Revisiting the Structural, Electronic, and Magnetic Properties of (LaO)MnAs: Effect of Hubbard Correction and Origin of Mott-Insulating Behavior

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ABSTRACT: We study the structural, electronic, and magnetic properties of the antiferromagnetic-layered oxyarsenide (LaO)-MnAs system from the first-principle calculation. The increasing Hubbard energy (U) in the Mn 3d orbital induces the increasing local-symmetry distortions (LSDs) in MnAs₄ and OLa₄ tetrahedra. The LSD in MnAs₄ tetrahedra is possibly promoted by the second-order Jahn–Teller effect in the Mn 3d orbital. Furthermore, the increasing U also escalates the bandgap (E_g) and the magnetic moment of Mn (μ_B). The value of U = 1 eV is the most appropriate by considering the structural properties. This value leads to E_g and μ_B of 0.834 eV and 4.31 μ_B, respectively. The calculated μ_B is lower than the theoretical value for the high-spin state of Mn 3d (5 μ_B) due to the hybridization between Mn 3d and As 4p states. However, dₓᵧ states are localized and show the weakest hybridization with valence As 4p states. The Mott-insulating behavior in the system is characterized by the E_g transition between the valence and conduction dₓᵧ/dₓᵧ states. This work shows new physical insights for advanced functional device applications, such as spintronics.

1. INTRODUCTION

Layered oxypnictides (LaO)TPn (T = transition metals, Pn = P, As, Sb) have been extensively investigated because of their various properties. Doping F in (LaO)FeAs induces the superconducting behavior with the high Curie temperature (T_C). (LaO)NiAs exhibits the strong-coupling superconducting behavior with the enhanced T_C by F substitutional doping at O sites. Behaving as the itinerant ferromagnetic material, (LaO)CoAs exhibits the possible crossover of 3D-to-2D fluctuations above 150 K. (LaO)ZnP (Pn = P, As, Sb) shows the semiconducting behavior, where its structural, electric, and electronic properties are strongly dependent on Pn substitution. It has been found that (LaO)ZnP shows diamagnetism, while (LaO)ZnAs and (LaO)ZnSb show paramagnetism. (LaO)MnPn (Pn = P, As, Sb) exhibits the insulating behavior based on the temperature (T)-dependent electrical resistivity (4–300 K). As one of the manganese-based layered oxypnictides, the (LaO)MnAs system consists of [LaO] and [MnAs] layers stacked along the c-axis direction with the space group P4/nmm. As (La) ions tetrahedrally surround Mn (O) ions, this leads to LaMn₄ and OLa₄ tetrahedra. [LaO] layers show the covalent bonding between La and O atoms, while [MnAs] layers show the ionic bonding between Mn and As atoms based on the synchrotron X-ray powder diffraction (SXRD) measurement and the first-principle calculation. At room temperature (RT), doping holes into [MnAs] layers changes the antiferromagnetic insulating to ferromagnetic metallic behaviors. The doping was performed by inducing defects in [LaO] layers. Achieving x ≈ 0.3, the (LaO)₁₋ₓMnAs system exhibits the metallic behavior for T < 150 K. The (LaO)₁₋ₓMnAs system shows interesting properties. It exhibits the giant negative magnetoresistance up to −24% at 200 K as well as the G-type antiferromagnetic behavior with the Néel temperature (T_N) above RT, which is 360(1) K. In the system, Mn 3d spins aligned ferromagnetically along the c axis and antiferromagnetically along the ab plane based on the neutron diffraction measurement. The (LaO)₁₋ₓMnAs system also exhibits the Mott-insulating behavior, which is partly contributed by the superexchange interaction between Mn and As ions. The Mott-insulating behavior is related to the half-filled d orbital (d⁵) in the system. The previous first-principle
calculation has shown that the insulating behavior is strongly correlated by the G-type magnetism at the ground state, while the metallic behavior is correlated with the ferromagnetic state. The insulating or semiconductor behaviors are indicated by the bandgap \(E_g\) transition, which is mainly contributed by the valence and conduction Mn 3d states.

