preparation procedure similar to that of the $SrMoO_3$ sample was used. The details of this procedure were published elsewhere. The high pressure of sintering technique is effective to provide metastable $Mo^{3+}$ and $Rh^{4+}$ states. From x-ray diffraction measurements, it was confirmed that all the samples have a single phase. From dc resistivity and magnetization measurements, it was also found that their electric and magnetic properties are consistent with the previous reports.

Just before optical measurements, we polished the sample surfaces up to 0.3 μm. Then, we measured reflectivity spectra from 5 meV to 30 eV at room temperature. In the energy region between 5 meV and 0.6 eV, we used a conventional Fourier transform spectrophotometer. Between 0.5 eV and 6.0 eV, we used a grating spectrophotometer. And, in the deep ultraviolet region above 6.0 eV, we used synchrotron radiation from the normal incidence monochromator beam line at Pohang Accelerator Laboratory. After the optical measurements, thin gold films were evaporated onto the samples and used for making corrections for light scattering loss from the rough sample surfaces.

In order to obtain $\sigma(\omega)$ from the measured reflectivity spectra, we performed the Kramers-Kronig (KK) analysis. It was known that the KK analysis for the highly anisotropic polycrystalline samples could provide incorrect $\sigma(\omega)$. However, all of our 4$d$ TMO have the slightly distorted perovskite structure and their optical constants should be nearly isotropic, so the KK analysis could be applied without any problem. For the analysis, the reflectivity below 5 meV was extrapolated with the Hagen-Rubens relation for the metallic samples and with a constant value for the insulating $SrZrO_3$ sample. For a high frequency region, the reflectivity value at 30 eV was used for reflectivities up to 40 eV, above which $\omega^{-4}$ dependence was assumed. To check the validity of our KK analysis, we independently determined $\sigma(\omega)$ using spectroscopic ellipsometry techniques in the photon energy range of 1.5 - 5.5 eV. The $\sigma(\omega)$ data from the spectroscopic ellipsometry agreed quite well with the results from the KK analysis.

III. RESULTS AND DISCUSSIONS

A. Schematic diagrams of the electronic structures

Figure 1 shows schematic diagrams of the electronic structures of the perovskite-type $SrMO_3$ compounds, where the 4$d$ transition metal $M$ is either Zr, Mo, Ru, or Rh. Figure 1(a) shows a typical diagram of electronic structure for a $d^0$-insulator. $SrZrO_3$ is known to be a 4$d^0$-insulator with a bandgap between the O 2p- and the Zr 4$d$ t$_{2g}$-band. The e$_g$-band has a higher energy level by 10$D_q$ than the t$_{2g}$-band. Usually, the $Sr$ 4$d$-band is in a higher energy level than $M$ 4$d$-bands. As the atomic number of $M$ increases from Zr, extra 4$d$ electrons start to fill the t$_{2g}$-band partially without any significant change in the overall feature of the band structure. Here, the details of the partially-filled t$_{2g}$ orbitals can vary according to the el-el correlation. When the el-el correlation is quite weak, i.e., 4$d$ bandwidth $W \gg U$, the partially-filled band induces a band metallic state, as shown in Fig. 1(b). Since $SrMoO_3$ is a 4$d^2$-system and known to be a Pauli paramagnetic band metal, its electronic structure should resemble Fig. 1(b). On the other hand, when the el-el correlation is quite large, i.e., $U \gg W$, the partially-filled band is split into two Hubbard bands by $U$, which induces a Mott insulator. In the
intermediate state between two extreme cases, there can occur correlated metals, whose band diagram is shown in Fig. 1(c). In the low-spin configuration, the quasiparticle band is located at $E_F$ in addition to the Hubbard bands, and the $e_g$-band remains empty.

The electronic structure of SrRuO$_3$, a low-spin 4$d^2$-system, was investigated by earlier workers and known to follow Fig. 1(c). It was recently found that a 4$d^2$-system SrRhO$_3$ is a paramagnetic correlated metal with the low-spin configuration. Because the $W$ of SrRhO$_3$ is narrower than that of SrRuO$_3$, the Hubbard bands induced by the $el-el$ correlation are more dominant in SrRhO$_3$ than in SrRuO$_3$. So, the band diagram of SrRhO$_3$ can be also explained by Fig. 1(c).

