

## Half-metallic antiferromagnetic double perovskites: $\text{LaAVRuO}_6$ ( $A = \text{Ca, Sr, and Ba}$ )

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Based on the theoretical exploration of electronic structures, we propose that the ordered double perovskites  $\text{LaAVRuO}_6$  and  $\text{LaVO}_3/\text{ARuO}_3$  (001) superlattice ( $A = \text{Ca, Sr, and Ba}$ ) are strong candidates for half-metallic (HM) antiferromagnets (AFM's). We have shown that the HM-AFM nature in  $\text{LaAVRuO}_6$  is very robust regardless of (i) divalent ion replacement at  $A$  sites, (ii) oxygen site relaxation, (iii) the inclusion of the Coulomb correlation, and (iv) cation disorder. A type of the double exchange interaction is expected to be responsible for the half-metallicity and the antiferromagnetism in these systems.

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Since the observation of the room-temperature colossal magnetoresistance (CMR) phenomenon in  $\text{Sr}_2\text{FeMoO}_6$ ,<sup>1</sup> intensive research efforts have been devoted to understanding electronic and magnetic properties of double perovskites with  $A_2BB'O_6$  formula unit (f.u.). The high transition temperature  $T_C$  and the low field MR in double perovskites suggest the high spin polarization of conduction electrons and the half-metallic (HM) ground state.<sup>1,2</sup> In fact, the HM property is considered to be closely related to the CMR phenomena observed in various materials.<sup>3,4</sup> It has also been proposed that the double perovskites can be a suitable candidate for the HM antiferromagnet (AFM).<sup>5</sup> The HM-AFM is a nonmagnetic metal, but its conduction electrons are perfectly spin-polarized. The HM-AFM is expected to play a vital role in the advanced spintronic devices that utilize the spin polarization of the conduction carriers. Furthermore, the success in synthesizing the ordered  $\text{La}_2\text{CrFeO}_6$  as an artificial superlattice of (111) layers of  $\text{LaFeO}_3/\text{LaCrO}_3$  stimulates research on developing double perovskites with striking properties.<sup>6</sup> The purpose of present work is to search for candidate materials in double perovskites having the HM-AFM characteristics.

The first HM-AFM was proposed by van Leuken and de Groot<sup>7</sup> on the basis of the Heusler compound. Pickett<sup>5</sup> has also reported that the double perovskite  $\text{La}_2\text{VMnO}_6$  can be a promising candidate for the HM-AFM. According to the local spin-density approximation (LSDA) band calculation for  $\text{La}_2\text{VMnO}_6$ , only the minority  $t_{2g}$  bands of both V and Mn contribute to the density of states (DOS) near the Fermi energy  $E_F$ . The valence electron configurations are  $\text{Mn}^{3+}(3d^4)$  and  $\text{V}^{3+}(3d^2)$ , and the antiparallel alignment of the low spin  $\text{Mn}^{3+}$  ( $t_{2g}^3\uparrow t_{2g}^1\downarrow$ ,  $S=1$ ) and the  $\text{V}^{3+}$  ( $t_{2g}^2\downarrow$ ,  $S=1$ ) states yields zero total magnetic moment. The HM-AFM nature of  $\text{La}_2\text{VMnO}_6$  has not been tested experimentally yet. However, the low spin state of  $\text{Mn}^{3+}$  in the double perovskite seems to be rather unlikely. On the other hand, it has been speculated that mixed-cation double perovskites of  $AA'BB'O_6$  type might form ordered structures and provide good candidates for the HM-AFM.<sup>5</sup>

Motivated by the above theoretical and experimental works, we have explored the  $AA'BB'O_6$ -type double perovskites to search for possible HM-AFM's. We have chosen  $\text{LaAVRuO}_6$  (LAVRO:  $A = \text{Ca, Sr and Ba}$ ) as potential candidates. In the ionic picture, V and Ru ion are expected to be

trivalent  $\text{V}^{3+}(3d^2)$  and tetravalent  $\text{Ru}^{4+}(4d^4)$ , respectively. Then  $\text{V}^{3+}$  ion has the spin moment of  $2\mu_B$  in high spin state while  $\text{Ru}^{4+}$  ion has  $2\mu_B$  in low spin state, and so, if they are antiferromagnetically coupled, the total magnetic moment will be zero. Another valence configuration of  $\text{V}^{4+}(3d^1)$  and  $\text{Ru}^{3+}(4d^5)$ , albeit not so plausible, would also produce zero total magnetic moment.