In the electronic properties of \((\text{LaO})\text{MnAs}\), the conventional density-functional theory (DFT) provides the underestimated \(E_g\) value. The Hubbard energy \((U)\) correction can be carried out to correct the electronic properties. The term \(U\) is significant in changing \(E_g\) and moment magnetic of Mn ion \((\mu_{\text{Mn}})\). The previous calculation shows that \(E_g\) of the \((\text{LaO})\text{MnAs}\) system is increased by the \(U−J\) value and saturates for \(U−J\) more than 4 eV, which is large enough for the Mn 3d orbital.\(^{15}\) The term \(U\) can also correct the magnetic properties in terms of spin-state assignments in Mn 3d and structural properties.\(^{12}\) Using the local density approximation (LDA) + \(U\) method, the previous investigation shows that the value of \(U = 2\) eV for Mn 3d gives the consistent crystal volume structures of the \(Pr_{0.75}Na_{0.25}\text{MnO}_3\) system compared to the experimental data.\(^{15}\) For the same system, the change in \(U\) value for Mn 3d also significantly influences the crystal structure, electronic properties, the charge and spin densities, and the hybridization of Mn 3d and O 2p orbitals.\(^{16}\)

As the \((\text{LaO})\text{MnAs}\) system shows the antiferromagnetic semiconducting behaviors, it is expected to be suitable for spintronic application. The antiferromagnetic semiconductors are suggested to be promising for spintronics since these semiconductors provide the higher magnetic ordering temperature than the diluted magnetic semiconductors.\(^{17}\) Furthermore, the semiconductor behavior in an antiferromagnetic material can be used for measuring the anisotropic magnetoresistance. Alongside the electrical resistance measurement, they provide the charge and spin-dependent transport for spintronics.\(^{18}\) Furthermore, the antiferromagnetic behavior is suggested to be suitable for spintronic applications since the materials show no parasitic magnetic fields. The antiferromagnetic materials exhibit the fast antiferromagnetic state switching and are insensible under external magnetic fields. The semiconducting behavior provides \(E_g\), which is suitable for applications in electronic devices.\(^{19}\) Regarding the structural properties, the local-symmetry distortion (LSD) in MnAs\(_4\) and OLa\(_4\) tetrahedra has not been explored yet. Moreover, the contribution of orbital states to the antiferromagnetic insulating behaviors is yet to be explored. For instance, the role of sub-Mn 3d states to the behaviors is not clear despite the remarkable contribution of Mn 3d states.

In this paper, we study the structural, electronic, and magnetic properties of the \((\text{LaO})\text{MnAs}\) system, calculated by first principles based on the density-functional theory (DFT). The structural properties are systematically investigated, which include the LSD in both MnAs\(_4\) and OLa\(_4\) tetrahedra. Then, the electronic and magnetic properties are discussed in terms of the band structure and magnetic moment at Mn sites. Finally, energy-dependent total and projected density of states (DOS) are revealed to find the electronic properties of each orbital in the system.

2. CALCULATION DETAILS

The Quantum ESPRESSO code\(^{20}\) was employed to calculate the structural and electronic properties of \((\text{LaO})\text{MnAs}\) with the space group of \(P4\)/\(mm\) (no. 129).\(^{21}\) Figure 1 visualizes the crystal structure model of the systems, which shows MnAs\(_4\) \((i = 1, 2)\) and OLa\(_4\) tetrahedra and is modeled using VESTA.\(^{22}\) All-electron potentials are implemented by the ultrasoft pseudopotentials within the Vanderbilt scheme.\(^{23}\) The calculation carried out the plane-wave method within the generalized gradient approximation (GGA) employing the Perdew–Burke–Ernzerhof (PBE)-type exchange–correlation functional energy.\(^{24}\) The properties of various systems have previously been calculated using this method.\(^{25,26}\) As the initial magnetic state, the magnetic orders of Mn1 and Mn2 are antiferromagnetic along the \(ab\) plane and ferromagnetic along the \(c\) axis directions.\(^{8}\) The present work employed the initial structural properties of \(a = 4.11920\) Å, \(c = 9.04312\) Å, \(z_{\text{As}} = 0.13247\), and \(z_{\text{Lat}} = 0.66879\) from our previous report.\(^{2}^{27}\) First, using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm,\(^{28}\) a full optimization of structural properties was performed with a threshold force of \(10^{-3}\) Ry/Bohr \((\sim 0.03\) eV/Å). Using the Broyden mixing scheme,\(^{27}\) the self-consistent-field (SCF) calculation carried out a threshold energy, cut-off kinetic energy, and \(k\)-point mesh of \(10^{-4}\) Hartree \((\sim 2.72\times 10^{-3}\) eV), 60 Rydberg \((\sim 816\) eV), and \(9\times 9\times 4\), respectively.

