Electronic structure and magnetic properties of NaOsO$_3$

Yongping Du,$^1$ Xiangang Wan,$^{1,2,*}$ Li Sheng,$^1$ Jinming Dong,$^1$ and Sergey Y. Savrasov$^2$

$^1$National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, China
$^2$Department of Physics, University of California, Davis, One Shields Avenue, Davis, California 95616, USA

(Received 15 January 2012; published 16 May 2012)

A comprehensive investigation of the electronic and magnetic properties of NaOsO$_3$ has been made using first-principle calculations in order to understand the importance of Coulomb interaction, spin-orbit coupling, and magnetic order in its temperature-induced and magnetic-related metal-insulator transition. It is found that its electronic structure near the Fermi energy is dominated by strongly hybridized Os 5$d$ and O 2$p$ states. Despite of the large strength of spin-orbit coupling, it has only small effect on the electronic and magnetic properties of NaOsO$_3$. On the other hand, the on-site Coulomb repulsion affects the band structure significantly, but a reasonable $U$ alone cannot open a band gap. Its magnetism is itinerant, and the magnetic configuration plays an important role in determining the electronic structure. Its ground state is of a G-type antiferromagnet, and it is the combined effect of $U$ and magnetic configuration that results in the insulating behavior of NaOsO$_3$.

DOI: 10.1103/PhysRevB.85.174424

I. INTRODUCTION

It is well known that the Coulomb interaction among 3$d$ electrons in transition-metal oxides (TMOs) is substantially important, which includes peculiar properties, such as metal-insulator transition, colossal magnetoresistance, and high critical temperature superconductivity. Because the 5$d$ orbitals are highly extended compared to those in the 3$d$ systems, it is natural to expect that the electronic correlations are weak and have only negligible effect in the 5$d$ compounds. However, recent theoretical and experimental works have given the evidence on the importance of Coulomb interactions here. On the other hand, the spin-orbit coupling (SOC) in the 5$d$ transition-metal elements is expected to be strong due to the large atomic number. Hence, due to the interplay of electron correlations and strong spin-orbit interactions, various anomalous electronic properties have been observed/proposed in the 5$d$ transition oxides, such as $J_{\text{eff}} = 1/2$ Mott state, giant magnetoelectric effect, high-$T_c$ superconductivity, Weyl semimetal with Fermi arcs, Axion insulator with large magnetoelectric coupling, topological insulator, correlated metal, Kitaev mode, etc.

One class of the well-studied 5$d$ compounds are the osmates, For example, the physical properties of Cd$_2$Os$_2$O$_7$ are quite intriguing. It has been found that Cd$_2$Os$_2$O$_7$ is metallic at room temperatures, while undergoing a metal-insulator transition (MIT) at about 230 K. Experiments reveal that this MIT is continuous and purely electronic. Moreover, it is coincident with a magnetic transition of antiferromagnetic (AFM) character. Therefore, experimentalists argue that Cd$_2$Os$_2$O$_7$ is the first well-documented example of a pure Slater transition. Its exact magnetic ground-state configuration is still unknown due to the strong magnetic frustration of the pyrochlore lattice. Therefore, theoretical evidence of the Slater transition in this compound is still lacking.

Recently, using high-pressure technique, Shi et al. synthesized another osmate: NaOsO$_3$. Similar to Cd$_2$Os$_2$O$_7$, NaOsO$_3$ also exhibits a temperature-induced MIT, which is again accompanied by a magnetic ordering without any lattice distortion. However, better than Cd$_2$Os$_2$O$_7$, NaOsO$_3$ has a simple perovskite structure, consequently being free from the complication induced by magnetic frustration. Therefore, NaOsO$_3$ provides a unique platform to understand the temperature-induced and magnetic-related MIT. Based on the experimental crystal structure, Shi et al. also perform the band-structure calculation for this compound. They find that both LDA and LDA + SOC calculation give the paramagnetic solution. Their numerical results show that Coulomb $U$ is not efficient, and AFM correlation is essential to open the band gap. Recently, experimental and theoretical evidence of the importance of electronic correlation and spin-orbit coupling in 5$d$ transition-metal compounds has been found. Therefore, a comprehensive investigation of the effect of the Coulomb interaction, SOC, and magnetic order on its electronic structure and MIT is still an interesting problem, which we address in the present work.

