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Comparative study of the electronic structures of SrMO₃ (M = Ti, V, Mn, Fe, and Co; M = Zr, Mo, Ru, and Rh) by O 1s x-ray absorption spectroscopy

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Abstract

We obtained O 1s x-ray absorption spectra of perovskite SrMO₃ (M = Zr, Mo, Ru, and Rh) to investigate general trends of the electronic structures of the partially filled 4d compounds in comparison with 3d ones (M = Ti, V, Mn, Fe, and Co). The parameter values for the crystal electric field, $10Dq$, and hybridization strength, V_{pd} , are estimated from the configuration interaction cluster model calculation with full ionic multiplets (CICM), showing a systematic change with the increase of the d electron number. The calculated spectra of the 4d compounds from the CICM show good agreement with the measured spectra in the t_{2g} region, but give a considerable deviation in the e_g region, implying orbitally dependent correlation effects.

(Some figures in this article are in colour only in the electronic version)

Transition metal oxides (TMOs) have become important material sources, showing numerous intriguing physical phenomena [1]. Many of the phenomena, such as high temperature superconductivity [2], metal-insulator transition [3], colossal magneto-resistivity [4], etc, have been observed in 3d TMOs. Basically these phenomena are believed to be related to the so-called correlation effects originating from the localized feature of the 3d orbitals of these 3d transition metal (TM) elements. Meanwhile, it has been a traditional belief that 4d orbitals are so spatially spread that 4d TMOs do not have strong correlation effects and the electronic structure can be understood with the one-electron band picture.

However, the discovery of superconductivity in Sr₂RuO₄ changed the traditional expectation [5], and spurred studies on the strongly correlated nature of 4d TMOs, especially ruthenates, molybdates, and rhodates. Now numerous cases on the correlation effects of 4d TMOs have been established, but systematic studies on general features of partially filled 4d orbitals in comparison with 3d ones are still relatively rare [6]. This approach is useful for searching novel materials because these general features can serve as a good guide to comprehensively understanding the physical properties of TMOs.

Soft x-ray absorption spectroscopy (XAS) is a powerful tool for investigating the unoccupied electronic structure of compounds containing transition metal or rare-earth metal

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elements that have the highly localized feature of 3d or 4f orbitals. Unfortunately, the elevated sensitivity of XAS to 3d compounds, especially at the 3d TM L_{2,3}-edge, rapidly decreases at the 4d TM M_{2,3}-edge due to the spatial spread of the 4d orbitals. As a consequence, soft XAS loses its benefits for 4d TM compounds. In the oxides case, however, XAS is still an appropriate probe. Because the O 2p orbitals are strongly hybridized with the TM 4d orbitals and the sensitivity of XAS to the O 1s → 2p transition is quite strong, detailed information about the unoccupied states of the TM 4d orbitals can be obtained by measuring absorption coefficients at the O K-edge of the TMOs. In this study, we investigated the electronic structures of perovskite SrMO₃ (M = Zr, Mo, Ru, and Rh) by O 1s XAS and compared these structures to those of 3d SrMO₃ (M = Ti, V, Mn, Fe, and Co) to understand the general features of the 4d TMOs in comparison with 3d ones. Two important parameter values, the crystal electric field (CEF) splitting energy (10Dq) and hybridization strength (V_{pd}) between the TM d and O 2p orbitals were extracted through configuration interaction cluster model analysis with full ionic multiplets. The analysis results imply that the correlation effects of the 4d TMOs are moderate and orbital dependent.

The polycrystalline SrMO₃ (M = Zr, Mo, Ru, and Rh) were synthesized by the standard solid state reaction method or high pressure technique. All of the samples were confirmed to be a single phase by powder x-ray diffraction measurements. The dc resistivity and magnetization measurements were also consistent with previous reports [7]. The XAS measurements were performed at the Dragon Beamline of the National Synchrotron Radiation Research Center in Taiwan. The chamber pressure and sample temperature were kept at ~10⁻⁹ Torr and 250 K, respectively. The incoming photons were set to have ~98% linear polarization with a 0.2 eV energy resolution. The samples were fractured *in situ* to obtain a clean surface. The spectra were recorded in the total electron yield mode and normalized by the photon flux to have the same intensities in the region well above the threshold.