3. RESULTS AND DISCUSSION

3.1. Structural Properties. Figure 2a shows the \(U\) dependencies of \(a\) and \(c\) compared to that of the previous experiment.\(^{28}\) The increase in \(U\) induces the increase in \(a\) and \(c\) with the decreasing of the gradients \(\Delta a/\Delta U\) and \(\Delta c/\Delta U\). It is found that the values of \(U = 1\) and 0 eV respectively induce the closest \(a\) and \(c\) to those of the previous report. The result also shows that \(c\) is more sensitive to the change of \(U\) than \(a\). The increments of \(a\) and \(c\) have also been obtained in the rutile and anatase TiO\(_2\) systems with the tetragonal crystal structure. It is well known that the term \(U\) expands their unit cell volume.\(^{29,30}\) However, the increments of \(a\) and \(c\) of the rutile TiO\(_2\) system are almost linear, which are in contrast to that of the \((\text{LaO})\text{MnAs}\) system in the present work.\(^{25,29}\) Figure 2b
shows the $U$ dependences of the ratio $c/a$. The increase in $U$ from 0 to 1 eV promotes the sharp decrease in $c/a$. For $1 < U < 4$ eV, $c/a$ is decreased with the minimum value at $U = 3$ eV and then reaches its maximum at $U = 4$ eV. For $U > 4$ eV, $c/a$ is decreased with the sharper gradient than that of the range of $1 < U < 3$ eV. We find that $c/a$ is in a good agreement with that of the experiment for $U = 6$ eV. However, this value is too large for the Mn site. The present work does not consider the effect of $U$ of the La 4f orbital since its presence has no effect in changing $E_g^{13}$. Therefore, the term $U$ of La 4f is negligible.

Figure 2c presents the $U$ dependences of the $c$-axis coordinate of La ($z_{La}$) and As atoms ($z_{As}$). The value of $U = 1$ eV induces the closest $z_{La}$ and As atoms $z_{As}$ to those of the previous report. This result shows the increasing thickness of [MnAs] layers since both $c$ and $z_{As}$ increase due to the $U$ increment. Furthermore, one can assume that the Mn 3d orbital should not have a very large $U$ value in the system.

Based on Figure 2, bond lengths and bond angles in the (LaO)MnAs system are presented in Figure 3. Figure 3a presents the $U$ dependences of bond lengths between La and O sites ($l_{La-O}$) as well as between La and As sites ($l_{La-As}$). It is shown that the increase in $U$ induces the increase in $l_{La-O}$ and $l_{La-As}$ with the decreasing of the gradients $\Delta l_{La-O}/\Delta U$ and $\Delta l_{La-As}/\Delta U$. The increasing $l_{La-O}$ and $l_{La-As}$ are in line with
the increases in \( a \) and \( c \). It is found that \( \frac{l_{\text{Os}-\text{O}}}{l_{\text{Os}-\text{A}}} \) and \( \frac{l_{\text{Mn}-\text{A}}}{l_{\text{Mn}-\text{O}}} \) are close to the experimental results for \( U = 1 \) and 2 eV, respectively. Figure 3b shows the \( U \) dependences of bond length between Mn and As sites \( (l_{\text{Mn-As}}) \). The increase in \( U \) induces the increase in \( l_{\text{Mn-As}} \) with the decreasing of the gradient \( \Delta l_{\text{Mn-As}}/\Delta U \). The value of \( U = 1 \) eV induces the closest \( l_{\text{Mn-As}} \) to that of the experiment. Figure 3c shows the \( U \) dependences of bond angle between La and O sites \( (\theta_{\text{La-O}}) \) as well as As sites \( (\theta_{\text{As-La}}) \). Centered at Mn sites, two bond angles between Mn and As sites \( (\theta_{\text{Mn-As}}) \), which are \( \alpha \) and \( \beta \), are also presented as the function of \( U \) in Figure 3d. The increase in \( U \) induces the increase in \( \theta_{\text{Mn-As}} \) and \( \theta_{\text{As-La}} \), while \( \alpha \) is decreased. The value of \( U = 1 \) eV promotes the closest \( \theta_{\text{Mn-As}} \) and \( \theta_{\text{As-La}} \) to that of the experiment, while \( \theta_{\text{As-La}} \) is close to the experimental result for \( U = 2 \) eV.

