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Electronic structures and magnetic properties of LaAVMoO$_6$ (A=Ca,Sr,Ba): Investigation of possible half-metallic antiferromagnets

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We have investigated electronic structures and magnetic properties of double perovskite LaAVMoO$_6$ (A=Ca,Sr,Ba). The normal metallic and ferrimagnetic states are found to be ground states, contrary to the experimental speculation of possible candidates for a half-metallic antiferromagnet. We have shown that the metallic and ferrimagnetic nature of LaAVMoO$_6$ is very robust regardless of divalent ion replacement at A site (A=Ca,Sr,Ba), the Coulomb correlation interaction, and superlattice stackings. On the other hand, we have found that the oxygen site relaxation would lead to the nearly half-metallic electronic structure but still in the ferrimagnetic state.

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Recent report[1] of the room-temperature ($T_C \sim 415$ K) colossal magnetoresistance (CMR) in the ordered double perovskite Sr$_2$FeMoO$_6$ has attracted a great deal of attention owing to possible technological application. The origin of the room-temperature CMR is considered to be closely related to the half-metallic property.[1,2] Also the half-metallic antiferromagnet (HM-AFM), which is a half-metal with zero net magnetization, has been proposed theoretically in the double perovskite systems.[3,4] The HM-AFM is expected to play an important role in the spintronic devices using the spin-polarized conduction carriers. Since the first theoretical prediction of Heusler-based HM-AFM by van Leuken and de Groot[5] there have been several reports on the search for candidates of HM-AFM based on the double perovskite[3,4] and thiospinel[6] systems.

There have also been experimental attempts to synthesize the HM-AFM based on double perovskite structure. Following the theoretical proposal by Pickett,[3] Androulakis *et al.*[7] synthesized single-phase polycrystalline La$_2$MnVO$_6$ samples. However, Mn^{3+} ions prefer the high spin state in contrast to the theoretical prediction of the low spin state, and the system turns out to be a ferrimagnetic insulator with finite magnetization. More recently, Uehara *et al.*[8] synthesized double perovskite compounds LaAVMoO$_6$ (A=Ca,Sr,Ba) and speculated that LaCaVMoO$_6$ and LaSrVMoO$_6$ would be possible HM-AFMs. A signature of antiferromagneticlike transitions were observed at T=120 K and T=130 K for Ca and Sr samples, respectively, and metallic behaviors were seen in the temperature dependent resistivity at $T > 70$ K for Ca and at $T > 20$ K for Sr samples. Based on these results, they claimed that the samples with A=Ca and Sr, especially the part of the samples where V and Mo are structurally ordered, can be promising candidates for the HM-AFM having V^{3+}(S=1) and Mo^{4+}(S=1) valence and spin states.

To explore whether LaAVMoO$_6$ is really a HM-AFM or not, we have investigated electronic structures of double perovskite LaAVMoO$_6$ (A=Ca,Sr,Ba) using both the local spin-density approximation (LSDA) and the LSDA+U (U, Coulomb interaction) scheme on the basis of the linearized muffin-tin orbital (LMTO) band method. We have considered two kinds of superlattices of LaVO$_3$/SrMoO$_3$ having the layered structures of stacking along the [111] and [001] directions. The [111] stacking corresponds to the ordered double-perovskite structure LaAVMoO$_6$, in which each Mo atom has six V neighbors, and vice versa. In the [001] stacking, each Mo atom has four Mo and two V neighbors, while each V atom has four V and two Mo neighbors.

Orthorhombic LaVO$_3$ is known to be a Mott insulator with the antiferromagnetic ordering. Hence the Coulomb correlation interaction between V 3d electrons needs to be taken into account in the band calculation for LaVO. Indeed the insulating behavior of LaVO$_3$ was well described by the LSDA+U method.[4] On the other hand, orthorhombic CaMoO$_3$ and cubic perovskites SrMoO$_3$ and BaMoO$_3$ have normal metallic and Pauli paramagnetic properties.[9–11] Hence the Coulomb correlation interaction between Mo 4d electrons can be neglected.