We have investigated electronic structures of mixed-cation double perovskites LAVRO ( $A = \text{Ca, Sr, Ba}$ ) using both the LSDA and the LSDA +  $U$  ( $U$ : Coulomb correlation interaction) scheme on the basis of the linearized muffin-tin orbitals band method.<sup>8</sup> We have considered LAVRO as a combined form of  $\text{LaVO}_3$  and  $\text{ARuO}_3$  perovskites.  $\text{LaAVRO}$  with the antiferromagnetic coupling of V and Ru spins corresponds to a superlattice having the layered structure of stacking along the [111] direction, as in  $\text{La}_2\text{CrFeO}_6$ . In the [111] stacking, each Ru atom has six V neighbors, and each V atom has six Ru neighbors. In reality, the fabrication of LAVRO film along the [111] direction may not be easy due to the absence of proper substrate and the cation disorder effect.<sup>9</sup> Hence, in this work, we have also considered  $\text{LaVO}_3/\text{ARuO}_3$  superlattice stacking along the [001] direction to investigate the stable electronic and magnetic structures. In the [001] stacking of  $\text{LaVO}_3/\text{ARuO}_3$  superlattice, each Ru atom has four Ru and two V neighbors, while each V atom has four V and two Ru neighbors. By considering two stacking structures, one can expect to simulate the effect of the cation disorder on the electronic structures.

$\text{LaVO}_3$  is known to be a Mott insulator with the antiferromagnetic ordering.<sup>10</sup> Due to partially filled  $t_{2g}$  states ( $3d^2$ ) of  $\text{V}^{3+}$  ion, the Coulomb correlation and relatively weaker Jahn-Teller interactions play roles in stabilizing a typical orbital ordering in  $\text{LaVO}_3$ .<sup>11</sup> Hence the band calculation should take into account the  $3d$  electron Coulomb correlation to describe the Mott insulating nature of  $\text{LaVO}_3$ .<sup>12,13</sup> Indeed, with  $U=5.0$  eV and  $a/c=0.95$  tetragonal distortion from the cubic symmetry, we have found that  $\text{LaVO}_3$  becomes an insulator.<sup>14</sup> It has been reported that, with hole doping in  $\text{LaVO}_3$  ( $\text{LaAVO}_3$ :  $A = \text{Ca, Sr}$ ), the insulator-to-metal transition occurs with the collapsed orbital ordering.<sup>15,16</sup>

Both  $\text{CaRuO}_3$  and  $\text{SrRuO}_3$  exhibit metallic conductivity.  $\text{CaRuO}_3$  has an orthorhombically distorted perovskite structure with  $\text{GdFeO}_3$  type ( $Pbnm$ ).<sup>17</sup>  $\text{SrRuO}_3$  also has an orthorhombic crystal structure.<sup>17</sup> For the magnetic property

TABLE I. The equilibrium lattice constants ( $a$ ) and the total energy difference ( $\Delta E$  in eV/f.u.) between the ferrimagnetic and paramagnetic states.  $M_{\text{tot}}$  is the total magnetic moment in  $\mu_B$  per f.u., and  $M_V$  ( $M_{\text{Ru}}$ ) are local magnetic moments at V (Ru) sites.

