Electronic and Magnetic Structures of Ba$_2$$MReO_6$ (M = Mn, Fe, Co, and Ni)

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Electronic structures of ordered double perovskites Ba$_2$$MReO_6$ (M = Mn, Fe, Co, and Ni) are investigated by using the linearized muffin-tin orbitals band method in the local spin-density approximation (LSDA) and the LSDA+U method. The half-metallic ferrimagnetic ground states are obtained for M = Fe and Ni in the LSDA+U, whereas the insulating ground state is obtained for M = Mn in the LSDA+U incorporating the spin-orbit interaction. For M = Co, the antiferromagnetic ground state is stabilized in the LSDA+U by invoking the structural distortion.

1. Introduction

The colossal magnetoresistance (CMR) phenomenon has been firstly found in manganese oxides with perovskite structure [1] and also its derivative structures. However, the low operating temperatures ($T_C < 250$ K) in these materials hinder the practical applications. Therefore, the room temperature CMR phenomena in ordered double perovskites Sr$_2$FeM'O$_6$ (M' = Mo and Re) are essentially interesting to overcome such a problem [2-13].

The replacement of the B cation in the perovskite ABO_3 structure by two different kinds of cations results in the ordered double perovskite structure as $A_2B'B''O_6$. This structure still retains the over-all cubic symmetry and the octahedral environment at the B cation sites.

Compound of the type A_2^{2+}FeMoO$_6$ with the ordered perovskite structure have been reported with A = Ca, Sr, and Ba [4, 5]. For A = Sr and Ba, the tunneling magneto-resistance (TMR) phenomena is observed, but not for A = Ca in the ceramic phase. As changing the A cation from Ba to Sr and Ca, the cubic symmetry turns into the tetragonal and the orthorhombic symmetry. Ito *et al.* [13] have reported the structural and magnetic properties of Sr$_2$$MMoO_6$ (M = Mn, Fe, Co): antiferromagnetic semiconductor for M = Mn, Co and ferrimagnetic metal for M = Fe.

In contrast to active researches done on the Mo-based

double perovskite, studies on Re-based compounds are relatively scarce [14-17]. Sleight *et al.* [14] investigated magnetic and electronic characteristics of the ordered double perovskite Ba$_2$$MReO_6$ (M = Mn, Fe, Co, and Ni). The magnetic features of them are somewhat similar to the Mo-based double perovskites: ferrimagnetic for M = Mn, Fe, Ni, and antiferromagnetic for M = Co. These Re-based double perovskites supply strong evidence for the half-metallic characteristics of integer magnetic moments. The measured magnetic moments are close to integer values, 3.91 μ_B, 3.06 μ_B, and 1.03 μ_B for M = Mn, Fe and Co, respectively.

Although both Sr$_2$FeMoO$_6$ and Sr$_2$FeReO$_6$ exhibit seemingly similar electronic and magnetic characteristics, it should be noted the differences of electronic states of Mo 4d and Re 5d ions. A major difference between Mo and Re oxides is electronic configuration: Mo^{5+} has 4d^1 electron configuration, whereas Re^{5+} has 5d^2. Hence the conduction carrier density of Re system is expected twice larger than that of Mo system, while the localized spins of Fe 3d electrons remain similarly in both oxides. This will have an influence on the magnetotransport behavior, in view of the fact that the low-field MR in ferromagnetic metals depend on the charge-carrier density [18]. Further, the spin-orbit (SO) interaction in Re ion would be important to produce the sizable orbital magnetic moment of Re ion [19, 20].

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2. Computational Method

The linearized muffin-tin orbitals (LMTO) band structure calculations have been performed for cubic double perovskites BaMReO$_6$ (M = Mn, Fe, Co, and Ni). The employed experimental lattice constants are 8.181 Å, 8.050 Å, 8.078 Å, and 8.053 Å for M = Mn, Fe, Co, and Ni, respectively. The density of states (DOS) were obtained by using both the local spin-density approximation (LSDA) and the LSDA + U including the SO interaction [21]. The on-site Coulomb interactions U and the exchange interaction J parameters in the LSDA + U calculations are U = 3~5 eV for Mn, Fe, Co, Ni, and 2.0 eV for Re, respectively, and J = 0.89 eV for all the cases.