Cubic perovskite SrMO₃ is an ideal system for a systematic study of how an increase of the principal quantum number from 3 to 4 has an effect on the electronic structure of the TMOs. All of the TM ions are under the same conditions except for the number of partially filled d electrons as the atomic number increases from Zr (Ti) to Rh (Co). The simple O_h symmetry of the ligand field in MO₆ octahedra provides a relatively simple analysis scheme based on the cluster model for interpretation of the O 1s x-ray absorption spectra. Since the application of XAS to 3d TMOs in the early studies [8, 9], the interpretations in numerous XAS studies have been based on a cluster model or the configuration interaction cluster model with full ionic multiplets (CICM), an evolved form of the simple cluster model [10].

In the CICM that we employed in this work, only a cubic MO₆ octahedron was considered. The initial ground state of the TM d electrons is given by $|g\rangle = a_1|d^n\rangle + a_2|d^{n+1}\underline{L}\rangle$, where d^n and \underline{L} denote an n d electrons occupied state and one ligand hole (unoccupied) state, respectively. Similarly, the final one-electron absorbed states are given by $|f_i\rangle = b_1|\underline{c}d^{n+1}\rangle + b_2|\underline{c}d^{n+2}\underline{L}\rangle$, where \underline{c} denotes the oxygen 1s core

hole state. In order to take the full ionic multiplets into account, we express both the initial state Hamiltonian and final states Hamiltonian as follows; $H = \sum_i \epsilon_{di} d_i^\dagger d_i + \sum_i \epsilon_{pi} p_i^\dagger p_i + \sum_{ijkl} U_{ijkl} d_i^\dagger d_j^\dagger d_l d_k + \sum_{ij} V_{ij} d_i^\dagger p_j + \text{H.c.}$, where $i \sim l$, label spin and orbital-quantum numbers. The ligand 2p orbitals are assumed to be symmetry-adapted to d orbitals. Here, d_i^\dagger (p_i^\dagger) creates an electron on a transition metal d (ligand 2p) orbital and the orbital energies are given by ϵ_d (ϵ_p). V_{ij} and U_{ijkl} are the nearest-neighbor metal–oxygen hopping energy and the Slater integrals, respectively. The Hamiltonians are directly diagonalized to obtain the initial ground state and the final states with the eigenenergies, respectively. We calculate the absorption spectrum by $I_{O\ 1s}(\omega) = \sum_{i,j} |\langle f_i | p_j^\dagger | g \rangle|^2 \delta(E_f - E_g - \hbar\omega)$, where i is a running index for all final states, E_g the initial ground state energy, and E_f the final state energy, respectively. If the core hole interactions are assumed to be ignorable, this corresponds to a transition from an O 1s core state to a ligand 2p hole state in a single electron picture. The obtained delta-function-like peaks are broadened with a Lorentzian profile whose width is energy dependent in order to simulate a core hole lifetime effect. After all, the Hamiltonians are parametrized with the crystal electric field (10Dq), the charge transfer energy ($\Delta = E(d^{n+1}\underline{L}) - E(d^n)$), the Slater–Koster integrals ($V_{pd\sigma}$), and the Slater integrals (U_{ijkl}), again expressed in terms of the on-site Coulomb energy (U) and Slater–Condon parameters (F_{dd}^2 , F_{dd}^4). In an undistorted cubic perovskite, $V_{t2g} = -2V_{pd\pi}$ and $V_{eg} = \sqrt{3}V_{pd\sigma}$. If $V_{pd\sigma} = -2.16V_{pd\pi}$ is assumed, according to Harrison’s rule all hybridization strengths are expressed in terms of $V_{pd\sigma}$, but we used $V_{pd\sigma}$ and $V_{pd\pi}$ as independent parameters in order to reflect the lattice distortion effects and deviation from Harrison’s rule [11]. The calculated spectra are qualitatively fitted to the measured spectra until they show the best agreement. More detailed information about the CICM is available in [10].

In perovskite SrMO₃ (M = Zr, Mo, Ru, and Rh), the transition metal M is nominally tetravalent, so the number of d electrons is 0 in Zr, 2 in Mo, 4 in Ru, and 5 in Rh. Because the TM atom occupies the center of a MO₆ octahedron, the five d orbitals are split into triply degenerate t_{2g} orbitals and doubly degenerate e_g orbitals due to the crystal electric field (CEF) with O_h symmetry as shown in the schematic diagram of figure 1. The O 1s XAS spectrum of SrMoO₃ is displayed in figure 1 together with the calculated spectrum from the CICM. The spectrum can be roughly divided into three regions, 529–536 eV, 536–541 eV, and 541–547 eV. Each region corresponds to the unoccupied Mo 4d, Sr 4d, and Mo 5sp states, respectively. The consistency of these assignments is checked with the other XAS spectra of the 4d TMOs, as shown in figure 2.