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 4$d$ SrMO$_3$ systems. From such interband transitions, we can estimate some physical parameters: a charge transfer energy $\Delta_{pd}$ 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 $M_4d$ $e_g$ transitions. On the other hand, the $U$ value should be estimated from the $d$-$d$ transition between two Hubbard bands, which should be much weaker than the $p$-$d$ transitions.

**B. Assignment of interband transitions in the SrMO$_3$ compounds**

Figure 2 shows $\sigma(\omega)$ of SrZrO$_3$ up to 20 eV. It is clearly shown that this insulating 4$d^0$-compound has a large optical gap of $\sim 5.6$ eV, consistent with the previous reports. This value is larger by $\sim 2$ eV than the bandgap of SrTiO$_3$, i.e., 3.4 eV. Distinct interband transitions are observed around 8 eV and 12 eV. To our knowledge, there has been no band calculation report on this compound, so we assigned these interband transitions by referring to the band structure of SrTiO$_3$, which is a 3$d^1$ insulator. The dotted line in Fig. 2 represents $\sigma(\omega)$ of SrTiO$_3$. Its overall features are very similar to that of SrZrO$_3$, but with $\sim 2.5$ eV shift to lower energy. K. van Benthem et al. assigned the peaks around 5 eV and 9 eV of SrTiO$_3$ as O $2p \rightarrow Ti$ 3$d$ $t_{2g}$ and O $2p \rightarrow Ti$ 3$d$ $e_g$ transitions, respectively. They also claimed that the higher frequency peak should come from O $2p \rightarrow Ti$ 3$d$ $e_g$ and/or Sr $4d$. Similarly, we can assign the peaks around 8 eV and 13 eV in SrZrO$_3$ as O $2p \rightarrow Zr$ 4$d$ $t_{2g}$ and O $2p \rightarrow Zr$ 4$d$ $e_g$ transitions, respectively. Note that these assignments are consistent with the energy diagram of a band insulator, shown in Fig. 1(a). By using the positions of the strong peaks, we can approximately estimate $\Delta_{pd} \sim 8$ eV and $10Dq \sim 5$ eV in SrZrO$_3$, which are larger than the values for SrTiO$_3$ (i.e., $\Delta_{pd} \sim 5$ eV and $10Dq \sim 4$ eV).

![Figure 2. Room temperature $\sigma(\omega)$ of 4$d^0$ SrZrO$_3$ (the solid line) up to 20 eV. The $\sigma(\omega)$ of 3$d^0$ SrTiO$_3$ (the dotted line), quoted from Ref. 21, is also displayed with a 2.5 eV shift to higher energy for comparison with SrZrO$_3$.](image-url)

Figure 3 shows $\sigma(\omega)$ of the SrMO$_3$ series, with $M =$ Zr, Mo, Ru, and Rh, up to 12 eV. The $\sigma(\omega)$ of SrRuO$_3$ is quoted from our previous paper. The insulating SrZrO$_3$ has a relatively large optical gap. For other metallic compounds, $\sigma(\omega)$ below 1.0 eV have zero-frequency spectral weights, which decrease with the increasing atomic number of $M$. The coherent mode of the band metallic SrMoO$_3$ can be fitted well by the Drude model with a plasma frequency of $\sim 2.8$ eV and a scattering rate of $\sim 0.3$ eV. For other correlated metallic SrRuO$_3$ and SrRhO$_3$, the low frequency $\sigma(\omega)$ decreases more slowly than the $1/\omega^2$-dependence which is predicted by the Drude model. This behavior, which have often been observed in many correlated metals, indicates that the incoherent character in the mid-infrared region might be rather strong.