The calculated equilibrium lattice constant of LaSrVMoO$_6$ in the LSDA, 7.875 Å, is close to the average value of the calculated equilibrium lattice constants of its parent materials, 7.810 Å of LaVO$_3$ and 7.915 Å of SrMoO$_3$. Furthermore the calculated equilibrium lattice constants are very close to experimental lattice constants: 7.89 Å for LaSrVMoO$_6$,[8] 7.84 Å for LaVO$_3$,[12] and 7.95 Å for SrMoO$_3$.[11] We have found that the ferrimagnetic state of the G type ([111] antiferromagnetic ordering of V and Mo ions) is the ground state for LaSrVMoO$_6$. In the G type, neighboring V and Mo ions are antiferromagnetically polarized. We will discuss the other types of the antiferromagnetic ordering later in Fig. 5. The total energy of the ferrimagnetic state of LaSrVMoO$_6$ is lower than the paramagnetic state by 0.102 eV/f.u and then the ferromagnetic state[13] at the experimental lattice constant. Similarly, LaCaVMoO$_6$ and LaBaVMoO$_6$ also have the ferrimagnetic ground state.

Figure 1 presents the LSDA total densities of state (DOS) for ferrimagnetic phase of LaAVMoO$_6$ (A=Ca,Sr,Ba) ([111] stacking of LaVO$_3$/AMoO$_3$), calculated at their experimental lattice constants. All of them have normal metallic nature. Furthermore, distinctly from experimental speculation,[8] the total magnetic moments do not vanish for all three cases. Total magnetic moments are $\sim$0.84, $\sim$0.69,

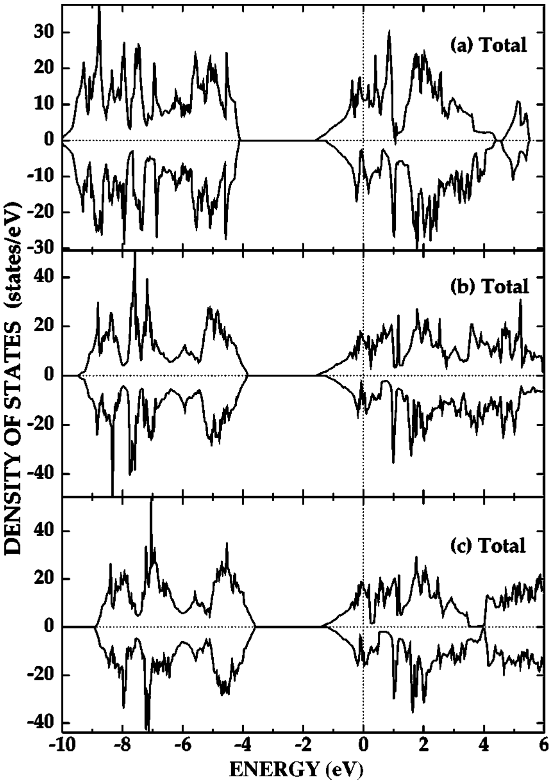

FIG. 1. The LSDA total DOS of LaAVMoO$_6$. (a) A=Ca, (b) A=Sr, and (c) A=Ba. They are obtained at the experimental lattice constants, 7.82, 7.89, and 7.98 Å for Ca, Sr, and Ba, respectively.

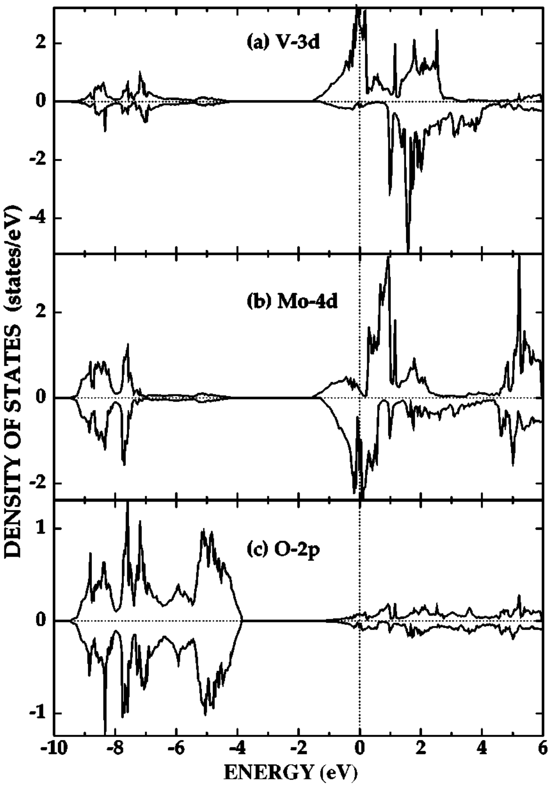

FIG. 2. The LSDA PLDOS of LaSrVMoO$_6$ ([111] stacking of LaVO$_3$/SrMoO$_3$). (a) V 3d, (b) Mo 4d, and (c) O 2p.

