Electronic Structures, Magnetism, and Phonon Spectra in the Metallic Cubic Perovskite BaOsO₃

Myung-Chul Jung¹ and Kwan-Woo Lee¹

¹ Department of Applied Physics, Graduate School, Korea University, Sejong 339-700, Korea
² Department of Display and Semiconductor Physics, Korea University, Sejong 339-700, Korea

(Dated: July 23, 2014)

By using ab initio calculations, we investigated a cubic perovskite BaOsO₃ and a few related compounds that have been synthesized recently and formally have a metallic $d^5$ configuration. In BaOsO₃, which shows obvious three-dimensional fermiology, a nonmagnetism is induced by a large spin-orbit coupling (SOC), which is precisely equal to an exchange splitting $\sim 0.4$ eV of the $t_{2g}$ manifold. However, the inclusion of on-site Coulomb repulsion as small as $U' \approx 1.2$ eV, only 1/3 of the $t_{2g}$ bandwidth, leads to the emergence of a spin-ordered moment, indicating that this system is on the verge of magnetism. In contrast to BaOsO₃, our calculations suggest that the ground state of an orthorhombic CaOsO₃ is a magnetically ordered state due to the reduction of the strength of SOC (about a half of that of BaOsO₃) driven by the structure distortion, although the magnetization energy is only a few tenths of meV. Furthermore, in the cubic BaOsO₃ and BaRuO₃, our full-phonon calculations show several unstable modes, requiring further research.

PACS numbers: 71.20.Be, 71.20.Dg, 75.50.Cc, 71.18.+y

I. INTRODUCTION

Transition metal oxides show abundant phenomena involved in the interplay among charge, spin, orbital, and lattice degrees of freedom. Recently, the effects of spin-orbit coupling (SOC) have been intensively investigated in the $t_{2g}$ manifold of an MO₃ octahedral structure ($M=5d$ transition metals). In the atomic limit, a large SOC leads to transforming the $t_{2g}$ manifold into an effective angular momentum of $|\mathcal{L}|=\frac{1}{2}$.

A conventional SOC picture says that a $d^4$ system is a trivial nonmagnetic insulator in the large SOC limit, which may be suitable for a nonmagnetic (NM) and nonmetallic NaIrO₃. However, two interesting studies have recently appeared. Khalilullin suggested a van Vleck-type Mott insulating state due to excitations between a singlet $J=0$ state and triplet $J=1$ states. Meetei et al. proposed unusual Mott insulators of a charge-disproportionated ferromagnetic (FM) $J=1$ state as well as a FM $J=2$ state, as including effects of correlation. One may expect different physical phenomena for a metallic $5d^4$ system such as BaOsO₃, which will be focused on in this research.

Several decades ago, Chamberland and Sarkozy synthesized a body-centered cubic KSB₀₃-type and a 6$H$ hexagonal phase. Although no detailed information of the crystal structures and the physical properties is available, the 6$H$ hexagonal phase, which is a semiconductor with an activation energy of 0.39 eV, follows the Curie-Weiss behavior above 100 K (no measurement has been done below this temperature). The observed effective moment is 2.81 $\mu_B$, which is very close to the spin-only value for $S=1$, indicating negligible effects of SOC for such a large structure distortion. Very recently, Shi et al. synthesized a distortion-free cubic perovskite phase using a technique of high temperature ($\sim 2000$ K) and high pressure (17 GPa). The resistivity is metallic but indicates a small upturn at 50 K, which may be due to the polycrystallinity of the sample. The heat capacity measurement shows a metallic behavior, but can be fitted well by a linear combination of the Debye and the Einstein models, suggesting a complicated behavior in phonon modes around 300 K. Shi et al. also synthesized two orthorhombic, isovalent perovskites CaOsO₃ and SrOsO₃. CaOsO₃ shows complicated electronic properties, whereas SrOsO₃ has metallic characteristics in both the resistivity and the heat capacity measurements. The resistivity data of CaOsO₃ is semiconductor-like, but $\ln \rho(T)$ does not follow typical models of $T^{-1}$ or $T^{-1/4}$ forms. Also, the heat capacity contains itinerant electronic character even at very low $T$. It was claimed that CaOsO₃ is near a Mott insulating state. For the magnetic properties, these three osmates commonly follow the Curie-Weiss susceptibility, though no order moment has been observed. At low $T$, the susceptibility measurements of CaOsO₃ and SrOsO₃ show larger enhancement than that of BaOsO₃, indicating more magnetic tendencies in these two orthorhombic osmates.