The observed peaks of the SrMO$_3$ compounds can be assigned according to their electronic structures shown in Fig. 1. It is noted that, according to the Fermi golden rule, the $p$-$d$ transition should be dominant in $\sigma(\omega)$. The assignments for the SrZrO$_3$ peaks were already given. For SrMoO$_3$, the 5.0 eV and 8.5 eV peaks are observed clearly, as shown in Fig. 3(b). These two peaks can be assigned as O $2p \rightarrow Mo$ 4$d$ $t_{2g}$ and O $2p \rightarrow Mo$ 4$d$ $e_g$ transitions. For SrRuO$_3$, the 3.0 eV, 6.0 eV, and 10 eV peaks shown in Fig. 3(c) can be assigned as O $2p \rightarrow Ru$ 4$d$ $t_{2g}$, O $2p \rightarrow Ru$ 4$d$ $e_g$, and O $2p \rightarrow Sr$ 4$d$ transitions, respectively, according to our previous report. Note that the $d$-$d$ transition between the lower and the upper Hubbard bands is located around 1.7 eV, but too weak to be clearly seen in this compound.
It is interesting to observe systematic trends in the interband transitions of the SrMO$_3$ series. As it goes from SrZrO$_3$ to SrRhO$_3$, all of the p-d transitions shift to lower energies. In the photon energy region up to 12 eV, only the O 2$p$ → M 4$d$ $t_{2g}$ transition is observed in SrZrO$_3$, but the O 2$p$ → M 4$d$ $e_g$ transition is additionally observed in SrMoO$_3$. And, in SrRuO$_3$ and SrRhO$_3$, the O 2$p$ → Sr 4$d$ transition as well as the O 2$p$ → M 4$d$ transition are observed. Note that as the atomic number of M increases, the O 2$p$ → M 4$d$ transitions shift to the lower energy side. In addition, the peak interval between the O 2$p$ → M 4$d$ transitions and the O 2$p$ → M 4$d$ $e_g$ transitions decreases. These interesting trends in peak positions should be originated from the systematic changes of $\Delta_{pd}$ and $10Dq$.

C. Systematic trends in $\Delta_{pd}$ and $10Dq$

Figure 4(a) shows a systematic trend in the $\Delta_{pd}$ values, which are estimated from the position of the O 2$p$ → M 4$d$ $t_{2g}$ transition. As the atomic number increases, $\Delta_{pd}$ decreases. According to J. B. Torrance et al.’s work with the ionic model, the change of $\Delta_{pd}$ with the atomic number of a transition metal is attributed mainly to the change in electronegativity (or ionization energy) of a transition metal; as the electronegativity of a transition metal becomes larger, the $\Delta_{pd}$ decreases. So, the decrease of $\Delta_{pd}$ in 4$d$ SrMO$_3$ can be explained by the larger electronegativity of M with its atomic number increasing.

Figure 4(b) shows a systematic trend in the $10Dq$ values, which are estimated from the peak position difference between the O 2$p$ → M 4$d$ $t_{2g}$ and the O 2$p$ → M 4$d$ $e_g$ transitions. The $10Dq$ of SrZrO$_3$ is approximately estimated to be ~ 5 eV, as shown in Fig. 2. The $10Dq$ value of SrMoO$_3$, ~ 3.8 eV, is comparable to that in Mo 4d-bands of double perovskite Sr$_2$FeMoO$_6$, ~ 4 eV, from x-ray absorption spectroscopy. SrRhO$_3$ is estimated to have $10Dq$ ~ 2.6 eV, a little smaller than that of SrRuO$_3$, i.e., 3 eV. It is noted that the $10Dq$ decreases with the increasing atomic number of M. It is generally accepted that, as the overlap (or covalency) between the 2p- and the d-orbital becomes stronger, $10Dq$ becomes larger. So, the decrease of the $10Dq$ in the 4$d$ SrMO$_3$ series can be understood as the shrinking of the d-orbitals, and the resultant weakening of the covalency between the 4$d$-and the O 2$p$-orbitals with the increasing atomic number. For a quantitative analysis, we estimate the covalency strength as the $p$-d matrix element with the $\sigma$-bonding $V_{pd\sigma} \propto d_r^2 \frac{d_{M-O}^2}{d_r^2 + d_{M-O}^2}$, suggested by W. A. Harrison. Here, $d_r$ and $d_{M-O}$ are the radial size of the d-orbital and the distance between the M and the O ions, respectively. As shown in the inset of Fig. 4(b), the value of $d_r^2 d_{M-O}^2$ in the 4$d$ compounds decreases with increasing atomic number of M, consistent with the decrease of $10Dq$. This suggests that the $p$-d covalency should play
values of $\Delta_{pd}$ in the 3d Sr$M'O_3$ series are displayed as the open circles. Similar to the case of the 4d TMO, $\Delta_{pd}$ decreases as the atomic number of $M'$ increases. While there are no optical reports on metallic SrFeO and SrCoO$_3$, photoelectron spectroscopy (PES) results claimed that their $\Delta_{pd}$ values be nearly zero. However, the magnitudes of $\Delta_{pd}$ in 4d SrMO$_3$ are relatively larger than those of 3d SrM'O$_3$ with the same electron occupancy in $d$-orbitals. As mentioned earlier, the systematic change of $\Delta_{pd}$ is attributed to the change in electronegativity. The larger $\Delta_{pd}$ values in the 4d SrMO$_3$ series than those in the 3d SrM'O$_3$ series can be also explained by the smaller electronegativity for 4d transition metals.