	LaCaVRuO <sub>6</sub>	LaSrVRuO <sub>6</sub>	LaBaVRuO <sub>6</sub>
$a$ (Å)	7.767	7.867	7.965
$\Delta E$	-0.10	-0.24	-0.12
$M_{\text{tot}}$	0.00	0.00	0.00
$M_V$	-1.22	-1.26	-1.37
$M_{\text{Ru}}$	1.01	1.05	1.10

of CaRuO<sub>3</sub>, several conflicting results are reported.<sup>18–20</sup> According to the most recent report, CaRuO<sub>3</sub> is considered to be a paramagnetic metal.<sup>21</sup> On the other hand, SrRuO<sub>3</sub> is a ferromagnet with  $T_C \sim 160$  K and the magnetic moment  $M = 1.4 \pm 0.4 \mu_B$  per Ru atom.<sup>18,19</sup> BaRuO<sub>3</sub> is chemically related and isoelectronic to CaRuO<sub>3</sub> and SrRuO<sub>3</sub>, but its structure and electronic properties are very different. The crystal structure of BaRuO<sub>3</sub> belongs to the hexagonal perovskite family with various crystallographic forms,  $4R$ ,  $6R$ , and  $9R$ , according to the stacking sequence. The  $4R$ -BaRuO<sub>3</sub> shows a metallic resistivity behavior down to the lowest temperature, while the  $9R$ -BaRuO<sub>3</sub> shows a crossover to a more resistive state.<sup>22</sup> The magnetic states are paramagnetic for all BaRuO<sub>3</sub>.<sup>22,23</sup>

The LSDA equilibrium lattice constant of LaSrVRuO<sub>6</sub> (LSrVRO) turns out to be close to the average value of the lattice constants of its parent materials, LaVO<sub>3</sub> and SrRuO<sub>3</sub>.<sup>24</sup> The ferrimagnetic ground state is lower in energy than the paramagnetic state by 0.24 eV/f.u. for LSrVRO. Likewise, both LaCaVRuO<sub>6</sub> (LCaVRO) and LaBaVRuO<sub>6</sub> (LBaVRO) have the ferrimagnetic ground states too (see Table I). The total DOS of LAVRO ( $A = \text{Ca, Sr, and Ba}$ ) are presented in Fig. 1, which shows the HM-AFM nature of all three systems. As is well known,  $A$ -site atoms in  $ABO_3$  perovskite act as carrier reservoir and volume conserver. The interaction between  $A$  and neighboring atoms is so weak that many  $ABO_3$ 's even with different  $A$  share similar electronic properties. Indeed, as seen in Fig. 1, the DOS are similar for all LAVRO, even if the  $A$ -site atom is varied. Most interestingly, the antiparallel alignment of Ru and V magnetic moments yields zero total magnetic moment for all cases, by counting together the polarized magnetic moments of La,  $A$ , and O atoms. The local magnetic moments of Ru and V in LAVRO are provided in Table I.

For LSrVRO, as shown in Fig. 2, the energy gap of  $\sim 0.8$  eV opens between the occupied Ru  $t_{2g}$  and the empty V  $t_{2g}$  states in the spin-up bands. On the other hand, the spin-down bands are metallic and composed of  $t_{2g}$  states of Ru and V. The DOS of two  $t_{2g}$  states near  $E_F$  are similar in the weight and shape, indicating the large hybridization between Ru and V. Occupied  $t_{2g}$  states in Fig. 2 seem to reflect the nominal valences of V<sup>3+</sup> ( $d^2$ ) and Ru<sup>4+</sup> ( $d^4$ ), respectively. In fact, at Ru site, the spin-up bands are occupied by nearly three  $t_{2g}$  electrons, while the spin-down bands by about  $1.8t_{2g}$  electrons. At V site, the spin-down bands are

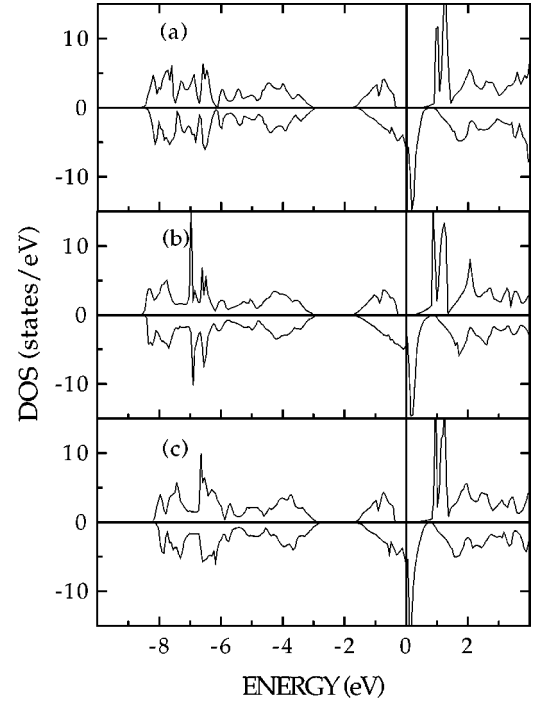


FIG. 1. The total DOS of LaAVRuO<sub>6</sub> in the LSDA. (a)  $A = \text{Ca}$ , (b)  $A = \text{Sr}$ , and (c)  $A = \text{Ba}$ .