3. Results

### 3.1. Ba$_2$MnReO$_6$

The LSDA electronic structure calculation produces the ferrimagnetic metallic state for Ba$_2$MnReO$_6$ (Fig. 1(a)). Spins of Mn and Re ions polarize antiferromagnetically, with the magnetic moment of 3.62 μ_B and −1.83 μ_B, respectively. The metallic result from the LSDA, however, does not agree with the insulating ground state in experiments. Therefore, one has to invoke some other mechanism to yield an insulating ground state. One possible mechanism is the Coulomb correlation effect. However, the LSDA + U method also gives the half-metallic ground state for Ba$_2$MnReO$_6$.

Hence we performed the LSDA + U + SO including the SO interaction. The DOS including the SO interaction shows a semiconducting ground state with a deep valley near the Fermi level (E_F) in agreement with the experiment (Fig. 1(b)). The spin and orbital magnetic moments at Re site are −1.07 μ_B and 0.33 μ_B, respectively. The total magnetic moment per formula unit (f.u.) is 4.38 μ_B with the spin contribution of 4.01 μ_B and the orbital contribution of 0.37 μ_B. The localized states near E_F correspond to the hybridized states mostly of Re t_{2g} and O 2p character.

3.2. Ba$_2$FeReO$_6$

The LSDA electronic structure calculation yields the ferrimagnetic half-metallic ground state for Ba$_2$FeReO$_6$ at the experimental lattice constant of a = 8.050 Å (Fig. 1(c)). The half-metallic nature from the LSDA is consistent with the experimental result of the metallic state for Ba$_2$FeReO$_6$. The DOS of Fig. 1(c) indicates that the exchange splittings $\Delta_{ex} \cong$ 3-4 eV at Fe and Re sites are larger than the crystal field splittings 10$Dq \cong$ 1 eV. Hence the high spin states are favorable at both sites: the majority spin bands (t_{2g} and e_g) at Fe are fully occupied
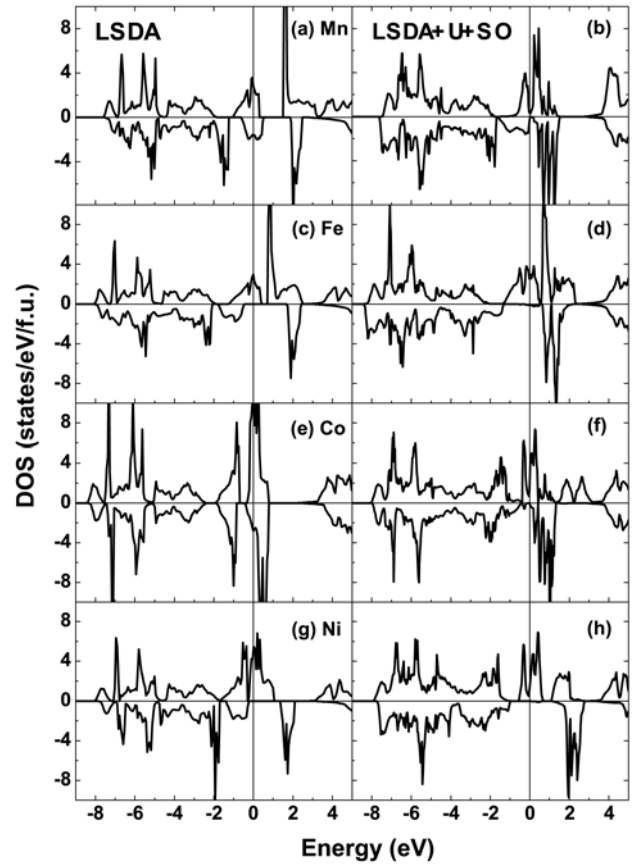
Fig. 1. The spin-polarized DOS of Ba$_2M$ReO$_6$ (M = Mn, Fe, Co, Ni) within the LSDA (Left) and the LSDA + U + SO (Right). The Fermi energy is chosen at 0.0 eV.

and the minority spin bands are partially occupied, and the majority bands at Re are empty and the minority spin bands are partially occupied. Therefore, one can expect that the spin-polarized tunneling between Fe t_{2g} and Re t_{2g} states near E_F becomes much more effective to yield the large MR ratio.