In Fig. 4(b), the reported values of 10$Dq$ in the 3d SrM'O$_3$ series are plotted as the open circles. The general trend of 10$Dq$ in the 3d series is also similar to that in the 4d series. It is interesting to see that the 10$Dq$ of 4d SrMO$_3$ is larger than that of 3d SrM'O$_3$. This behavior is consistent with the larger values of $d_{r}^{5}/d_{M-O}$ in 4d SrMO$_3$ than those in 3d SrM'O$_3$, shown in the inset. It is evident that the more extended 4d-orbitals induce stronger $p$-$d$ covalency, which causes the 10$Dq$ values of the 4d oxides to be larger than those of the 3d oxides.

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 10$Dq$ values in the 4d SrMO$_3$ series. The spin-configuration in TMO is determined according to the relative magnitude of 10$Dq$ and $J$: a high-spin configuration for 10$Dq < J$, and a low-spin configuration for 10$Dq > J$. It is known that some 3d TMO, such as Mn- and Fe-oxides, have a high-spin configuration. For example, the values of 10$Dq$ and $J$ in Mn-oxides are estimated to be 1.1 $\sim$ 1.8 eV and $\sim$ 3 eV, respectively. On the other hand, 4d TMO favor the low-spin configuration with the relatively larger 10$Dq$ and smaller $J$ due to the more extended 4d-orbitals. For Ru-oxides, the values of 10$Dq$ and $J$ are estimated to be 3 eV and 0.5 $\sim$ 0.6 eV, respectively. Although there is no report about $J$ in SrRhO$_3$, the large 10$Dq$ value of $\sim$ 2.6 eV strongly suggests that this compound should have the low-spin configuration. Because the Rh 4d-orbitals become more extended in the Rh$^{3+}$ state than in the Rh$^{4+}$ state, an insulating 4d$^{9}$ LaRhO$_3$ material with a Ru$^{3+}$ state is very likely to be a band-insulator which has fully-occupied $t_{2g}$ orbitals in the low-spin configuration.

In the 3d TMO, the character of the low energy charge excitations has been investigated intensively. According to Zaanan, Sawatzky, and Allen’s picture, the charge excitation should be the $d$-$d$ transition between the Hubbard bands, if $U < \Delta_{pd}$. This is classified as the Mott-Hubbard regime. If $U > \Delta_{pd}$, the low energy excitation should be a $p$-$d$ transition, and this regime is classified as the charge transfer regime. While the early 3d TMO are classified to be in the Mott-Hubbard regime ($U < \Delta_{pd}$), the late 3d TMO mainly fall in the

![Graph showing charge transfer energy and on-site Coulomb repulsion energy](image)

