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Electronic structure of double-perovskite transition-metal oxides

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Electronic structure has been investigated by reflectivity measurement for ordered-perovskite transition-metal oxides, Sr_2MMoO_6 ($M = \text{Cr, Mn, Fe, and Co}$). The ground states of the Co and Mn compounds are paramagnetic insulators, making a sharp contrast with the ferrimagnetic metallic $\text{Sr}_2\text{FeMoO}_6$. For all the compounds, we have observed intense optical transition at ~ 2 eV, which has been ascribed to the charge-transfer excitation from the $O2p$ state to the $\text{Mo}4d$ level. Based on the optical spectra, we argue the electronic structure of this class of compounds.

Transition-metal oxides with ordered double-perovskite structure, $A_2M\text{MoO}_6$, $A_2M\text{ReO}_6$ and $A_2M\text{WO}_6$ (A is a rare-earth metal and M is a transition metal) have begun to attract the interest of material scientists from the practical point of view as a magnetoresistive device. More than 300 compounds with double-perovskite structure, $A_2B'B''\text{O}_6$, have been synthesized,¹ in which the perovskite B sites are occupied alternately by different cations B' and B'' . Among them, $A_2\text{FeMoO}_6$ ($A = \text{Ca, Sr, and Ba}$) are known to be ferrimagnetic with critical temperature T_c ($= 330\text{--}420$ K),² which is higher than that of the doped manganites (maximum T_c is ≈ 360 K for $\text{La}_{0.4}\text{Sr}_{0.6}\text{MnO}_3$). Quite recently, Kobayashi *et al.*³ have observed room temperature magnetoresistance in $\text{Sr}_2\text{FeMoO}_6$ and $\text{Sr}_2\text{FeReO}_6$ due to the intergrain tunneling.⁴ Up to the present, many researchers^{2,3,5-9} have reported the structural, magnetic, and electrical properties of the double-perovskite transition-metal oxides, especially for the Fe-based compounds. To our knowledge, however, there is no spectroscopic investigation, which is indispensable not only to understand the electronic structure of the ordered perovskite, but to design the materials as a magnetoresistive device.

Among the double-perovskite transition-metal oxides, $\text{Sr}_2\text{FeMoO}_6$ ($\text{Sr}_2\text{FeReO}_6$) are metallic and ferrimagnetic with critical temperature $T_c \approx 420$ K (≈ 400 K). In these systems, Fe^{3+} ions ($3d^5$) behave as local spins, while the conduction band is occupied by the $4d(5d)$ electrons of Mo^{5+} (or Re^{5+}). The ferrimagnetism⁷ has been ascribed to the antiferromagnetic superexchange interaction between the $3d^5$ spins and $4d^1(5d^2)$ spins. Band calculation³ suggests a half-metallic feature for these compounds: there exists a gap for the up-spin density of state (DOS), while $\text{Fe}3d\text{--}\text{Mo}4d$ ($\text{Fe}3d\text{--}\text{Re}5d$) mixed state, which is strongly hybridized with the $O2p$ state, is observed around the Fermi level for the down-spin DOS. Itoh *et al.*⁸ have reported that $\text{Sr}_2\text{CoMoO}_6$ and $\text{Sr}_2\text{MnMoO}_6$ are paramagnetic insulators: the paramagnetic behavior has been ascribed to the absence of the $4d$ electrons in the hexavalent $\text{Mo}^{6+}(4d^0)$ ions.⁹

In this paper, we have investigated the electronic structure of the ordered-perovskite transition-metal oxides, Sr_2MMoO_6 ($M = \text{Cr, Mn, Fe, and Co}$). For all of the compounds, we have observed intense optical transition at ~ 2 eV. Judging from the band calculation³ as well as the M -independent transition energy, we have ascribed the tran-

TABLE I. Lattice constant and M -O bondlength (d_{M-O}) for $Sr_2M\text{MoO}_6$ ($M=\text{Cr, Mn, Fe, and Co}$) at 300 K. The crystal symmetry is cubic ($Fm\bar{3}m$; $Z=4$) for $M=\text{Cr, Fe, and Mn}$, and is tetragonal ($I4/mmm$; $Z=2$) for $M=\text{Co}$.