Through first-principles calculations, we will address the electronic structures and magnetic properties of the cubic BaOsO₃, which are substantially affected by SOC, structure distortion, and correlation effects. The cubic BaOsO₃ will be compared and contrasted to the orthorhombic CaOsO₃ to investigate the interplay between magnetism, SOC, and structure distortion. Besides, we performed full-phonon calculations to inspect the stability of the cubic phases of isovalent BaOsO₃ and BaRuO₃, which can be synthesized only by a technique of very high pressure and temperature.
the convergence carefully for this metallic system. In BaOsO$_3$ sampled with a very dense than 1 meV/a.u. (see below). The Brillouin zone was lattice or internal parameters until the forces were smaller GGA) functional. We also performed linear response phonon calculations, using quantum espresso with PBE-GGA ultrasoft-pseudopotential and the fully relativistic pseudopotential for GGA+SOC. These calculations were carried out with a $4 \times 4 \times 4$ $q$-mesh, a $24 \times 24 \times 24$ $k$-mesh, an energy cutoff of 45 Ry, and a charge cutoff of 450 Ry.

II. CALCULATION METHOD

Our calculations were carried out by using the experiment lattice parameter $a = 4.02573$ Å for BaOsO$_3$ with two all-electron full potential codes, fplo and wien2k. Both SOC and correlations have been considered within extensions of the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) functional. When necessary, we optimized the lattice or internal parameters until the forces were smaller than 1 meV/a.u. (see below). The Brillouin zone was sampled with a very dense $k$-mesh of $24 \times 24 \times 24$ to check the convergence carefully for this metallic system. In wien2k, the basis size was determined by $R_{mt} K_{max} = 7$ and the augmented plane wave (APW) radii of Ba 2.50, Os 2.08, O 1.7 (in units of a.u.).

We also performed linear response phonon calculations, using quantum espresso with PBE-GGA ultrasoft-pseudopotential and the fully relativistic pseudopotential for GGA+SOC. These calculations were carried out with a $4 \times 4 \times 4$ $q$-mesh, a $24 \times 24 \times 24$ $k$-mesh, an energy cutoff of 45 Ry, and a charge cutoff of 450 Ry.

III. RESULTS

A. Electronic Structure of BaOsO$_3$

First, we address the electronic structure of nonmagnetic (NM) BaOsO$_3$, since the ground state is NM when considering SOC. We discuss this in Sec. IIIC in detail.

The top of Fig. 1 displays the NM band structure of BaOsO$_3$, excluding SOC. The O $p$ states and the Os $t_{2g}$ manifold extend over the range of $-9$ eV to $0.5$ eV, relative to the Fermi energy $E_F$. As clearly visible in the corresponding DOS of Fig. 2(a), $E_F$ pinpoints at the $2/3$ filling of the $t_{2g}$ manifold, which is consistent with the $d^4$ configuration. The orbital-projected DOS of Fig. 2(a) shows strong hybridization between Os 5$d$ and O 2$p$ states: roughly $pd\sigma$ states at $-9$ eV to $-5$ eV ($0.5$ eV to $6$ eV), $pd\pi$ states at $-7.2$ eV to $-3$ eV ($-3$ eV to $1$ eV), and pure O $p\pi$ states at $-4.2$ eV to $-2.8$ eV. Here, the numbers inside the parentheses are for each antibonding states, usually denoted the $e_g$ and $t_{2g}$ manifolds, respectively. These bands below 1 eV were fitted by the tight-binding Wannier function technique implemented in fplo. We obtained two important parameters: $p\sigma$ hopping $t_{\sigma} = 1.32$ eV and direct oxygen-oxygen hopping $t'_\sigma = 0.14$ eV. The $t'_\sigma$ value is similar to that of BaRuO$_3$, but the value of $t_{\sigma}$ is about 10% larger than that of BaRuO$_3$, reflecting the wider extension of the 5$d$ orbital than the 4$d$ orbital. Remarkably, in the band structure, there are three nearly dispersionless bands around the $M$ point, in addition to a flat band just above $E_F$ along the $\Gamma - X$ line, which often appears due to a lack of $dd\delta$ hopping in conventional perovskites. The former three bands lead to sharp peaks at $-6$ eV, $-3.5$ eV, and $E_F$ in the DOS of Fig. 2(b), whereas the latter conduction band does not. The van Hove singularity at $E_F$ results from the quite flat band with the character of $pd\pi$ antibonding between Os $d_x^2$ and O $p_z$ orbitals along the $X - M$ line, which shows a large band mass of $m^* \approx -70$.  