Based on Figure 3, the local-symmetry distortion (LSD) in MnAs\(_4\) and OLa\(_4\) tetrahedra shifts with the increase in \( U \). For quantitatively describing the LSD, we carry out the LSD parameters.\(^{30}\) For the tetrahedron \( AX\(_4\) \), the first LSD parameter is the mean quadratic elongation \( (\lambda_{\text{tet}}) \) formulated as

\[
\lambda_{\text{tet}} = \frac{1}{4} \sum_{i=1}^{4} \left( \frac{l_{i}}{l_{0}} \right)^2 \quad \text{(dimensionless)}
\]

where \( l_{i} \) is the \( A-X \) bond length for an ideal \( AX\(_4\) \) tetrahedron with the same volume as that of the distorted tetrahedron and \( l_{0} \) is \( A-X \) bond lengths. The second parameter is the bond-angle variance \( (\theta_{\text{tet}}) \), expressed as

\[
\theta_{\text{tet}}^2 = \frac{1}{5} \sum_{i=1}^{6} (\theta_{i} - 109.4712^\circ)^2 \quad \text{(in }^\circ \text{)}
\]

where \( \theta_{i} \) is the \( X-A-X \) bond angles.\(^{30a}\) Notably, the bond angle 109.4712\(^\circ\) is possessed by the ideal tetrahedron.\(^{31}\) In the present work, both parameters are used for both MnAs\(_4\) and OLa\(_4\) tetrahedra as shown in Figure 4. Figure 4a shows that \( \lambda_{\text{tet}} \) of OLa\(_4\) is larger than that of MnAs\(_4\) for each \( U \) value. Figure 4b also depicts that \( \theta_{\text{tet}} \) of OLa\(_4\) is larger than that of MnAs\(_4\) for each \( U \) value. The increase in \( U \) induces the increases in \( \lambda_{\text{tet}} \) and \( \theta_{\text{tet}} \). The LSD possibly comes from the second-order Jahn–Teller (JT) effect since the 3d\(^{3}\) orbital cannot possess the first-order Jahn–Teller effect. This possible mechanism has been suggested in our previous reports.\(^{4b,32}\)

From the structural properties, the value of \( U = 1 \) eV is the most suitable value for the system in the present work. This value is used to discuss the electronic properties. Notably, this value induces the different result with that of previous experimental reports. However, this value is sufficient to obtain the closest structural properties to that of previous experiments. The next subsection will show more details regarding this issue.

### 3.2. Band Structures

Figure 5a shows the \( U \) dependence of indirect \( E_{\text{g}} \) of the (LaO)MnAs system, compared to that of the previous experiment, that is \( E_{\text{g}} \approx 1.4 \) eV.\(^{33}\) Since the system exhibits the antiferromagnetic behavior, spin-up and spin-down band structures have the same profile based on the calculation result. Then, we only present the band structure for a single spin orientation. The present work shows the maximum \( E_{\text{g}} \) because of the wider range in sweeping \( E_{\text{g}} \). The inset shows the band structure for \( U = 0 \) eV. We find the indirect \( E_{\text{g}} \) transition from the \( \Gamma \) to M point, which is in line with that of the previous calculation.\(^{33}\) This transition is used to show the trend of \( E_{\text{g}} \). The result depicts that the increase in \( U \) induces the increase in \( E_{\text{g}} \) with the maximum value at \( U = 8 \) eV (\( E_{\text{g}} = 1.348 \) eV) and the slight decrease in \( E_{\text{g}} \) for \( 8 < U < 10 \) eV. Although the value of \( U = 8 \) eV results in the closest \( E_{\text{g}} \) to that of the previous experiment, this \( U \) value induces the overestimated lattice parameters as shown in Figure 2. The increase in \( E_{\text{g}} \) is in alignment with that of the previous calculation, showing the saturation at \( U \) of 4 eV with the \( U \) range of \( 0-5 \) eV.\(^{15}\) Instead of depicting a saturation feature, the present work shows the maximum \( E_{\text{g}} \) because of the wider range in sweeping \( E_{\text{g}} \). On the other hand, for \( U = 1 \) eV, we find an \( E_{\text{g}} \) of 0.834 eV, which is \( \sim60\% \) of the experimental result. The value of \( U = 1 \) eV is more reasonable since it is the most suitable value for the structural properties. Moreover, the
underestimated $E_g$ is acceptable because of the limitation of the GGA method in describing $E_g$ in the electronic properties.\textsuperscript{34} Furthermore, the previous report shows that the small value of $U = 2$ eV for Mn 3d can give the suitable crystal volume structures of the $P_{6\bar{3}}N_{6\bar{3}}MnAs$ system compared to the experimental data.\textsuperscript{37}