II. METHOD

The electronic band structure calculations have been carried out by using the full potential linearized augmented plane-wave method as implemented in wien2k package. Local spin density approximation (LSDA) is widely used for various 4$d$ and 5$d$ TMOs and we therefore adopt it as the exchange-correlation potential. The muffin-tin radii for Na, Os, and O are set to 1.13, 1.02, and 0.90 Å, respectively. The basic functions are expanded to $R_{\text{mt}} K_{\text{max}} = 7$ (where $R_{\text{mt}}$ is the smallest of the muffin-tin sphere radii and $K_{\text{max}}$ is the largest reciprocal lattice vector used in the plane-wave expansion), corresponding to 1915 LAPW functions at the $\Gamma$ point. Using the second-order variational procedure, we include the SOC interaction, which has been found to play an important role in the 5$d$ system. A $10 \times 6 \times 10$ mesh is used for the Brillouin zone integral. The self-consistent calculations are considered to be converged when the difference in the total energy of the crystal does not exceed 0.1 mRy and that in the total electronic charge does not exceed $10^{-3}$ electronic charge at consecutive steps.

NaOsO$_3$ has an orthorhombic perovskite structure with space group of $Pmna$. There are four formula units (f.u.) per unit cell, and the 20 atoms in the unit cell can be classified
TABLE I. Numerical and experimental internal coordinates of NaOsO₃.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Calculation</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x</td>
<td>y</td>
</tr>
<tr>
<td>Na</td>
<td>0.0392</td>
<td>1/4</td>
</tr>
<tr>
<td>O1</td>
<td>0.4919</td>
<td>1/4</td>
</tr>
<tr>
<td>O2</td>
<td>0.2940</td>
<td>0.0428</td>
</tr>
</tbody>
</table>

as four nonequivalent crystallographic sites: Na, Os, O1, and O2 according to the symmetry. They are located at 4c, 4b, 4c, and 8d sites, respectively, and result in seven internal coordinates. From the x-ray diffraction experiment,¹¹ the lattice constants of NaOsO₃ are determined to be $a = 5.384$ Å, $b = 7.580$ Å, and $c = 5.328$ Å, respectively. Based on the experimental lattice parameters, we optimize all independent internal atomic coordinates until the corresponding forces are less than 1 mRy/a.u. We confirm that the Coulomb $U$ and SOC have only small effect on the crystal structure and list in Table I the internal atomic coordinates by LDA calculations. Our numerical internal coordinates are in good agreement with the experimental result, as shown in Table I.

III. RESULTS AND DISCUSSIONS

Using the experimental lattice constants and the numerical internal coordinates, we first perform nonmagnetic LDA calculation. The total density of states (TDOS), Os 5$d$ partial density of states (PDOS), O1 2$p$ PDOS, O2 2$p$ PDOS, and Na 2$s,2$p PDOS are plotted in Figs. 1(a)–1(e), respectively.

Our TDOS is very similar to that obtained based on the experimental crystal structure [see Fig. (4a) of Ref. 21]. The energy range, −9.0 to −2.4 eV is dominated by O1 2$p$ and O2 2$p$ bands with a small contribution from the Os 5$d$ state. Both Na 2$s$ and Na 2$p$ states, appearing mainly above 4 eV, have also considerable distribution between −9.0 and −2.4 eV, where the O 2$p$ state is mainly located, indicating the non-negligible hybridization between Na and O states despite that Na is highly ionic. The Os atom is octahedrally coordinated by six O atoms, making the Os 5$d$ band split into the $t_{2g}$ and $e_g$ states, and the $12t_{2g}$ bands are located from −2.8 to 1.2 eV, as shown in Fig. 2(a). Due to the extended nature of 5$d$ states, the crystal splitting between $t_{2g}$ and $e_g$ states is large, and the $e_g$ states are located about 2.0 eV higher than the Fermi energy ($E_F$) and disperse widely. While providing the basic features of the electronic structure, LDA produces a metallic state due to partially occupied Os 5$d$ $t_{2g}$ band.

The SOC of 5$d$ electrons is about 0.5 eV, which is one order of magnitude larger than that of 3$d$ electrons. Therefore, SOC usually changes the 5$d$ band dispersion significantly and plays an essential role in the gap opening of Sr₂IrO₄, as well as of pyrochlore iridates.⁴,⁵,⁹ In order to investigate the effect of SOC on the electronic structure, we compare the results obtained in the presence and absence of SOC, which are given in Fig. 2. The difference between the bands with and without SOC is small, as demonstrated in Fig. 2. For 5$d^3$ electronic configuration of Sr₂IrO₄ (Ref. 4) and A₂Ir₂O₇ ($A =$ Y or rare earth),³,⁶ where the $J_{eff} = 1/2$ picture is valid, SOC has a dramatic effect on the band structure. In NaOsO₃, Os occurs in its 5$^+$ valence and there are three electrons in its $t_{2g}$ band. Since $t_{2g}$ band is half filled, it is natural to expect the effect of SOC to be small. As shown in Fig. 1(a), the Fermi

FIG. 1. (Color online) Electronic density of states (DOS) from LDA calculations. Fermi energy $E_F$ is set to zero. (a) TDOS, (b) Os 5$d$ PDOS, (c) O1 2$p$ PDOS, (d) O2 2$p$ PDOS, (e) Na PDOS.