FIG. 1: (Color online) (a) GGA NM band structure of BaOsO$_3$ in the regime including O 2$p$ and Os 5$d$ orbitals. The bands above $0.5$ eV are the Os $e_g$ manifold. (b) Blowup GGA FM band structure (black solid lines are for spin up and green dot-dashed lines are for spin down), which is overlapped by the GGA+SOC one (red dashed lines). The horizontal dashed lines denote the Fermi energy $E_F$, which is set to zero.

FIG. 2: (Color online) Orbital-projected densities of states (PDOSs) per atom in (a) GGA, and (b) atom PDOSs in GGA and in (c) GGA+SOC of NM BaOsO$_3$. The corresponding FM DOS is not shown here, since this is very similar to that of NM, except for the positions of $E_F$‘s at $0.25$ eV and $-0.15$ eV for the spin-up and -down channels, respectively, relative to $E_F$ of NM. For NM, the single spin DOS at $E_F$ is $N(E_F) = 3.38$ states per eV.
This van Hove singularity enhances the magnetic instability (see below).

To investigate the effects of SOC, we carried out GGA+SOC calculations. The blowup band structure near $E_F$ denoted by (red) dashed lines in the bottom of Fig. 1 shows a strength of SOC of $\xi \approx 0.4$ eV, as measured near $E_F$, where SOC affects considerably. This value is largely reduced from the atomic value $\sim 2/3(\pi/a)$, containing $\sim 0.31$ holes. The $\Gamma$-centered spherical FS becomes more isotropic, although nodules appear in the (100) directions. The radius of the spherical FS decreases by $\sim 10\%$ to compensate for the reduction of the hole-like FSs, and attains a radius of $0.9\pi/a$, containing about 0.76 electrons.

Transport properties can be studied with the Fermi velocity and plasma frequency. For the GGA case, the root-mean-square of the Fermi velocity is $v_{F\text{rms}} = 2.71 \times 10^7$ cm/s, a typical value for a metal. The plasma energy $\hbar \Omega_{\text{pl,ii}}$, which is proportional to $v_{F\text{rms}} \sqrt{N(E_F)}$, is 4.55 eV. The inclusion of SOC increases $v_{F\text{rms}}$ to $3.63 \times 10^7$ cm/s, which is consistent with the fact that the bands around $E_F$ become more dispersive. So, the magnitude of the plasma energies is similar to the case neglecting SOC.

### C. Magnetic tendencies

Within GGA, FM with a total moment of 0.85 $\mu_B$ is energetically favored over NM, but the difference in energy is only 11 meV. We performed fixed spin moment calculations in GGA to investigate the stability of the FM state. We obtained $I = 0.79$ eV, leading to $I N(E_F) \approx 1.2$ with $N(E_F) = 1.53$ states/eV-spin for FM. This value, above unity of the Stoner criterion, is close to that of the cubic FM BaRuO$_3$ with the similar moment.

The bottom of Fig. 1 displays the enlarged FM band structure in GGA, showing that the exchange splitting of the $t_{2g}$ manifold is about 0.4 eV. Remarkably, this value is identical to the strength of SOC, resulting in a transition from FM to NM in this metallic $d^4$ system. Whenever including SOC our trials always converge to NM, which is consistent with the experiment.