Figure 5b presents the $U$ dependence of $\mu_{\text{Mn}}$ in the (LaO)MnAs system. The increase in $U$ induces the increase in $\mu_{\text{Mn}}$. We suggest that the increase in $\mu_{\text{Mn}}$ might be influenced by the increase in LSD relating to the increasing the second-order JT effect in the Mn$^{2+}$ case. This suggestion is based on the increasing $\mu_{\text{Mn}}$ due to the JT effect in the LaMnO$_3$ system. This suggestion will be elaborated in a future publication. However, for all $U$, $\mu_{\text{Mn}}$ values are higher than those of the previous experimental report, which is $3.34(2)$ $\mu_B$.\textsuperscript{9} For $U = 1$ eV, we find a $\mu_{\text{Mn}}$ of $4.31$ $\mu_B$, which is close to that of the other experimental report, i.e., $\sim 4.00$ $\mu_B$ at low $T$.\textsuperscript{35} From the theoretical point of view, Mn$^{2+}$ ion has the electron configuration of $[\text{Ar}]3d^44s^0$, leading to the theoretical magnetic moment of $5 \mu_B$ with the high-spin (HS) state ($S = 5/2, t_2g^0$). For the case of smaller tetrahedral crystal-field splitting energy ($\Delta_{\text{t}}$) between e and $t_2$ states than pairing energy between spins, only HS states are possible to exist in the 3d orbital. However, the low-spin (LS) state ($S = 1/2, t_2g^2$) can possibly exist in the tetrahedral coordination with a sufficiently large $\Delta_{\text{t}}$.\textsuperscript{36} The spin configurations of HS and LS states are illustrated in the inset of Figure 5b. For the Mn 3d orbital, as the counterpart of the HS state, the LS state can possibly exist for sufficiently large $\Delta_{\text{t}}$. It might be suggested that in the present work, the Mn 3d orbital exhibits the mixed HS–LS state, where the HS state portion is more pronounced for the higher $U$. Furthermore, the interaction between spins in the Mn 3d orbital can be considered into two possibilities. First, the interaction can be affected by the direct exchange between the nearest-neighboring Mn ions. Second, the interaction can be contributed by the superexchange with As ions. By extracting from Figure 2, we obtain $I_{\text{Mn–Mn}}$ of 2.92184 and 2.91271 Å for $U = 1$ eV and from the previous experiment.\textsuperscript{7} On the other hand, the body-centered cubic (bcc) δ–Mn and the face-centered cubic (fcc) γ–Mn crystals show $I_{\text{Mn–Mn}}$ of 2.66822 and 2.73155 Å between the nearest-neighboring Mn sites.\textsuperscript{37} These values imply that the direct exchange between Mn ions is not dominant in the (LaO)-MnAs system. The superexchange between Mn and As ions may provide the dominant contribution to the spin state. This suggestion is supported by the previous report suggesting that a lower $\mu_{\text{Mn}}$ than $5 \mu_B$ can be promoted by the substantial hybridization of As 4p and Mn 3d orbitals.\textsuperscript{7} We will clarify this suggestion in Section 3.3.

3.3. Projected Density of States. Figure 6a shows the total DOS of the (LaO)MnAs system for spin-up and spin-down orientations for $U = 1$ eV. In the approximate range of $-5$ to $-3$ eV, we find a large DOS peak for each spin orientation with a ripple feature. For the approximate range from $-3$ to $-0.5$ eV, two lower valence band peaks are shown near $E_F$. Above $E_F$, the result shows the conduction band in the approximate range from 0.4 to 2.5 eV with the two highest peaks at around 1.5 and 2.4 eV. The absence of state between the valence and conduction bands indicates $E_g$ shown in Figure 5a. For describing states contributing to both valence and conduction bands, we further present the projected DOS of orbitals involved in the system.