The measured spectrum can be qualitatively understood using a simple ionic model as follows. In the Mo⁴⁺ (4d²) case, when a 1s core electron is excited by an x-ray and occupies the partially filled 4d orbitals, there are four cases with a different energy as shown in figure 1: t_{2g}↑, t_{2g}↓, e_g↑, and e_g↓. The energy of the electron occupied in the t_{2g}↓ state increases by the Hund coupling energy (J_H). If we denote J to be an average exchange energy per electron pair with different spin states

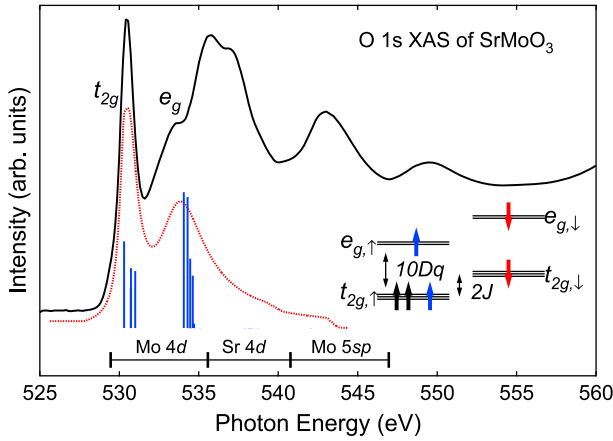


Figure 1. O 1s XAS spectra of SrMoO₃. The inset shows a schematic energy diagram and possible electron configurations.

there are two electron pairs in the $t_{2g\downarrow}$ case, so $J_H = 2J$. Similarly, in the $e_{g\uparrow}$ and $e_{g\downarrow}$ cases, the energy increases by $10Dq$ and $10Dq + 2J$, respectively. Thus, four distinct peaks are expected in the XAS spectrum. However, in 4d TMOs, because the exchange energy ($2J$) is much smaller than the CEF ($10Dq$), only two peaks in the Mo 4d region are as observed in figure 1. The CICM approach shows the same result. The blue bars in figure 1 represent the relative transition probabilities calculated from the final multiplet structure. The red dotted line is the calculated spectrum from the multiplets with Lorentzian broadening of $\text{FWHM} = 0.3 + 0.35|E - E_F|$ eV.

Figure 2(a) shows all of the measured O 1s XAS spectra of the 4d TMOs together with the spectra calculated by the CICM (red lines). The measured spectra are shifted by -528.0 eV for convenience. Below them, the lifetime broadened (0.5 eV) O p -projected unoccupied density of states (UDOS), calculated by the local density approximation (LDA) method, is plotted for comparison [12–14]. For SrMoO₃, no LDA result is available at present. It is noteworthy in figure 2 that the position of the M 4d states systematically moves to the lower photon energy side as the atomic number of M increases, while other states stay at nearly the same position. This is a good example of the chemical shift of the O 1s core hole binding energy in XAS. Figure 2(b) shows the O 1s XAS spectra of the 3d TMOs ($M = \text{Ti, V, Mn, Fe, and Co}$) taken from the literature [15–18]. In the plot, the first main peak of the spectra is set to 0 eV for convenience. The CICM calculation results (red lines) and UDOS (blue dotted lines) are also displayed below the spectra [15, 20, 19, 21, 22]. Neither the CICM calculations nor UDOS completely reproduce the XAS spectra of the 4d TMOs. This is quite in contrast to the prevailing agreement of the CICM calculation with the 3d TMOs as shown in figure 2(b).

SrZrO₃ is a band insulator with fully occupied O 2p and empty Zr 4d bands. The gap size is known to be ~ 5.4 eV [1]. The LDA calculation predicts an insulating phase with the 3.4 eV gap size. The electronic structure of the unoccupied states appears quite different from the measured structure, as shown in figure 2(a), but the CICM calculation reasonably reproduces the experimental spectrum. Here, the peak (\blacklozenge) at