and $\sim 0.54\mu_B$ for Ca, Sr, and Ba systems, respectively. It is also seen that, irrespective of A-site atoms, the electronic structures are similar, reflecting the weak interaction between A and neighboring atoms.

The projected local DOS (PLDOS) for ferrimagnetic phase of LaSrVMoO$_6$ is given in Fig. 2. Occupied states near the Fermi level E_F correspond to t_{2g} states of V and Mo ions. V ion has an intermediate spin state with nominal valence of 3+(d^2), whereas Mo ion has a low spin state with nominal valence of 4+(d^2). Local magnetic moments are $1.43\mu_B$ and $-0.62\mu_B$ for V and Mo, respectively. The reduced magnetic moment of Mo ion is due to the large hybridization between the spin-up V and Mo states.

We have checked the Coulomb interaction effect of V 3d electrons on the electronic structure of LaAVMoO$_6$, because LaVO$_3$ is known to be a Mott insulator, as stated above. As shown in Fig. 3(a), the LSDA+U band calculations with U=2.0 eV and J=0.95 eV for V 3d electrons yield the normal ferrimagnetic metallic states for all LaAVMoO$_6$ (A=Ca,Sr,Ba).[14] That is, the Coulomb correlation effect in d bands of LaAVMoO$_6$ is minor, because the band widths of V and Mo are rather wide.

We have investigated the electronic structure of different superlattice stacking of LaVO$_3$/AMoO$_3$ to examine the effect of structural disorder in LaAVMoO$_6$. Figure 3(b) shows that the [001] superlattice of LaVO$_3$/SrMoO$_3$ also has the metallic and ferrimagnetic ground state. The DOS becomes a bit broader than for the [111] case, because of extra hybridizations between the same ions for the [001] case.[4] As mentioned above, the [001] superlattice has the different local ordering of cations from the [111] superlattice. Thus this result suggests that the metallic and ferrimagnetic nature would be retained, even if some cation disorder exists in the layers.

We have also examined the effect of oxygen site relaxation in LaSrVMoO$_6$, which affects the magnetic properties of double perovskites.[4,15] We have considered the variations of d_{VO}/a (d_{VO}, bond length between V and O; a, lattice constant) from 0.24 to 0.27. Since d_{VO}/a=0.25 corresponds to the case of no relaxation, smaller and larger d_{VO}/a correspond to contractions of V and Mo contained octahedron, respectively. As d_{VO}/a increases from 0.24 to 0.27, the local magnetic moment of V ion in LaSrVMoO$_6$ increases from $0.77\mu_B$ to $2.49\mu_B$, while that of Mo ion decreases from $-1.22\mu_B$ to $-0.12\mu_B$. Note that, for d_{VO}/a=0.24, the magnetic moment of Mo ion is larger than that of V ion (see Fig. 4). Accordingly, total magnetic moment increases from $-0.59\mu_B$ to $2.17\mu_B$. That is, as the hybridization between d states of the transition metal and the O 2p states is enhanced, the local magnetic moment of the transition metal decreases, and vice versa. We have obtained that the Mo site contraction case has the lower total energy, which indicates that the oxygen ion would be relaxed toward the Mo site in the ground state. This is understandable because the hybridization of 4d orbitals with neighboring O 2p orbitals is stronger than that of 3d orbitals.