Compound	a (Å)	d_{M-O}/d_{M-M}	c (Å)	d_{M-O}/d_{M-M}
$Sr_2\text{CrMoO}_6$	7.8156(3)	0.234(3)		
$Sr_2\text{MnMoO}_6$	8.0056(1)	0.2639(7)		
$Sr_2\text{FeMoO}_6$	7.8882(4)	0.253(3)		
$Sr_2\text{CoMoO}_6$	7.8816(2) ^a	0.261(2)	7.9575(2)	0.264(4)

^aMultiplied by $\sqrt{2}$

sition to the charge-transfer excitation from the $O2p$ state to the unoccupied $Mo4d$ level. We further have found weak spectral weight down to ~ 0.2 eV, even in the insulating $Sr_2\text{CoMoO}_6$ and $Sr_2\text{MnMoO}_6$.

A series of ceramics compounds, $Sr_2M\text{MoO}_6$ ($M=\text{Cr, Mn, Fe and Co}$), was synthesized by solid state reaction in vacuum. Stoichiometric mixture of commercial SrO , Cr_3O_3 , Mn_3O_4 , Fe_2O_3 , CoO , MnO_3 , and Mo was well ground and calcined two times at 1000–1200°C for 2–3 h. To obtain x-ray powder data of good counting statistics with high angular resolution (full width of half maximum is about 0.03° in 2θ), synchrotron radiation x-ray powder experiments with an imaging plate (IP) as a detector were carried out by using the Large Debye-Scherrer Camera at SPring-8 BL02B2. A precipitation method was adopted in order to get a fine powder, which gives a homogeneous intensity distribution in the Debye-Scherrer powder ring. The fine powder was sealed in 0.2 mm ϕ quartz capillary, and the powder pattern was measured at 300 K. The wavelength of the incident x-ray is 0.4973 Å, and exposure time was 30 min. The crystal symmetry is found to be cubic ($Fm\bar{3}m$; $Z=4$) for $M=\text{Cr, Fe, and Mn}$, except for tetragonal $Sr_2\text{MnMoO}_4$ ($I4/mmm$; $Z=2$). We have analyzed thus obtained x-ray patterns with the RIETAN-97 β program,¹⁰ and listed the results in Table I. We have determined the oxygen position with assuming perfect ordering of the perovskite B site. In Fig. 1 are shown prototypical examples of the Rietveld refinement: (a) $Sr_2\text{MnMoO}_6$ ($Fm\bar{3}m$; $Z=4$) and $Sr_2\text{CoMoO}_6$ ($I4/mmm$; $Z=2$). The final refinements are satisfactory for both cases, in which the reliable factor R_1 is fairly typical of published ones ($R_1=5.05\%$ for $Sr_2\text{MnMoO}_6$ and 4.45% for $Sr_2\text{CoMoO}_6$).

Figure 2(a) shows the temperature dependence of magnetization M per a transition metal for $Sr_2M\text{MoO}_6$ ($M=\text{Cr, Mn, Fe, and Co}$). M was measured under a field of $\mu_0H=0.5$ T after cooling down to 5 K in the zero field (ZFC). A large M value is observed for the $M=\text{Fe}$ compound in the temperature range investigated (≤ 400 K), which is consistent with the high critical temperature ($T_c \approx 420$ K).^{2,5,3} The lower panel of Fig. 2 shows the magnetization curve at 5 K. The M value rapidly increased with the external field, and then saturated at $M_s \approx 3.1 \mu_B$ per Fe site, in agreement with Ref. 3. The M value of the Cr compound slightly increases below ~ 300 K [Fig. 2(a)]. However, the saturation magnetization M_s is $\approx 0.5 \mu_B$ per Cr site [(b)]. The other two compounds, that is, $Sr_2\text{MnMoO}_6$ and $Sr_2\text{CoMoO}_6$, do not show any trace of ferrimagnetic transition down to 5 K. The inset of Fig. 2(a) shows the inverse susceptibility χ^{-1} for