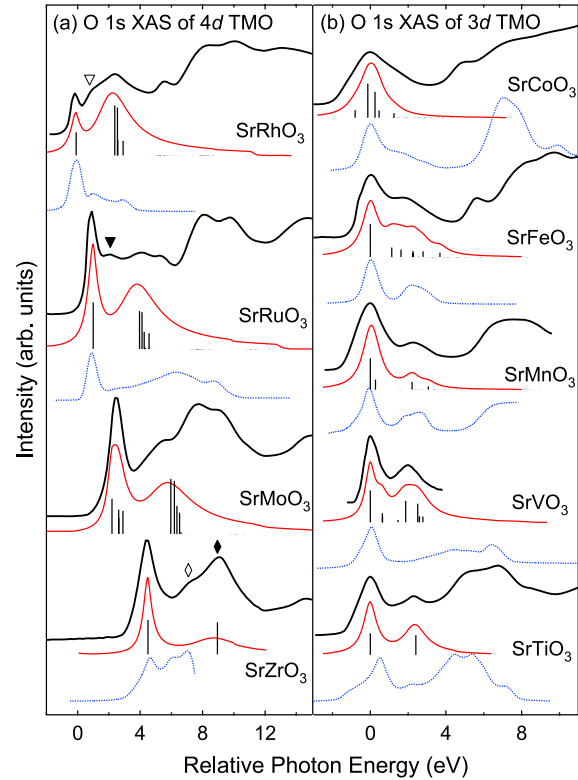


Figure 2. (a) O 1s XAS spectra of SrMO₃ ($M = \text{Zr, Mo, Ru, and Rh}$). The calculated spectra by CICM (red lines) and oxygen p -projected unoccupied density of states (UDOS) (blue dotted lines) are drawn below the measured spectra. The black bars represent the multiplet transition probabilities. (b) O 1s XAS spectra of SrMO₃ ($M = \text{Ti, V, Mn, Fe, and Co}$). The others are the same as (a). All experimental spectra for the 3d TMOs are taken from [15, 19, 20, 18].

9 eV is regarded as the Zr 4d e_g states and the shoulder peak (\blacklozenge) at 7 eV as a part of the Sr 4d states. In other words, the 9 eV structure is composed of the Zr 4d states and Sr 4d states. Then, we can explain why only the 9 eV peak (\blacklozenge) of ZrSrO₃ among the commonly observed Sr 4d structures of the 4d TMOs has a larger weight than the other peak at 7 eV. The $10Dq$ value, 4.2 eV, from the CICM calculation under this assignment is also consistent with the previously reported value, 5.0 eV, from the optical measurement [6].

In the SrMoO₃ case, two electrons occupy t_{2g} orbitals. The system becomes a paramagnetic metal. The XAS spectrum is reproduced from the CICM calculation with $10Dq = 3.3$ and $V_{pd\sigma} = 2.6$ eV, and is understood as described above. SrNbO₃ and SrTcO₃ are not available in this work. In the cases of SrRuO₃ and SrRhO₃, four and five electrons occupy the 4d states respectively, then two kinds of spin configuration, high spin and low spin, are possible for the ground state. The spin configuration is determined by the competition between the CEF energy ($10Dq$) and the Hund coupling energy (J_H). This energy is proportional to the Slater integrals (U_{ijkl}) in the model Hamiltonians. In the 4d TMOs, due to the spatial spread of the 4d orbitals, the $10Dq$ becomes larger and the J_H smaller, so the low spin configuration is energetically stable. Both CICM and LDA give the same result for the

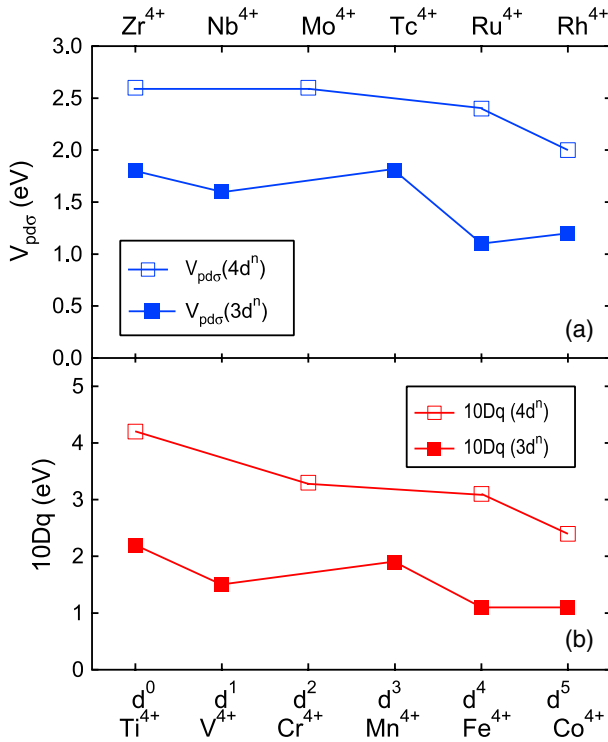


Figure 3. (a) Hybridization strength versus number of d electrons. (b) Crystal electric field versus number of d electrons.

