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Valency and Magnetic-Interaction Control Mechanism In Double-Perovskites Sr_2MMoO_6 (M =Cr, Mn, Fe, Co)

Noriaki Hamada[1] and Yutaka Moritomo[2]

[1] *Department of Physics, Faculty of Science and Technology, Science University of Tokyo, Yamazaki 2641, Noda, Chiba 278-8510, Japan*

[2] *Center for Integrated Research in Science and Engineering, Nagoya University, Furou-cho, Chikusa-ku, Nagoya, Aichi 464-8601, Japan*

Abstract. Recent crystal-structure analysis for Sr_2MMoO_6 (M =Cr, Mn, Fe, Co) implies that the Mo ionic state is 5+ for M = Cr and Fe, and is 6+ for M = Mn and Co. The Mo^{5+} ion makes the system ferromagnetic. The valency control of Mo is considered to be driven by the relative stability of Cr^{3+}, Mn^{2+}, Fe^{3+} and Co^{2+} ions.

Key words: Ordered perovskite, Valency, Magnetic order, Band structure calculation

1 Introduction

Double-perovskites Sr_2MMoO_6 (M = Cr, Mn, Fe, Co) exhibit a variety of magnetic and transport properties. Recent experiments have shown that the bond length of Mo-O is long for M = Cr and Fe, and is short for M = Mn and Co, as shown in Table 1 [1, 2, 3]. This fact implies that the Mo ionic state is 5+ for M = Cr and Fe, and is 6+ for M = Mn and Co. This observation is a key to understand the properties of these materials.

Table 1: Interatomic distances in Sr_2MMoO_6 (M = Cr, Mn, Fe, Co)

M	M-O (Å)	Mo-O (Å)
Cr	1.83	2.08
Mn	2.12	1.89
Fe	2.00	1.95
Co	2.04	1.89

These materials are ferromagnetic with high Curie temperatures for M = Cr and Fe, while those for M = Mn and Co are antiferromagnetic with very low Néel temperatures. If the Mo 4d t_{2g} band is filled partially, the hybridization between the Mo 4d states and the 3d states derives a strong ferromagnetic coupling between the 3d moments, as shown by Sarma *et. al.* [4], and Fang, Terakura and Kanamori [5, 6]. The Mo^{5+} ion produces the ferromagnetism, while only weak superexchange interaction works for the Mo^{6+} system.

To confirm those pictures for the valency and the magnetic interaction, we have performed the electronic band structure calculation by using the full-potential augmented plane wave (FLAPW) method on the basis of the LDA+U scheme [7].

2 Calculational scheme

We use an empirical version of the LDA+U scheme [7] to obtain a realistic energy spectrum of an electron. The empirical values of $U_{eff} = U - J$ for the d state are 2.4eV for Cr, 2.0eV for Mn, Fe and Co, and 1.0eV for Mo. The LDA exchange-correlation potential is evaluated by using an analytical form of Vosko, Wilk and Nusair [8]. The angular momentum in the spherical-wave expansion is truncated at l_{max} = 6 and 7 for the potential and the wave function, respectively.

The muffin-tin radii are 2.1 a.u. for the transition-metal atoms and 1.4 a.u. for the O atom. The energy cutoff parameters of the plane wave for the wave function are 12Ry for the wave function and 48Ry for the charge density and the potentials. We take 19 **k** points in

the irreducible Brillouin zone for the face centered cubic lattice.

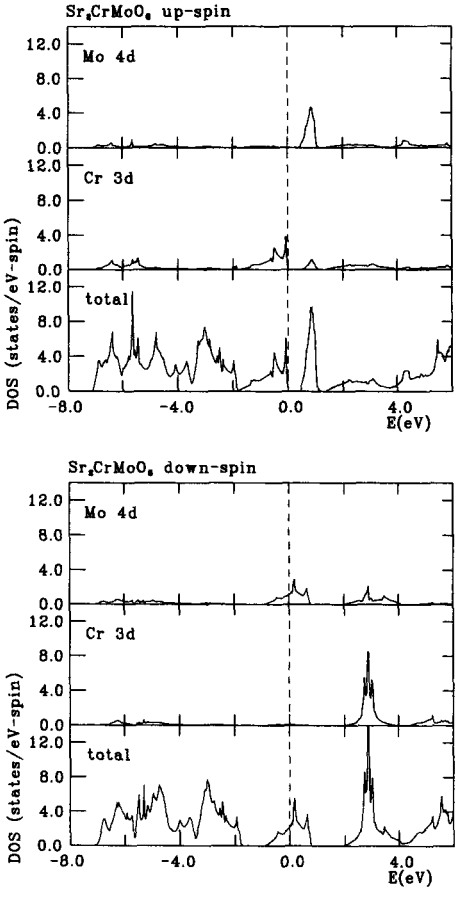

Figure 1: Total and partial DOS of Sr_2CrMoO_6 with the experimental lattice parameter. The energy zero is taken just at Fermi level.