FIG. 2. (Color online) Band structure of NaOsO₃, shown along the high-symmetry directions. (a) LDA, (b) LDA + SO.
level is located near a sharp peak in the DOS. The relatively high density of states at the Fermi energy \( N(E_F) \) suggests the possibility of a Stoner instability against ferromagnetism (FM). Therefore, we perform a spin polarized calculation; however, our LSDA + SO calculation with initial FM setup converges to the nonmagnetic state. Thus, consistent with Shi et al.,\(^{21}\) the FM state is not stable in LSDA + SO calculation.

Although the 5\( d \) orbitals are spatially extended, it has been found that the electronic correlations are important for 5\( d \) TMO.\(^{4,5}\) Moreover, the experiment reveal that NaOsO\(_3\) has a long-range magnetic order at low temperature.\(^{21}\) We therefore utilize LSDA + \( U \) scheme,\(^{31}\) which is adequate for searching for magnetically ordered insulating ground states.\(^{32}\)

Although the accurate value of \( U \) is not known for perovskite osmates, the estimates of the values of \( U \) have been recently obtained between 1.4 and 2.4 eV in layered Sr\(_2\)IrO\(_4\)/Ba\(_2\)IrO\(_4\).\(^{33}\) We generally expect the screening to be larger in three-dimensional (3D) systems than in two-dimensional (2D) ones, and one can image that \( U \) in NaOsO\(_3\) should be smaller than that in Sr\(_2\)IrO\(_4\)/Ba\(_2\)IrO\(_4\). We therefore perform LDA + \( U \) + SO calculation and vary parameter \( U \) between 0.5 and 2.0 eV. Numerical results show that the electronic correlations can stabilize the FM configuration and narrow the Os \( t_{2g} \) band. However, as shown in Fig. 3(a), our LDA + \( U \) + SO calculation with \( U = 2.0 \) eV still gives a metallic solution. Naively, one may expect that using larger Coulomb \( U \) will result in an insulating state. However, consistent with Shi et al.,\(^{21}\) our additional calculations show that increasing \( U \) cannot solve this problem, and even a quite large \( U \) (=6.0 eV) cannot open the band gap. Therefore, electronic correlations alone cannot explain the insulating behavior, and the MIT is not of a Mott type.

After studying the effect of SOC and \( U \), we subsequently investigate the effect of various magnetic orders. We considered four AFM configurations besides the FM state: A-type AFM state (A-AFM) with layers of Os ions coupled ferromagnetically in a given set of (001) planes but with alternate planes having opposite spin orientation; C-type AFM state (C-AFM) with lines of Os ions coupled ferromagnetically in a given direction (001) but with alternate lines having opposite spin orientation; G-type AFM state (G-AFM) with Os ions coupled antiferromagnetically with all of their nearest neighbors; D-type AFM state (D-AFM) where Os ions lying within alternating planes perpendicular to (001) direction are coupled ferromagnetically along either [010] or [100] directions while different lines are coupled antiferromagnetically. Same as with the FM setup, the LSDA + SO calculation with \( U = 0 \) for all considered AFM setups converges to the nonmagnetic metallic state.