**FIG. 4.** (a) Charge transfer energy $\Delta_{pd}$ and on-site Coulomb repulsion energy $U$, and (b) crystal field splitting energy 10$Dq$ in 4d SrMO$_3$ with $M$ = Zr, Mo, Ru, and Rh (solid symbols) and 3d SrM'O$_3$ with $M'$ = Ti, V, Mn, and Co (open symbols). Note that these parameters are estimated from the optical measurements only, except the 10$Dq$ value of SrCoO$_3$. In the inset of Fig. 4(b), the values of $d_{r}^{5}/d_{M-O}$ are estimated in the 3d and the 4d oxides. The values of $d_{r}$ are used from Ref. 25. We also estimated $d_{r}$ from the ionic size of $M^{4+}$ ($M^{4+}$). The results show the similar trends, except the case of SrFeO$_3$. The $d_{M-O}$ of the 3d compounds are used from Ref. 23. For the 4d oxides, because detailed structural analyses have not been done, we used the values of $d_{M-O}$ as half of the pseudo-cubic lattice constants, which are obtained from x-ray diffraction measurements. The pseudo-cubic lattice constants $a$ of SrZrO$_3$, SrMoO$_3$, SrRuO$_3$, and SrRhO$_3$ are 4.11 Å, 3.97 Å, 3.94 Å, 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)].

**D. Comparison with 3d transition metal oxides**

We also display the reported results on some 3d SrM'O$_3$ with a 3d transition metal $M'$= Ti, V, Mn, and Co in Fig. 4. Most of the displayed results were determined from $\sigma(\omega)$ in the same way as was adopted in this paper. Note that we include only the optical results except for the 10$Dq$ value of SrCoO$_3$. In Fig. 4(a), the values of $\Delta_{pd}$ in the 3d SrM'O$_3$ series are displayed as the open circles. Similar to the case of the 4d TMO, $\Delta_{pd}$ decreases as the atomic number of $M'$ increases. While there are no optical reports on metallic SrFeO and SrCoO$_3$, photoelectron spectroscopy (PES) results claimed that their $\Delta_{pd}$ values be nearly zero. However, the magnitudes of $\Delta_{pd}$ in 4d SrMO$_3$ are relatively larger than those of 3d SrM'O$_3$ with the same electron occupancy in $d$-orbitals. As mentioned earlier, the systematic change of $\Delta_{pd}$ is attributed to the change in electronegativity. The larger $\Delta_{pd}$ values in the 4d SrMO$_3$ series than those in the 3d SrM'O$_3$ series can be also explained by the smaller electronegativity for 4d transition metals.

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![Graph showing charge transfer energy and on-site Coulomb repulsion energy](image)
charge-transfer regime \((U > \Delta_{pd})\), implying some kind of crossover between the two regimes. This behavior is related to the increase of \(U\) and the decrease of \(\Delta_{pd}\) as the atomic number of a transition metal increases.

To find the character of the low energy charge excitation in the 4d \(\text{SrMO}_3\) series, we estimated the values of \(U\) from the position of the \(d-d\) transition between the Hubbard bands in \(\sigma(\omega)\). The values of \(U\) for \(\text{SrRuO}_3\) and \(\text{SrRuO}_3\) are estimated from the previous studies. Note that the \(U\) value obtained from \(\sigma(\omega)\) is usually somewhat smaller than that measured from PES, due to the exciton effects, but its difference between optical spectroscopy and PES is usually less than 1.0 eV.