occupied by about  $1.6t_{2g}$  electrons, while the spin-up bands are nearly empty. Hence, the electron configurations become V<sup>3.4+</sup> ( $3d^{1.6}$ ) and Ru<sup>3.2+</sup> ( $4d^{4.8}$ ). It is thus likely that two valence states of V<sup>3+</sup>/Ru<sup>4+</sup> and V<sup>4+</sup>/Ru<sup>3+</sup> are nearly degenerate.

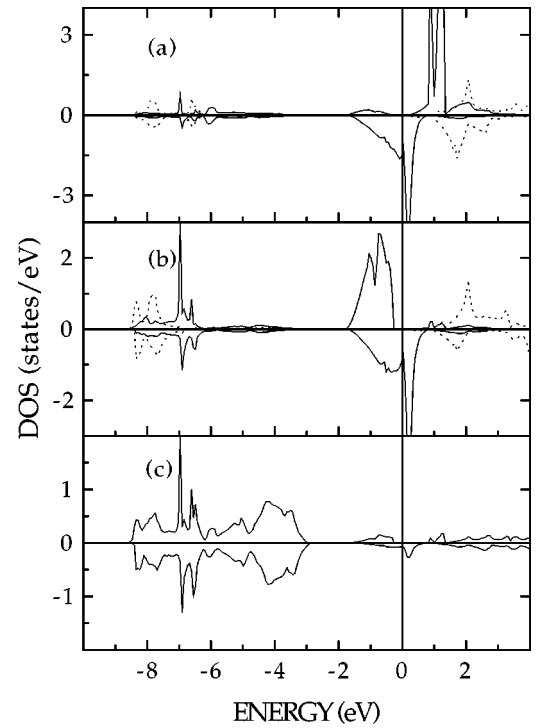


FIG. 2. The orbital projected DOS of LaSrVRuO<sub>6</sub> in the LSDA. Solid and dotted lines in (a) and (b) denote  $t_{2g}$  and  $e_g$  states, respectively. (a) V  $3d$ , (b) Ru  $4d$ , and (c) O  $2p$ .

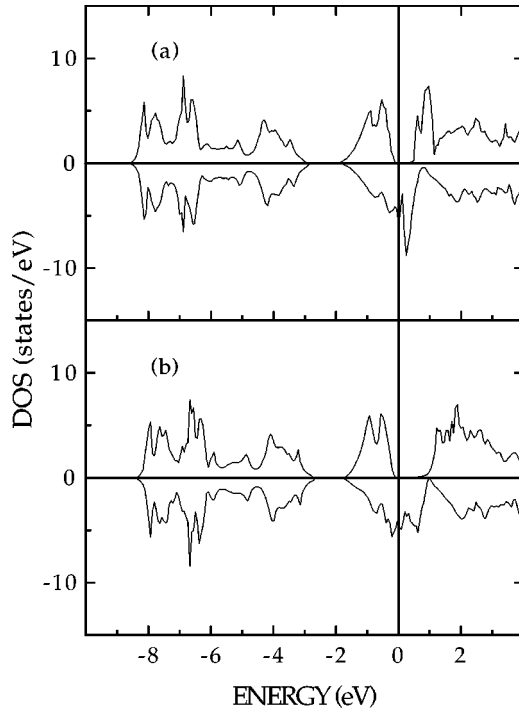


FIG. 3. The total DOS of  $\text{LaSrVRuO}_6$  with the oxygen site relaxation of  $d(\text{V-O})/d(\text{Ru-O})=0.9$  (a) in the LSDA and (b) in the LSDA+ $U$  ( $U=3.0$  eV for V 3d electrons).