On the other hand, the nonzero Coulomb interaction \( U \) of Os 5\( d \) is found to stabilize the AFM configuration. Our calculation confirms that the magnetic order has a significant effect, and for a reasonable \( U \) (=2.0 eV), G-AFM configuration is the only insulating solution, as shown in Fig. 3. Moreover, regardless the value of \( U \), the G-AFM configuration always has the lowest total energy. Thus, we believe G-AFM configuration is the magnetic ordering state observed by the experiment.\(^{21}\) With increasing \( U \) the band structure will change, but only when \( U \) is larger than 1.0 eV does the G-AFM solution become insulating. The DOS from \( U = 1.0 \) eV [see Fig. (4c) of Ref. 21] is similar to that from \( U = 2.0 \) eV [see Fig. 3(b) of present work], which again indicates that the Coulomb \( U \) is not sufficiently efficient to open the band gap. It is found that the magnetic moment is mainly located at the Os site, and despite of strong hybridization between Os 5\( d \) and O 2\( p \), the site is basically nonmagnetic (less than 0.003 \( \mu_B \)). The numerical data for \( U = 2.0 \) eV are given in Table II. For the 5\( d^1 \) electronic systems such as BaIrO\(_3\), Sr\(_2\)IrO\(_4\), pyrochlore iridates, etc., it has been found that due to the strong spin-orbit entanglement in 5\( d \) states, the magnetic orbital moment is about twice larger than the spin moment,\(^{4,5,9,34}\) even in the presence of strong crystal-field and band effects. Contrary to 5\( d^3 \) systems, the obtained orbital moment for NaOsO\(_3\) is much smaller than its spin moment, showing again that SOC effect is small for this 5\( d^3 \) electronic configuration case. As shown in Table II, the magnitude of magnetic moment is sensitive to the magnetic configuration, indicating the itinerant nature of magnetism. For the same \( U \) value, the G-AFM configuration always has the largest magnetic moment among the considered states. However, as shown in Table II, our numerical magnetic moment (0.83 \( \mu_B \)) is much smaller than the experimental one.\(^{21}\) For an itinerant magnet, one may still fit the \( \chi(T) \) curve by the Curie-Weiss law, but cannot estimate the magnetic moment accurately based on the Curie-Weiss constant.\(^{35}\) Thus, the experimental magnetic moment may not be reliable. The energy difference between various magnetic configurations is large, which is consistent with the observed high magnetic transition temperature (about 410 K),\(^{21}\) although here one cannot estimate the interatomic exchange interaction and \( T_N \)
based on the difference between total energies accurately as in the local moment systems. Since the G-AFM configuration is the only insulating state, it is easy to understand that both magnetic and electronic phase transitions occur at the same temperature and our calculation indeed confirms that the MIT of NaOsO₃ is a Slater-type transition.

IV. SUMMARY

In summary, we have investigated the detailed electronic structure and magnetic properties of NaOsO₃ using a full potential linearized augmented plane-wave method. Our results show that the electronic structure near the Fermi energy $E_F$ is dominated by strongly hybridized Os 5d and O 2p states. Despite its big value the SOC has only weak effect on the band structure and magnetic moment. The electronic correlations alone cannot open the band gap, and the low-temperature phase of NaOsO₃ is not a Mott-type insulator. The magnetic ground state configuration has an important effect on the conductivity, and the ground state is a G-type AFM insulator. It is the interplay of the Coulomb interaction and magnetic ordering that result in the insulating behavior of NaOsO₃.

Note added in proof. After submission of this work, we became aware of a paper by Calder et al. where NaOsO₃ is studied experimentally. The agreement between our theory and experiment is fairly good: (1) Our theoretical magnetic ground state configuration has been confirmed by the experiment; (2) numerical magnetic moment at Os (0.83 $\mu_B$) is close to the experimental value (1.01 $\mu_B$); (3) SOC is not important for NaOsO₃, this theoretical result agrees with the measurement; (4) Our theoretical conclusion (the MIT of NaOsO₃ is a Slater-type transition) is consistent with the experimental result.

ACKNOWLEDGMENTS

The work was supported by the National Key Project for Basic Research of China (Grants No. 2011CB922101 and No. 2010CB923404), NSFC under Grants No. 91122035, No. 11174124, and No. 10974082. The project also funded by Priority Academic Program Development of Jiangsu Higher Education Institutions. S.Y.S was supported by DOE SciDAC Grant No. SE-FC02-06ER25793 and by DOE Computational Material Science Network (CMSN) Grant No. DE-SC0005468.

TABLE II. Spin ⟨S⟩ and orbital ⟨O⟩ moment (in $\mu_B$), as well as the total energy $E_{tot}$ per unit cell (in eV), for several magnetic configurations, as calculated using LDA + $U$ + SO method with $U = 2.0$ eV. $E_{tot}$ is defined relative to the G-AFM configuration.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>G-AFM</th>
<th>FM</th>
<th>C-AFM</th>
<th>A-AFM</th>
<th>D-AFM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{tot}$</td>
<td>0</td>
<td>0.243</td>
<td>0.186</td>
<td>0.282</td>
<td>0.205</td>
</tr>
<tr>
<td>⟨S⟩</td>
<td>0.94</td>
<td>0.22</td>
<td>0.54</td>
<td>0.29</td>
<td>0.20</td>
</tr>
<tr>
<td>⟨O⟩</td>
<td>−0.11</td>
<td>−0.01</td>
<td>−0.04</td>
<td>−0.03</td>
<td>−0.03</td>
</tr>
</tbody>
</table>

*Corresponding author: xgwan@nju.edu.cn


3W. Pickett, Rev. Mod. Phys. 61, 433 (1989).


26 J. C. Slater, Phys. Rev. 82, 538 (1951).