We also performed the LSDA + U including the SO interaction, and the spin and orbital magnetic moments at Re are −1.57 μ_B and 0.35 μ_B, respectively. However, the electronic feature does not change much from that without the SO interaction.

3.3. Ba$_2$CoReO$_6$

The ferrimagnetic metallic ground state is obtained in the LSDA at the experimental lattice constant a = 8.078 Å (Fig. 1(e)). In BaCoReO$_6$, the exchange splitting at Co site is negligible while that at Re site is ~0.5 eV, which are much smaller than the crystal field splittings of ~1.2 eV at Co and ~4 eV at Re, and so results in the low spin state. The total energy is lower by 0.01 Ry/f.u in the low spin state than in the high spin state. In addition, the

ferromagnetic state, where the spin directions of Co and Re are parallel, is only a bit higher in the total energy by ~0.01 Ry/f.u. than the ferrimagnetic ground state. However, the experimental ground state of Ba$_2$CoReO$_6$ is semiconducting, which is different from metallic in the LSDA.

The LSDA + U calculation gives the ferromagnetic ground state for Ba$_2$CoReO$_6$, which does not seem to agree with the experiment [14]. Hence we also performed the LSDA + U including the SO interaction. The electronic feature, however, does not change much from that without the SO interaction. To resolve this problem, we examined a lattice distortion effect. We assumed a tetragonal structure of $a/c = 0.70$ with the same volume as the cubic structure. Interestingly, the LSDA + U calculation for the tetragonal Ba$_2$CoReO$_6$ yields the zero total magnetic moment per f.u. with compensated local magnetic moments of 1 μ_B at Co and -1 μ_B at Re in agreement with the experimental data [14]. That is, a structural transition from cubic to tetragonal phase results in the magnetic state transition from ferromagnetic to antiferromagnetic.

3.4. Ba$_2$NiReO$_6$

For Ba$_2$NiReO$_6$, the LSDA calculation yields the ferromagnetic ground state at the experimental lattice constant $a = 8.053$ Å. The ferrimagnetic spin state is slightly higher in the total energy by 0.005 Ry/f.u. than that of the ferromagnetic state. However, the total magnetic moment of 3.0 μ_B in the ferromagnetic state is too larger than the experimental moment of 1.0 μ_B f.u. [14]. Therefore we apply the LSDA + U method to Ba$_2$NiReO$_6$ and obtained a correct ferrimagnetic state with the magnetic moment of 1.0 μ_B in agreement with the experiment [14]. The states near E_F are mainly from Re t_{2g} and the contribution from Ni $3d$ is negligible (Fig. 1(h)). Therefore, it is hard for carriers to hop between Ni and Re directly.

4. Conclusion

Electronic structures of double perovskite Ba$_2$$MReO_6$ were investigated by using the LSDA and the LSDA + U method. The LSDA + U calculations describe well the correct ferrimagnetic ground state for Ba$_2$MnReO$_6$, Ba$_2$FeReO$_6$, Ba$_2$NiReO$_6$ and the antiferromagnetic ground state for Ba$_2$CoReO$_6$. The SO interaction plays an important role in Ba$_2$MnReO$_6$ to make the system insulating. In Ba$_2$CoReO$_6$, the structural transition is invoked for the antiferromagnetic state. Also the incorporation of the SO interaction is essential in Ba$_2$$MReO_6$ system to describe properly the orbital contribution of Re ions to the mag-

netic moment.

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