spin configuration. However, neither the CICM nor the LDA satisfactorily reproduces the XAS spectra. The deviation is severe in the e_g states, implying orbital dependent correlation effects. Based on the Ru and Rh cases, the correlation effects in the 4d TMOs are expected only in the t_{2g} states. The peak (∇) at 1 eV in SrRhO₃ and the peak (\blacktriangledown) at 2 eV in SrRuO₃ are not explained by the multiplet structure. Rather, they seem to originate from the band structure based on the oxygen p-projected UDOS presented in figure 2(a). A recent polarization dependent XAS study has reported the large splits of the e_g states in the layered ruthenium oxides and the importance of lattice distortion for the electronic structure [23]. The deviation from the CICM analysis in the e_g region is probably attributable to the band effects induced by the abnormally large splitting of the e_g states. However, there is an opposite view arguing that the peak (\blacktriangledown) at 2 eV in SrRuO₃ is a correlation-induced peak. This issue is still open [24].

Figure 3 displays two important parameters estimated from the CICM analysis: the hybridization strength between the TM d orbitals and O 2p orbitals ($V_{pd\sigma}$) and the CEF energy ($10Dq$), as a function of the d electron number. The estimated $10Dq$ values are very comparable to those of the optical conductivity data [6]. The parameter values used in this analysis are listed in table 1. Here, the U and Δ are not used as fitting parameters because of the insensitivity to O 1s XAS spectra. They were taken from the literature [6, 18, 17, 19, 23]. In figure 3, a systematic change of the electronic structure of the 3d and 4d TMOs is clearly revealed through the changes of the two parameter values. The larger $10Dq$ and $V_{pd\sigma}$ of the 4d TMOs than those of 3d TMOs can be understood by the delocalized nature of the 4d orbitals. The spatial spread

Table 1. Parameter values used in this work.

	$10Dq$ (eV)	$V_{pd\sigma}/V_{pd\pi}$ (eV)	F_{dd}^2, F_{dd}^4 ^a	U (eV)	Δ (eV)
Zr (d ⁰)	4.2	2.6/−1.1	—	—	7.5
Mo (d ²)	3.3	2.6/−1.4	0.2	2.0	3.5
Ru (d ⁴)	3.1	2.4/−1.5	0.2	2.0	3.3
Rh (d ⁵)	2.4	2.0/−1.2	0.2	2.0	2.5
Ti (d ⁰)	2.2	1.8/−1.1	—	—	4.5
V (d ¹)	1.5	1.6/−1.0	0.4	3.6	3.5
Mn (d ³)	1.9	1.8/−0.90	0.75	7.1	3.5
Fe (d ⁴)	1.1	1.1/−0.60	0.45	7.5	0.0
Co (d ⁵)	1.1	1.2/−0.55	0.40	7.5	−2.0

^a F_{dd}^2 and F_{dd}^4 are the ratios to the Hartree–Fock value of the Slater–Condon parameters.

increases the overlapped integrals between the TM 4d and O 2p orbitals, thus increasing hybridizations. Also, the closer to the O anions, the stronger a d electron feels the CEF, so the delocalized 4d orbitals have larger $10Dq$. The decreasing tendency of the $10Dq$ and $V_{pd\sigma}$ with the increase of d electron number can be understood by the shrinking of the orbital with increase of atomic number if we properly take the bond length dependence into account [6]. If the atomic number increases, the nuclear charge also increases, then the average size of the d orbitals becomes smaller. Because a smaller orbital means a spatially less extended nature, the $10Dq$ and $V_{pd\sigma}$ become smaller by the same argument above.

In summary, we have presented the O 1s XAS spectra of perovskite SrMO₃ (M = Zr, Mo, Ru, and Rh) and compared them with the UDOS and the CICM calculation results. The comparison results imply that the 4d TMOs have moderate and orbitally dependent correlation effects. Larger CEF energies and hybridization strengths than those of the 3d TMOs are obtained from the CICM analysis, which explains the prevailing low spin configurations of partially filled 4d TMOs. These parameter values systematically decrease as the number of d electrons increases, which can be understood by the spatial shrink of the d orbitals.

Acknowledgments

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