Figure 6. (a) Total density of states (DOS) of the (LaO)MnAs system. (b) Projected DOS of La 5d, La 4f, and O 2p, and (c) Mn 3d ($i = 1, 2$) are also presented. In (c), DOS summation of Mn 1 3d and Mn 2 3d states is presented in the dashed line. Spin-up and spin-down states are denoted by † and ‡, respectively. Notably, the value of $U = 1$ eV is used.

The projected DOS data are presented in Figure 6b,c. Figure 6b shows the projected DOS of La 5d, La 4f, and O 2p states. We find that La 5d and O 2p states are deeply located in the valence band at around $-4$ eV. With the deep separation between both states and Fermi level ($E_F$), electrons in [LaO]$^+$ layers are difficult to excite to the conduction band. On the other hand, La 4f states are localized at 2.4 eV, indicating that the La 4f orbital is empty. This result leads to an insulating behavior in these layers. Furthermore, the presence of insulating [LaO]$^+$, as well as the conducting [MnAs]$^-$ layers indicated by the capability of electrons to be excited from the valence to the conduction bands through $E_F$ (see Figure 6c), shows that the (LaO)MnAs system is a natural superlattice. Some layered systems reported as the natural superlattice show the potential application for the thermoelectric power.\textsuperscript{25c,38} However, we do not find any reference showing any evidence of potential application for thermoelectricity. Figure 6c shows the projected DOS of Mn 3d ($i = 1, 2$) and As 4p states. The valence Mn 1 3d and Mn 3 3d states contribute to the large DOS peak at around $-4$ eV. Above them, Mn 1 3d and Mn 2 3d states contribute to the lower peaks, which hybridize with As 4p states. Our results are in line with the valence-band photoemission (PE) spectrum reported by Higashiya et al. The measurement was performed using X-ray photoelectron spectroscopy (XPS) with a horizontally polarized X-ray photon energy of 9.9 keV. The PE spectrum of (LaO)MnAs indicates that O 2p states and Mn 3d states are located at around $-5$ eV. On the other hand, Mn 3d states hybridize with As 4p states and contribute to the region between $-3.5$ eV and $E_F$.\textsuperscript{39}

From Figure 6c, the conduction band shows that Mn 1 3d and Mn 2 3d states dominate from 0.4 to 2.0 eV. The result shows that the conduction band minimum (CBM) and valence band maximum (VBM) mainly come from Mn 3d and As 4p.
states. It is shown that, at the VBM, the portion of Mn 3d and As 4p states is almost the same, indicating that $E_g$ transition can occur from between Mn 3d states. This result pronounces the Mott insulator characteristics.\textsuperscript{11b} We suggest that the presence of As 4p states at around VBM is induced by their strong hybridization with Mn 3d. This result supports our suggestion in the previous subsection that the lower $\mu_{\text{Mn}}$ can be induced by the hybridization between Mn 3d and As 4p states.\textsuperscript{9} Furthermore, the DOS shape of Mn 2 3d has the mirrored shape of the DOS shape of Mn 1 3d states, showing the antiferromagnetic behavior localized at Mn 1 and Mn 2 sites. It is remarkably shown that for the Mn 1 site, all the spin-up and spin-down Mn 1 3d states are almost located at the valence and conduction bands, respectively. This feature indicates that all sub-Mn 1 3d orbitals are occupied by five spin-up electrons, depicting the HS state. For the same reason, all sub-Mn 2 3d orbitals are occupied by five spin-down electrons as the result of the G-type antiferromagnetic ordering of Mn\textsuperscript{2+} ions.\textsuperscript{15} In the range of $−2.5$ to $−0.5\text{ eV}$, both spin-up and sub-Mn 3d orbital is occupied, indicating a very small contribution of LS state due to the strong hybridization between spin Mn 3d and As 4p states. This result confirms the previous suggestion that the spin state in the Mn 3d orbital is mainly contributed by the superexchange between Mn and As ions. However, the presence of both the occupied sub-Mn 3d orbital might also imply the Mn oxidation state of $3+$. We suggest that the possible oxidation state corresponds to a theoretical $\mu_{\text{Mn}}$ of 4 $\mu_B$ for the HS state ($S = 2$) of the Mn\textsuperscript{3+} 3d\textsuperscript{0} orbital and close to the calculated $\mu_{\text{Mn}}$ for small $U$. This suggestion follows the simple rules for the Heusler compounds,\textsuperscript{30} where Mn tends to exhibit a large value of $\mu_{\text{Mn}}$ with the nominal electron configuration of Mn\textsuperscript{3+}: [Ar] 3d\textsuperscript{4} and the oxidation state of $3+$.\textsuperscript{35}