erate to produce a type of the double exchange (DE) interaction.<sup>25</sup> That is, the hopping of itinerant  $t_{2g}$  spin-down electrons between Ru-V sites yields the kinetic-energy gain so as to induce the ferrimagnetism between Ru-V spins. This mechanism explains both the half-metallicity and the ferrimagnetism in  $\text{LSrVRO}$ . Note that the spins of itinerant carriers are antiparallel to the localized Ru spins ( $t_{2g}^3 \uparrow$ ), satisfying the Hund rule in the low spin state, as in  $\text{Sr}_2\text{FeMoO}_6$  and  $\text{Sr}_2\text{FeReO}_6$ .<sup>26,27</sup>

We have examined the effect of oxygen site relaxation, which is an important factor in double perovskites. In the case of recently synthesized mixed-cation double perovskite:  $\text{LaSrMRuO}_6$  ( $M=\text{Zn, Mg}$ ),<sup>28</sup> the oxygen site is reported to be relaxed with  $d(\text{Ru-O})/d(\text{M-O})=0.96$ . This value is similar to those observed in other double perovskites.<sup>1,29</sup> The inclusion of oxygen site relaxation for  $\text{LSrVRO}$  with  $d(\text{Ru-O})/d(\text{V-O})=0.96$  produces essentially the same electronic structure as in the case of the ideal structure, that is, the HM-AFM nature is retained. In addition, we have also considered the case of opposite oxygen site relaxation of  $d(\text{V-O})/d(\text{Ru-O})=0.9$  [see Fig. 3(a)]. In this case, the magnetic moments of both V and Ru are reduced ( $M_{\text{V}}=-0.65$  and  $M_{\text{Ru}}=0.55\mu_B$ ), but the HM-AFM nature is still retained.

Since the band widths of Ru and V are relatively wide, one expects that the correlation effect in  $d$  bands of LAVRO would be minor. However, as described above,  $\text{LaVO}_3$  is known to be a Mott insulator. Hence, it might be necessary to examine the correlation effect of V 3d electrons in the electronic structure of LAVRO. Figure 3(b) provides the DOS for  $\text{LSrVRO}$  using the LSDA+ $U$  method with  $U=3.0$  eV and  $J=0.87$  eV for V 3d electrons. Here  $d(\text{V-O})/d(\text{Ru-O})$

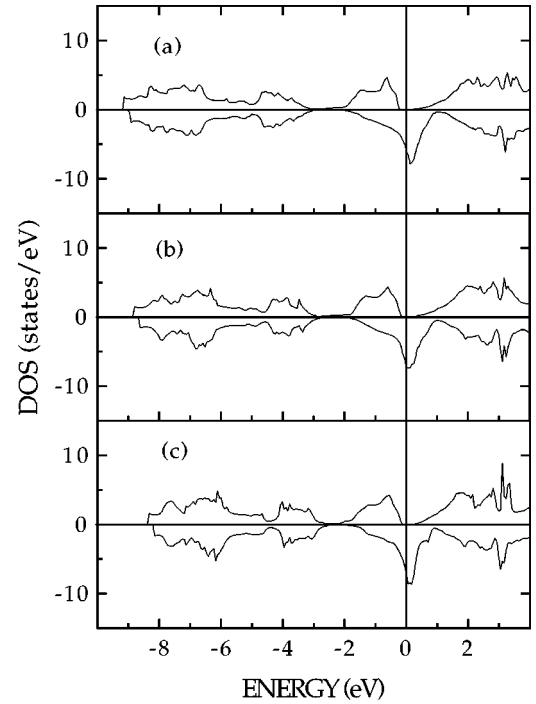


FIG. 4. The total DOS of  $\text{LaVO}_3/\text{ARuO}_3$  in the LSDA+ $U$  ( $U=2.0$  eV for V 3d and  $U=1.0$  eV for Ru 4d electrons). (a)  $A=\text{Ca}$ , (b)  $A=\text{Sr}$ , and (c)  $A=\text{Ba}$ .