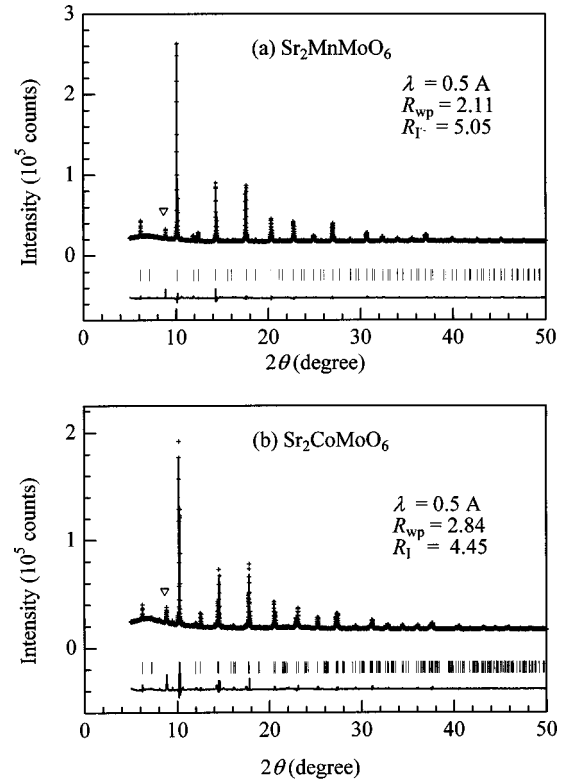


FIG. 1. The whole x-ray powder pattern (cross) at 300 K for (a) $Sr_2\text{MnMoO}_6$ and (b) $Sr_2\text{CoMoO}_6$. Solid curve shows the results of the Rietveld refinement with (a) cubic ($Fm\bar{3}m$; $Z=4$) and (b) tetragonal ($I4/mmm$; $Z=2$) structure. Open triangle indicates MnO_3 impurity.

$Sr_2\text{MnMoO}_6$ and $Sr_2\text{CoMoO}_6$. The $\chi^{-1}-T$ curve well obeys the Curie-Weiss law except for the low temperature region (≤ 40 K) of the Co compound. Effective moments μ_{eff} for the Mn and Co compounds are estimated to be $\approx 5.74 \mu_B$ and $\approx 5.23 \mu_B$, respectively. The magnitude of the μ_{eff} value implies $S=4-5$ per Mn (Co) site, and suggests that Mn (Co) ions take trivalent ($Mn^{3+}; d^4$) or divalent ($Mn^{2+}; d^5$) [high-spin trivalent ($Co^{3+}; d^6$) or tetravalent ($Co^{4+}; d^5$)] states. The magnetic behaviors for Mn and Co compounds are quantitatively consistent with the work done by Itoh *et al.*⁸

The above-mentioned magnetic behaviors seem to correlate with the transport properties. In Fig. 3 we show the temperature dependence of resistivity ρ . For four-probe resistivity measurements, the sample was cut into a rectangular shape, typically of $3 \times 2 \times 1$ mm³, and electrical contacts were made with a heat-treatment-type silver paint. Heat treatment has been done in vacuum. The $\rho-T$ curve for $Sr_2\text{FeMoO}_6$, which is a ferrimagnetic up to T_c (≈ 420 K), shows a metallic behavior up to 400 K. In Table II are shown the interrelation between the magnetic and transport properties of double-perovskite transition-metal compounds. Looking at Table II, one may notice that the high- T_c compounds, that is, $Sr_2\text{FeMoO}_6$, $Sr_2\text{CrMoO}_6$, and $Ba_2\text{FeReO}_6$ have a relatively low $\rho_{298\text{K}}$ value ($\leq 8 \times 10^{-2} \Omega\text{cm}$). Such a correlation suggests that the itinerant carriers, not the superexchange interaction, mediates the ferromagnetic coupling between the local $3d$ spins, e.g., by double-exchange mechanism.

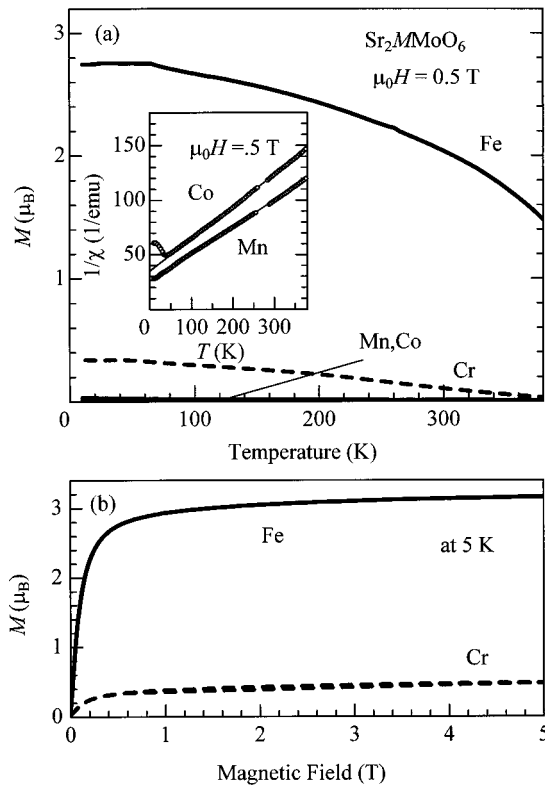


FIG. 2. (a) Temperature and (b) field dependence of magnetization M per a transition metal for Sr_2MMoO_6 ($M = \text{Cr}, \text{Mn}, \text{Fe},$ and Co). M was measured under a field of 0.5 T after cooling down to 5 K in the zero field (ZFC). Inset shows temperature variation of inverse susceptibility χ^{-1} for $\text{Sr}_2\text{MnMoO}_6$ and $\text{Sr}_2\text{CoMoO}_6$. Straight lines are the results of the least-square fitting.