Figure 4 presents the change of total DOS by varying d_{VO}/a. For d_{VO}/a=0.24 in the top of Fig. 4, Mo ion has more occupied electrons, and so the magnetic moment of Mo

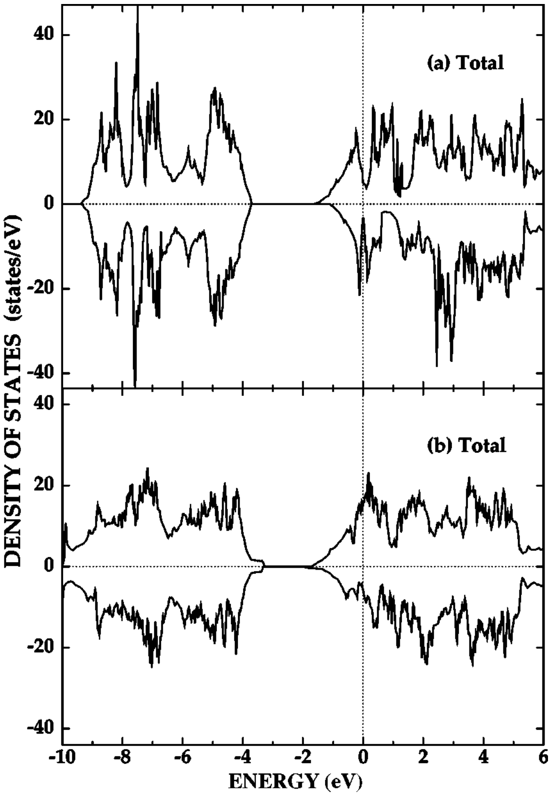

FIG. 3. (a) Total DOS of $LaSrVMoO_6$ obtained by using the LSDA+U (U=2.0 eV for V 3d electrons). (b) LSDA total DOS of $LaVO_3/SrMoO_3$ superlattice stacking along [001].

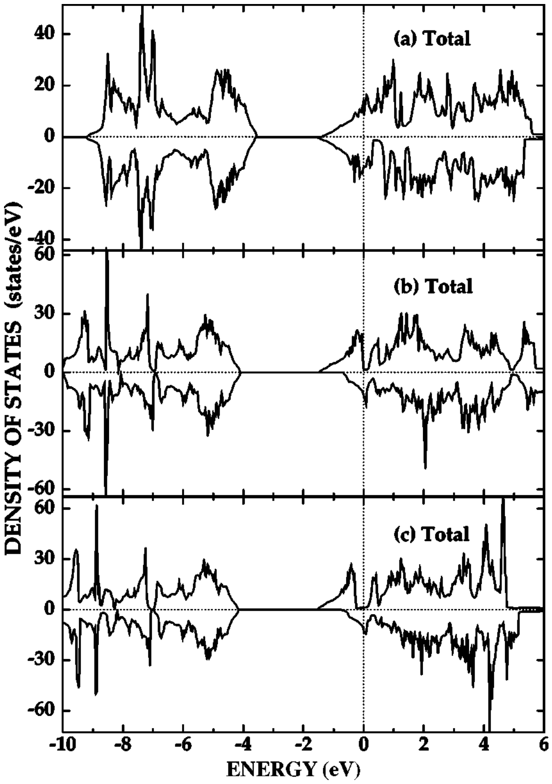

FIG. 4. The LSDA total DOS of $LaSrVMoO_6$ with the oxygen site relaxation. (a) $d_{VO}/a=0.24$, (b) $d_{VO}/a=0.265$, (c) $d_{VO}/a=0.27$.

ion is larger than that of V ion. Noteworthy in Fig. 4 is the nearly half-metallic electronic structure realized for $d_{VO}/a=0.27$. The half-metallic nature is not complete, having the non-integral total magnetic moment of $2.17\mu_B$/f.u. The nearly half-metallic electronic structure in this case is caused by the increase of electron occupancy at V ions through the oxygen site relaxation. Indeed, nominal valences change from $3+(d^2)$ to $2+(d^3)$ for V ions and from $4+(d^2)$ to $5+(d^1)$ for Mo ions. Accordingly, the spin-up t_{2g} band of V ion becomes fully occupied to exhibit the nearly half-metallic electronic structure. The half-metallic property is enhanced by the Coulomb correlation effect. This feature indicates that the oxygen site relaxation plays an important role in determining the electronic structure of the double perovskite $LaAVMoO_6$ (A=Ca,Sr,Ba) systems. Note, however, that the ferrimagnetic phase is still the ground state in this nearly half-metallic case.