Although the strength of correlation is still unclear in this system, the linear specific coefficient ratio of $\gamma_{\text{exp}}/\gamma_0$
D. Interplay among structure distortion, SOC, and magnetism

A structure distortion of the \(M4O_6\) octahedron from the ideal one reduces the strength of SOC. So, one may expect a magnetic ordering to emerge in the orthorhombic perovskite \(CaOsO_3\) with relatively small structure distortion since the NM ground state of the cubic \(BaOsO_3\) is purely due to effects of SOC. In GGA, FM with the moment of \(0.82 \mu_B/\text{Os}\) has lower energy by 6 meV/f.u. than NM, which is consistent with our fixed spin moment calculations. The obtained Stoner parameter \(I = 0.76\) eV is a little smaller than in \(BaOsO_3\), but \(I N(E_F)\) is almost identical to that of \(BaOsO_3\). This indicates similar magnetic tendencies in both \(CaOsO_3\) and \(BaOsO_3\), when ignoring SOC.

Figure 4 shows the blowup PDOS in both GGA and GGA+SOC, which indicate the exchange splitting of the \(t_{2g}\) manifold of about 0.3 and 0.1 eV for GGA and GGA+SOC, respectively. This reduction of 0.2 eV is almost identical to the strength of SOC in \(CaOsO_3\), which is only a half of that of \(BaOsO_3\). Consistent with this reduction, the inclusion of SOC reduces the moment by 50% and leads to a little magnetization energy, by only a few tenths of meV, although FM remains favored. A Stoner parameter in GGA+SOC can be estimated by \(I \sim 1/N(E_F) = 0.35\), which is a half of the GGA value. Our results suggest that the unusual magnetism, observed in the experiment, in the orthorhombic \(CaOsO_3\) results from emerging magnetic ordering induced by reducing the strength of SOC.

E. Phonon instability

Through first principles calculations, Rahman et al. suggested that two types of Jahn-Teller distortions in a cubic and isovalent \(BaFeO_3\), which are related to an antiferroic distortion of either Os or O ions along the c-axis, lead to a magnetic phase transition. In the cubic \(BaOsO_3\), our calculations show that these distortions...
are energetically unfavored, which is consistent with the phonon dispersion (see below). As mentioned in the introduction, however, the measurement of the specific heat suggested an unusual behavior.\textsuperscript{\texttt{1\texttt{5}}} Thus, we carried out linear response phonon calculations for our GGA optimized and a few compressed volumes, using both GGA and GGA+SOC.

Within GGA, we obtained several imaginary frequencies throughout all regimes (not shown here). Even for the inclusion of SOC, most of these unstable modes still survive, as given in the top of Fig. \texttt{6}. As often observed in cubic perovskites,\textsuperscript{\texttt{2\texttt{6}}} there are unstable modes, corresponding to the tilting of oxygens (triplet $R_{25}$, 36i cm$^{-1}$) and the rotation of in-plane oxygens (singlet $M_3$).\textsuperscript{\texttt{2\texttt{7}}} The latter appears at $\sim$ 600 cm$^{-1}$ in the compressed volume. Structure distortions involving these modes have been intensively investigated in several perovskites by Amisi \textit{et al.} and He \textit{et al.}\textsuperscript{\texttt{2\texttt{6},\texttt{2\texttt{8}}}} who suggest the gadolinium orthoferrite GdFeO$_3$-type structural distortion as the stablist one. However, in BaOsO$_3$ the GdFeO$_3$-type distortion is energetically unfavored. The most unstable modes of doublet 180i cm$^{-1}$ appear midway of the $\Gamma$–$X$ line, and are involved in the transverse acoustic mode, in which a displacement of one of the planar oxygens along the [110] direction is dominant. There are a few additional unstable modes along the $M$–$\Gamma$ and the $\Gamma$–$R$ lines. The latter is similar to the instability of the transverse acoustic mode observed in the possible charge-density-wave (CDW) Y$_3$Co.\textsuperscript{\texttt{2\texttt{9}}} However, consistent with the strong three-dimensionality in BaOsO$_3$, no indication of CDW is observed in our calculations. We also performed these calculations with two compressed volumes, which are 4% and 8% smaller than the optimized value, to investigate effects of pressure on the instability. The former corresponds to the experimental value. As shown in the top of Fig. \texttt{6}, most of the unstable modes remain nearly unchanged, indicating that volume contraction does not play an important role in the instability. The complicated phonon instability seems to be of interest, requiring further studies in both theoretical and experimental viewpoints, although this is not an issue covered in this research.