In Fig. 4 are shown the optical conductivity $\sigma(\omega)$ spectra at 300 K obtained by the Kramas-Kronig transformation of reflectivity spectra. Near-normal incident reflectivity measurements were made using a Fourier-type interferometer (0.05–0.75 eV) and a grating-type monochromator (0.6–5.0 eV). The sample surface with diameter of $\sim 4\text{--}5\text{ mm}^2$ was polished like a mirror with polishing sheets. The sharp peak

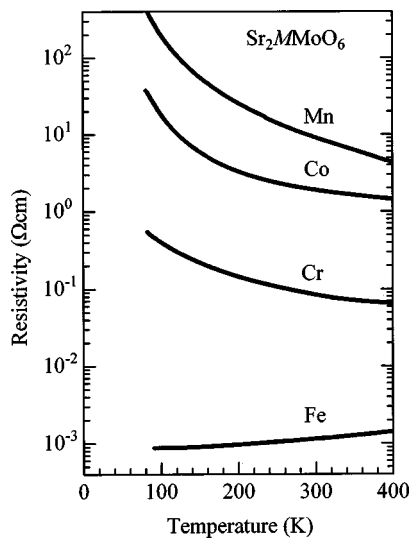


FIG. 3. Temperature dependence of resistivity ρ for Sr_2MMoO_6 ($M = \text{Cr}, \text{Mn}, \text{Fe},$ and Co).

TABLE II. Correlation between the magnetic and transport properties for Sr_2MMoO_6 and Ba_2MReO_6 . T_c , M_s and $\rho_{298\text{ K}}$ denote critical temperature for the ferrimagnetic transition, saturation magnetization, and resistivity at 298 K, respectively.

Compound	T_c (K)	M_s (μ_B)	$\rho_{298\text{ K}}$ (Ωcm)	Reference
$\text{Sr}_2\text{CrMoO}_6$	~ 300	0.5	8×10^{-2}	this work
$\text{Sr}_2\text{MnMoO}_6$			2×10^0	this work
$\text{Sr}_2\text{FeMoO}_6$	420	3.1	8×10^{-3}	2 and this work
$\text{Sr}_2\text{CoMoO}_6$			9×10^0	this work
$\text{Ba}_2\text{MnReO}_6$	105	3.9	6×10^4	9
$\text{Ba}_2\text{FeReO}_6$	334	3.1	9×10^{-4}	9
$\text{Ba}_2\text{CoReO}_6$			3×10^1	9
$\text{Ba}_2\text{NiReO}_6$	18	1.0	4×10^0	9

at $\sim 0.05\text{ eV}$ is due to the optical phonon (breathing-type $M\text{-O}$ stretching vibration). The $\sigma(\omega)$ spectra for $\text{Sr}_2\text{FeMoO}_6$ has a large Drude component below $\sim 1.2\text{ eV}$ consistently with the metallic behavior (Fig. 3), while the other three compounds show an insulating feature. In the insulating compounds ($M = \text{Cr}, \text{Mn},$ and Co), we observed intense transition bands at $\sim 2\text{ eV}$. A trace of the corresponding transition is observed even in the metallic $\text{Sr}_2\text{FeMoO}_6$, though the transition is rather burred. Such an M -independent spectral feature around $\sim 2\text{ eV}$ makes a sharp contrast with the perovskite-type transition-metal oxides, such as LaMO_3 ,¹¹ and LaSrMO_4 ,¹² and indicates that the $M3d$ level is not related to the $\sim 2\text{ eV}$ transition. Judging from the band calculation,³ we have ascribed the transition to the charge-