Figure 7 presents the projected DOS of sub-Mn 1 3d and sub-Mn 2 3d orbitals ($d_{x^2}$, $d_{y^2}$, $d_{zx}$, $d_{zy}$, $d_{x^2} − y^2$, $d_{z^2}$), respectively, in the (LaO)MnAs system for $U = 1\text{ eV}$. We find that all the sub-Mn 3d orbitals are separated at different energy levels. This result is obtained despite the fact that the HS state significantly dominates the Mn 3d orbital, indicating the absence of the JT effect. We suggest that the separations between sub-Mn 3d orbitals may be induced by the second-order JT effect.\textsuperscript{41} This effect may contribute to the LSD in MnAs\textsubscript{4} tetrahedra. Furthermore, [La\textsuperscript{3+}]\textsuperscript{3-} and [MnAs\textsubscript{3-}]\textsuperscript{3-} layers fit each other in the interface between both layers. This mechanism may lead to the LSD in OLa\textsubscript{4} tetrahedra, as MnAs\textsubscript{4} tetrahedra are distorted. In Figure 7a, we find that the spin-up valence and conduction $d_{xy}$ states have the highest peaks at $−3.84$ and $1.50\text{ eV}$, respectively, at which these two peaks tend to be localized. This result suggests the exchange splitting of around $5.35\text{ eV}$.

On the other hand, the other sub-Mn 1 3d orbitals tend to spread along with the valence and conduction band. Figure 6c shows that the energy level of $−3.84\text{ eV}$ is very close to the lowest DOS valley of As 4p states. Therefore, we roughly suggest that, alongside the localization, the valence $d_{xy}$ states also show the weakest hybridization with the valence As 4p states. This feature is in contrast to the conduction band, where the highest peak of $d_{xy}$ states is in the close energy level to that of As $4p$ states. The result of the Mn 2 site is the same as that of the Mn 1 site with an opposite spin direction as shown in Figure 7b. For both Mn 1 and Mn 2 sites, the Mott-insulating behavior is characterized by the $E_g$ transition between the valence and conduction $d_{xy}$ states.

4. CONCLUSIONS

The structural, electronic, and magnetic properties of the antiferromagnetic (LaO)MnAs system have been comprehensively investigated. The first-principle calculation shows that the increase in $U$ in the Mn 3d orbital induces the increment of the LSD at MnAs\textsubscript{4} and OLa\textsubscript{4} tetrahedra, where the LSD at OLa\textsubscript{4} is more pronounced than that of MnAs\textsubscript{4} tetrahedra. Since Mn 3d is half occupied, the LSD at MnAs\textsubscript{4} tetrahedra is induced by the possible second-order JT effect. It is also shown that the increase in $U$ induces the increase in $E_g$, which has the maximum value at $U = 8\text{ eV}$, and $\mu_{\text{Mn}}$. Based on the structural properties, the value of $U = 1\text{ eV}$ is the most appropriate value for the system in the present work despite the underestimated $E_g$ of 0.834 eV. This $U$ value also results in a $\mu_{\text{Mn}}$ of 4.31 $\mu_B$, respectively. Furthermore, the lower $\mu_{\text{Mn}}$, than the theoretical value for the HS state is promoted by the strong hybridization between Mn 3d and As 4p states. Among all the sub-Mn 3d orbital, we find that the valence $d_{xy}$ states show the less pronounced hybridization with valence As 4p states. Both valence and conduction $d_{xy}$ states are localized at $−3.84$ and $1.50\text{ eV}$, respectively. Moreover, it is suggested that the Mott-insulating behavior in the system is characterized by the transition between $d_{xy}/d_{xy}$ states at the valence band maximum and conduction band minimum. From the projected DOS, the second-order JT is suggested by the separations between all sub-Mn 3d states, where $d_{x^2}$ and $d_{y^2}$ states are at the same energy levels. Finally, this work presents the new insights of the properties of the system, which are essential for future functional device applications.

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Notes
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