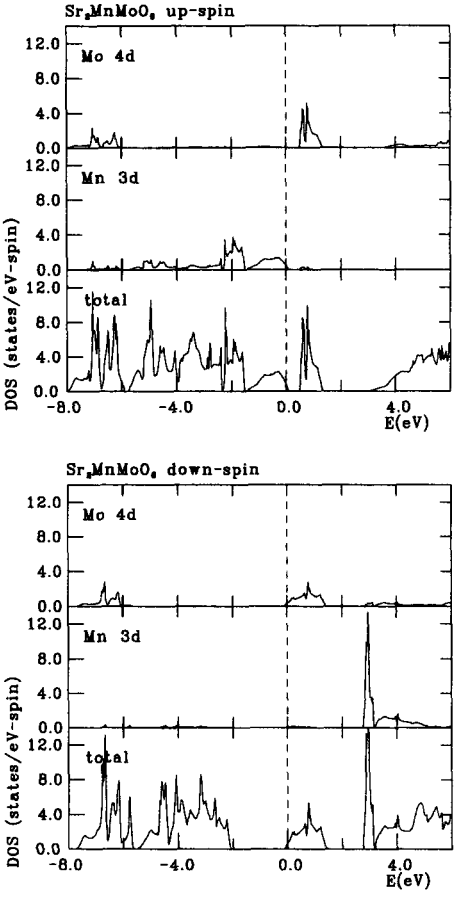

Figure 2: Partial DOS of Sr_2MnMoO_6 with the experimental lattice parameter.

3 Band Structure

We have performed the band structure calculation of ferromagnetic states in order to study the ionic states of Cr, Mn, Fe, Co and Mo.

Figure 1 shows the total and the partial densities of states (DOS) for Sr_2CrMoO_6. The Cr t_{2g} band is fully occupied (at ~ -1eV) for up spin, and is unoccupied (at $\sim +3$eV) for down spin. This means that the Cr ionic state is 3+. The Mo t_{2g} band is unoccupied for up spin, and is partially occupied by one electron for down spin. We can say that the Mo ionic state is 5+.

Figure 2 shows the total and the partial DOS for Sr_2MnMoO_6. The Mn 3d band is almost fully occupied for up spin, and is unoccupied for down spin; the Mn ionic state is 2+. The Mo t_{2g} band is unoccupied for both spins; the Mo ionic state is 6+. The system is expected to be an insulator.

Figure 3 shows the total and the partial DOS for Sr_2FeMoO_6. The Fe 3d band is fully occupied for up spin, and is almost unoccupied for down spin; the Fe ionic state is 3+. The Mo t_{2g} band is unoccupied for up spin, and is partially occupied by one electron for down spin. We can say that the Mo ionic state is 5+. The situation of this Mo t_{2g} band is similar to the Cr case. The down-spin Fe t_{2g} band is, however, located near the Fermi level, and is merged into the Mo t_{2g} band. The state of the Mo band has a considerable component of the Fe t_{2g} state. This means that the ionic states are $(3-\delta)+$ and $(5+\delta)+$ for Fe and Mo, respectively ($\delta > 0$). This subtle ionic state of this system is different

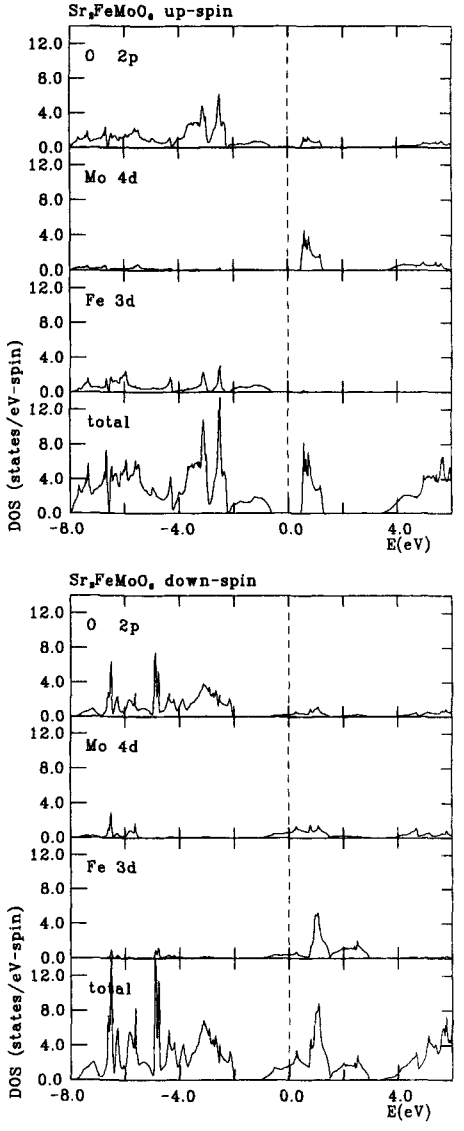

Figure 3: Total and partial DOS of Sr_2FeMoO_6 with the O atom located at the midpoint between Fe and Mo.