$=0.9$  is assumed as in Fig. 3(a). The LSDA+ $U$  yields no qualitative difference in electronic and magnetic properties from those of the LSDA. Magnetic moments of V and Ru are somewhat enhanced,  $-1.01$  and  $0.81\mu_B$ , respectively, but the HM-AFM nature is maintained in this case too.

In Fig. 4 we have plotted the DOS of  $\text{LaVO}_3/\text{ARuO}_3$  [001] superlattice in the LSDA+ $U$  calculation. We have employed  $U=2.0$  eV and  $J=0.87$  eV for V 3d and  $U=1.0$  eV and  $J=0.87$  eV for Ru 4d electrons, respectively. Interestingly, still in [001] superlattice, the HM-AFM is the ground state. It is seen that the DOS are a bit broader than those of double perovskite LAVRO. It is because extra hybridizations between the same ions (La-La, V-V, A-A, Ru-Ru) exist in the  $\text{LaVO}_3/\text{ARuO}_3$  [001] superlattice. This result reveals that the HM-AFM nature of LAVRO is maintained even though there may be some cation disorder in the layers.<sup>30</sup> Therefore,  $\text{LaVO}_3/\text{ARuO}_3$  [001] superlattice film would be a very promising candidate for the HM-AFM, provided it can be synthesized successfully.

Table I indicates that  $\text{LSrVRO}$  out of three candidates is the most promising, because it has the largest total energy difference between the ferrimagnetic state and the paramagnetic state. It was reported that the epitaxial thin films of parent materials,  $\text{SrRuO}_3$  and  $\text{LaVO}_3$ , can be grown on  $\text{LaAlO}_3$  substrates.<sup>31,32</sup> Further,  $\text{SrRuO}_3$  and  $\text{LaVO}_3$  are isostructural and the lattice constants are quite close. Once  $\text{LSrVRO}$  is synthesized, one thing to be checked is the Curie temperature  $T_C$ . Note that  $T_C$  of  $\text{SrRuO}_3$  is  $\sim 165$  K and the Néel temperature  $T_N$  of  $\text{LaVO}_3$  is  $\sim 140$  K, which may imply that  $T_C$  of  $\text{LSrVRO}$  is at most  $\sim 165$  K. We, however, expect that  $T_C$  of  $\text{LSrVRO}$  could be as high as  $T_C$  of

$\text{Sr}_2\text{FeMoO}_6$  ( $T_C=419$  K), in view of their similar electronic structures with relevant  $t_{2g}$  states near  $E_F$  and the seemingly operative DE mechanisms. In the DE mechanism,  $T_C$  is proportional to the band width of itinerant carriers. We would like to note that the band width of the spin-down  $t_{2g}$  states in  $\text{LSrVRO}$  ( $\sim 2$  eV) is as large as that of  $\text{Sr}_2\text{FeMoO}_6$ . In addition, according to the simple Kanamori-Goodenough rule, the possible superexchange interaction between neighboring V-Ru  $t_{2g}$  states ( $\text{V}^{3+}$ - $\text{Ru}^{4+}$ ) would yield the ferrimagnetic interaction, suggesting that the ferrimagnetic DE is strengthened further by the superexchange to enhance the HM-AFM nature.

In conclusion, we have proposed that the mixed-cation double perovskite system  $\text{LAVRO}$  ( $A = \text{Ca}, \text{Sr}, \text{and Ba}$ ) are

strong candidates for the HM-AFM's. The HM-AFM nature in  $\text{LAVRO}$  is very robust regardless of various factors:  $A$ -site ions (Ca, Sr, and Ba), the oxygen site relaxation, the Coulomb correlation effect, and the cation disorder. We have also shown that the  $\text{LaVO}_3/\text{ARuO}_3$  [001] superlattice would be a HM-AFM. A type of the double exchange interaction is operative in these systems to yield the half-metallicity and the antiferromagnetism.  $\text{LSrVRO}$  is expected to be the most promising candidate for a HM-AFM with high  $T_C$ . It is thus very desirable to test experimentally the HM-AFM nature of the mixed-cation double perovskite  $\text{LSrVRO}$  and the  $\text{LaVO}_3/\text{SrRuO}_3$  [001] superlattice film.

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