To search for possible nonmagnetic and metallic phases for $LaAVMoO_6$ as observed in the experiment, we have considered other antiferromagnetic structures, such as the C type of [110] antiferromagnetic ordering and the A type of [001] antiferromagnetic ordering. In the C type, V and Mo ions along the chain are ferromagnetically polarized, but neighboring chains are antiferromagnetically coupled. In the A type, V and Mo ions in the plane are ferromagnetically polarized, but neighboring planes are antiferromagnetically coupled. Due to these magnetic configurations, both types have vanishing total magnetic moment in the unit cell. The total energy comparison in the LSDA reveals that, within the

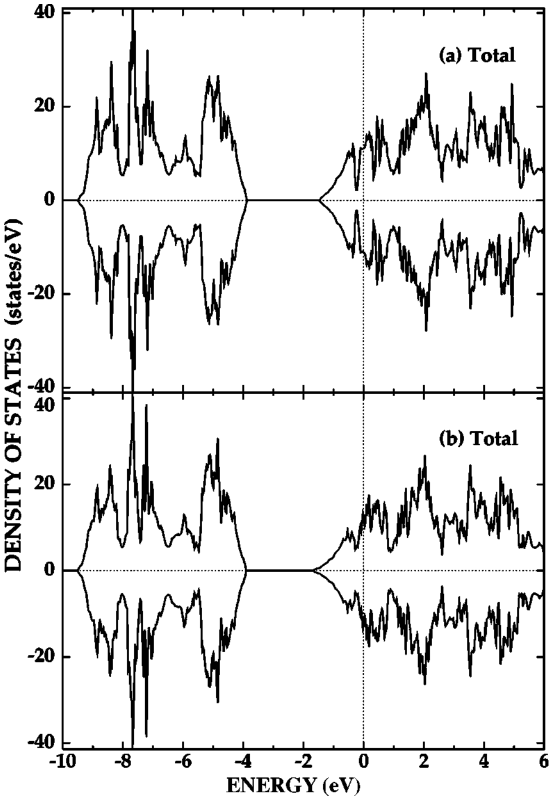

FIG. 5. The LSDA total DOSs of $LaSrVMoO_6$ (a) in the C type and (b) in the A type of antiferromagnetic ordering.

numerical uncertainty, the *C* type antiferromagnetic ordering is as stable as the *G* type ferrimagnetic ordering at the experimental lattice constant of LaSrVMoO$_6$. But the *A* type ordering is a bit less stable than the *G* type. The magnetic moments of V and Mo ions along the chain of the *C* type are 1.55 and 0.90μ_B, and those in the plane of the *A* type are 1.54 and 0.78μ_B, respectively. However, as shown in Fig. 5, the *C* type as well as the *A* type has the normal metallic electronic structure, not the half-metallic electronic structure. These results suggest that the experimental result[8] leaves room for other interpretations, and so further experiments are requested to clarify the real magnetic ground state of La*A*VMoO$_6$.

Finally, we have estimated the formation energy for LaSrVMoO$_6$. The enthalpy of formation is obtained to be positive, 0.49 eV/f.u., which implies that bulk LaSrVMoO$_6$ will not be stabilized in nature. This may explain why the degree of cationic ordering of V and Mo ions is very small, only about 26%.[8] Therefore, for the synthesis of double perovskite LaSrVMoO$_6$ compounds, the unequilibrium growing methods would be necessary, such as the molecular beam epitaxy method.

In conclusion, we have shown that the ordered double perovskite system La*A*VMoO$_6$ (A=Ca,Sr,Ba) are not HM-AFMs but normal metallic ferrimagnets. The metallic and ferrimagnetic nature of La*A*VMoO$_6$ is very robust regardless of various factors, such as *A*-site ions (Ca, Sr, and Ba), the Coulomb correlation effect, cation disorder, and the superlattice stacking order. On the other hand, the large oxygen site relaxation toward Mo site would give rise to the half-metallic electronic structure in the ferrimagnetic phase. We have found that bulk phase of ordered La*A*VMoO$_6$ would not be stable in nature, and so, to investigate metallic and nonmagnetic properties of the La*A*VMoO$_6$ systems more carefully, the film samples are preferred to be synthesized.

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