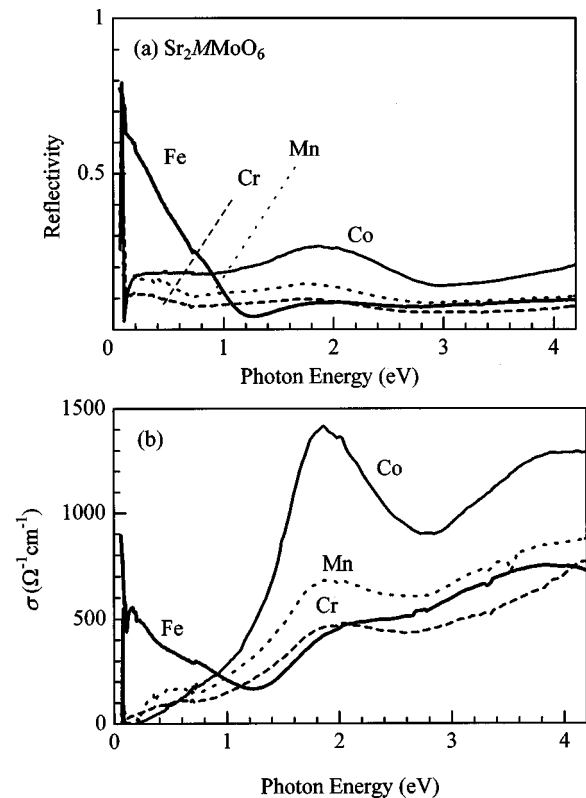


FIG. 4. (a) Reflectivity and (b) optical conductivity $\sigma(\omega)$ spectra for Sr_2MMoO_6 ($M = \text{Cr}, \text{Mn}, \text{Fe},$ and Co) at 300 K.

transfer (CT) excitation from the $O2p$ state to the unoccupied $Mo4d$ level. The pinned excitation energy of the CT transition suggests the same Mo valence state, i.e., Mo^{5+} [$4d$ (Ref. 1)], for these compounds. In this picture, the transition metal takes trivalent state M^{3+} , which is consistent with the observed μ_{eff} values of paramagnetic Sr_2MnMoO_6 and Sr_2CoMoO_6 . Optical gap is estimated to be ~ 0.2 eV for the Mn and Co compounds, and ~ 0.1 eV for the Cr compound. These gap energies are much smaller than the extrapolated energy (~ 0.8 eV) of the intense CT transition, suggesting that the weak spectral weight near the optical gap should be ascribed to different transition. Such a weak spectral weight is reminiscent of the Mott gap transition, as is observed in $LaTiO_3$ and $LaVO_3$.¹¹ For example, in $LaTiO_3$, the Mott excitation is observed down to ~ 1 eV below the intense CT transition (~ 4 eV) from the $O2p$ state to the $Ti3d$ level.

Here, we refer to an alternative interpretation of the $\sigma(\omega)$ spectra shown in Fig. 4. One can think of the situation in which the valence of Mn and Co ions is closer to the divalent state, and that of Mo ion to hexavalent (d^0) state; this would naturally explain the insulating nature of the Co and Mn compounds.⁹ Such a situation is supported by (i) long M -O bondlength (see Table I) and (ii) absence of the magnetic ordering except for the low temperature region (see Fig. 2). Furthermore, band calculation based on the local density approximation (LDA)¹³ suggests divalent states of the Co and Mn ions in the ordered-perovskite structure. How do we understand the $\sigma(\omega)$ spectra with this divalent picture? The

key may be the Mo-O bondlength d_{Mo-O} ; the d_{Mo-O} value becomes shorter in the Co and Mn compounds. With decrease of d_{Mo-O} , hybridization between the $Mo4d$ and $O2p$ enhances. Accordingly, the actual $O2p$ band has considerable $Mo4d$ character in Sr_2CoMoO_6 and Sr_2MnMoO_6 . In this sense, the $Mo4d$ orbitals are partially filled even in the *nominally* hexavalent Mo^{6+} ion. This is why the peak positions of the two CT excitations, that is, from the $O2p$ band to the Mo^{5+} level and to the *nominally* Mo^{6+} level, nearly coincide.

In summary, we have systematically investigated the electronic structure of ordered-perovskite transition-metal oxides, Sr_2MMoO_6 ($M = Cr, Mn, Fe, \text{ and } Co$). The obtained spectra apparently suggest the same Mo valence state, i.e., Mo^{5+} ($4d^1$), for these compounds. However, the above-mentioned argument suggests an important role of the $2p$ - $4d$ hybridization, which strongly couples with the Mo-O bondlength d_{Mo-O} . More elaborated investigations are under progress, to understand the electronic structure as well as the origin of the magnetic interaction of the double-perovskite transition-metal oxides.

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