In Fig. 4(a), the values of \(U\) for the 4d \(\text{SrMO}_3\) series are plotted as solid triangles. It appears that the magnitude of \(U\) in 4d \(\text{SrMO}_3\) is relatively smaller than that in 3d \(\text{SrM}′\text{O}_3\). As shown in Fig. 4(a), the value of \(U \sim 2\) eV in \(\text{SrVO}_3\) is comparable to those of \(\text{SrRuO}_3\) and \(\text{SrRhO}_3\), 1.6 - 1.7 eV. Generally, the \(U\) value increases as the size of the \(d\)-orbitals decreases. Because the \(d\)-orbital shrinks as the atomic number increases, the late 3d \(\text{SrM}′\text{O}_3\), such as \(\text{SrFeO}_3\) and \(\text{SrCoO}_3\), are expected to have larger \(U\) than the early 4d \(\text{SrVO}_3\), as has been confirmed by many PES studies. From this, it is clear that the \(U\) value of \(\text{SrRuO}_3\) and \(\text{SrRhO}_3\) should be smaller than those of \(\text{SrFeO}_3\) and \(\text{SrCoO}_3\). So, we can say safely that 4d \(\text{SrMO}_3\) have smaller \(U\) than 3d \(\text{SrM}′\text{O}_3\), which is quite natural due to the more extended nature of the 4d-orbitals.

The larger value of \(\Delta_{pd}\) than \(U\) indicates that all of the 4d \(\text{SrMO}_3\) compounds investigated in this study belong to the Mott-Hubbard regime. From our studies on \(\text{SrRuO}_3\) and \(\text{SrRhO}_3\), the magnitude of \(\Delta_{pd}\), 2.6 - 3.0 eV, is larger than that of \(U\), 1.6 - 1.7 eV, which indicates that even these compounds belong to the Mott-Hubbard regime. This implies that these 4d TMO can be used for investigating the Mott-Hubbard transition with the \(el-el\) correlation. Indeed, the importance of the \(el-el\) correlation has been observed in ruthenates and molybdates. This was rather surprising, since it was thought that the \(el-el\) correlation effects should be insignificant in 4d TMO due to the extended nature of the 4d-orbitals. And, due to the small value of \(U\), the multiplicity of the 4d orbitals might play an important role in physical properties of some 4d TMO. It is highly desirable to reinvestigate physical properties of some 4d TMO in view of the correlation effects.

IV. SUMMARY

We reported quantitative studies on physical parameters such as charge transfer energy \(\Delta_{pd}\), on-site Coulomb repulsion energy \(U\), and crystal field splitting energy \(10Dq\) of the perovskite-type of various 4d \(\text{SrMO}_3\) \((M = \text{Zr, Mo, Ru, and Rh})\) by optical conductivity analyses. While the systematic changes of these parameters with the transition metal are similar to those for the case of 3d transition metal oxides, their magnitudes are different; the \(\Delta_{pd}\) and the 10\(Dq\) values are relatively larger, while the \(U\) value is relatively smaller. These behaviors are explained by the more extended character in 4d-orbitals than in 3d-orbitals, which distinguishes the physical properties of the 4d compounds from those of the 3d ones. The relatively larger 10\(Dq\) is closely related to the low-spin configuration in 4d \(\text{SrMO}_3\). Due to the relatively smaller \(U\) and larger \(\Delta_{pd}\), it is very likely that most 4d transition metal oxides lie in the Mott-Hubbard regime. Although their \(U\) values are relatively small, some intriguing physical phenomena with the correlation effects could occur in 4d transition metal oxides.

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As the Madelung potential difference between a transition metal and O sites, $\Delta V_M$ increases, so does $\Delta_{pd}$. Because the lattice constants of 4$d$ SM$O_3$ are larger than those of 3$d$ SM$O_3$, $\Delta V_M$ is expected to be smaller in 4$d$ SM$O_3$ than in 3$d$ SM$O_3$. So, the contribution of $V_M$ cannot explain the larger $\Delta_{pd}$ of 4$d$ SM$O_3$ than those of 3$d$ SM$O_3$. 

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26. So, the quantity, $\eta_{pd} = d_{pd}^{1.5}/d_{M^{(M')}O}^{1.5}$, represents the anisotropic covalency strength of the O 2$p$ orbitals with the $t_{2g}$- and the $e_g$-orbitals. So, the quantity, $d_{pd}^{1.5}/d_{M^{(M')}O}^{1.5}$ can be a parameter related to the $10Dq$ between the $t_{2g}$- and the $e_g$-orbitals.
27. From PES results, the $U$ value of SrMoO$_3$ is $\sim 3$ eV while that of SrFeO$_3$ is $\sim 7.8$ eV.
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