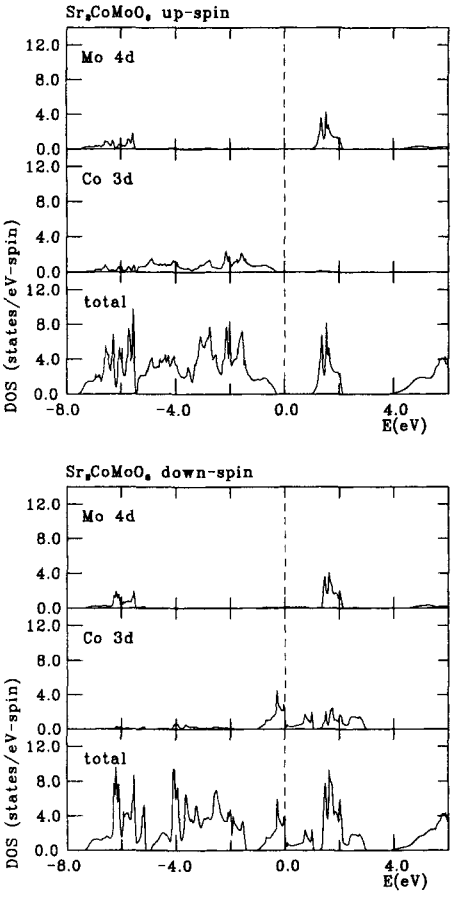

Figure 4: Partial DOS of Sr_2CoMoO_6 with the experimental lattice parameter.

from the other systems of Cr, Mn, and Co. The oxygen ion is slightly nearer to the Mo ion than to the Fe ion, actually (See Table 1).

Figure 4 shows the total and the partial DOS for Sr_2CoMoO_6. The up-spin Co 3d band is fully occupied and the down-spin Co t_{2g} band is partially occupied by two electrons. The Mn ionic state is, therefore, 2+. The Mo t_{2g} band is unoccupied for both spins; the Mo ionic state is 6+. In this case, the crystal structure is tetragonal actually [1], and the Co^{2+} high-spin state is stabilized by the cooperative Jahn-Teller distortion; we have a pseudogap at the Fermi level. If we take into account an appropriate self-energy correction, we will have a real gap. This is consistent with the insulating property.

4 Magnetic Structure

If a state is located at the Fermi level and is partially occupied, the state between magnetic ions produces a strong ferromagnetic interaction between those magnetic moments [6]. In the present case, the state deriving the ferromagnetism is the Mo t_{2g} state [4, 5]. For the Fe system, the down-spin Fe t_{2g} states are strongly hybridized with the down-spin Mo t_{2g} states through O $2p\pi$ states. Actually, there exists a considerable amplitude of down-spin Fe t_{2g} states around the Fermi level. For the Cr system, the t_{2g} hybridization between Cr and Mo

is large for up spin.

For the Mn and the Co systems, the Mo 4d states are unoccupied. The Kanamori-Terakura ferromagnetic interaction does not exist, and, therefore, the system shows very weak antiferromagnetism.

Table 2: Magnetic moments (μ_B) in ferromagnetic phases of Sr_2MMoO_6 (M = Cr, Mn, Fe, Co)

M	M	Mo	total
Cr	2.19	-0.40	2.00
Mn	4.25	0.09	4.92
Fe	3.86	-0.36	4.00
Co	2.62	-0.01	3.00

Table 2 shows the magnetic moments in muffin-tin spheres and the magnetization. For the Cr and the Fe systems, the Mo moment is about 0.4 μ_B, which is induced by the 3d moments. For the Mn and the Co systems, the Mo moment is almost zero, which is consistent with the Mo^{6+} ionic state.

5 Concluding Remarks

The relative positions of the t_{2g} and the e_g bands to the Mo t_{2g} band determines the stable ionic states of Mo and the 3d transition metal atom. The stable ionic states are Cr^{3+}, Mn^{2+}, Fe^{3+} and Co^{2+}. The Mo^{5+} ion produces ferromagnetism for the Cr^{3+} and the Fe^{3+} systems by the Kanamori-Terakura mechanism.

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