For comparison, phonon calculations were carried out in the cubic BaRuO$_3$, which is cubic even at temperature as low as 10 K.\textsuperscript{\texttt{3\texttt{0}}\texttt{,\texttt{3\texttt{1}}}} The bottom of Fig. \texttt{6} displays our results, which show very similar behavior to that of BaOsO$_3$. It is unclear yet why these phonon spectra show serious instabilities, although both the cubic BaOsO$_3$ and BaRuO$_3$ phases are experimentally stable. One possible scenario is that quantum fluctuations would stabilize the cubic phase in both systems, as discussed for some cubic perovskites.\textsuperscript{\texttt{3\texttt{0},\texttt{3\texttt{1}}}} This is true, only when the difference in energy between the cubic phase and a distorted phase is very small. Also, the instability may be related to the unusual behavior in the specific heat and the fact that these cubic systems can be synthesized only by a technique of extreme conditions.

\textbf{IV. DISCUSSION AND CONCLUSION}

Comparing the experimental linear specific heat coefficient $\gamma_{exp}$=18 mJ/mol-K$^2$ of CaOsO$_3$ with our theoretical values, there is an enhancement of a factor of two to three, implying a moderate correlation. Within the GGA+SOC+U approach, applying $U_{eff}$ to Os ions in CaOsO$_3$ leads to an insulating state at $U_{eff}$ $\approx$0.8 eV via a half-metallic state at $U_{eff} = 4$ eV. It may imply that this system is near an insulating state, resulting in the atypical electrical properties of CaOsO$_3$.

In conclusion, we have investigated the effects of SOC
on the magnetism of a few metallic 5$d^4$ systems synthesized recently. The cubic BaOsO$_3$ shows a transition from a Stoner-type FM to NM incurred by SOC, of which the strength is identical to the exchange splitting of the $t_{2g}$ manifold. However, at small $U^c \approx 1.2$ eV in GGA+SOC+U calculations, a small magnetic moment revives, suggesting that BaOsO$_3$ is an incipient magnet. On the other hand, our results indicate that the orthorhombic and isovalent CaOsO$_3$ magnet. We anticipate this fact to be true for the isostuctural and isovalent SrOsO$_3$. These results are consistent with a spin-ordered state observed very recently in a distorted double perovskite Sr$_2$YIrO$_6$ with 5$d^4$ $t_{3g}$ ions. Our findings indicate that these systems are good examples to investigate the interplay between magnetism, lattice, SOC, and correlation. Further research is required to clarify these issues from both the theoretical and experimental viewpoints.

V. ACKNOWLEDGMENTS

We acknowledge P. Giannozzi and C.-J. Kang for useful discussions on phonon instabilities, and W. E. Pickett for fruitful communications in the early stage of this research. This research was supported by NRF-2013R1A1A2A10008946.

---

* Electronic address: mckwan@korea.ac.kr

1 K.-W. Lee and W. E. Pickett, EPL 80, 37008 (2007), and references therein.
2 T. Dodds, T.-P. Choy, and Y. B. Kim, Phys. Rev. B 84, 104439 (2011).
3 G. Chen and L. Balents, Phys. Rev. B 84, 094420 (2011).
4 K.-W. Lee and W. E. Pickett, Phys. Rev. B 77, 115101 (2008).
5 M.-C. Jung, Y.-J. Song, K.-W. Lee, and W. E. Pickett, Phys. Rev. B 87, 115119 (2013).
6 H. Matsuura and K. Miyake, J. Phys. Soc. Jpn. 82, 073703 (2013).
7 B. J. Kim, H. Jin, S. J. Moon, J.-Y. Kim, B.-G. Park, C. S. Leem, J. Yu, T. W. Noh, C. Kim, S.-J. Oh, J.-H. Park, V. Durairaj, G. Cao, and E. Rothenberg, Phys. Rev. Lett. 101, 076402 (2008).
8 B. J. Kim, H. Ohsumi, T. Komesu, S. Sakai, T. Morita, H. Takagi, and T. Arima, Science 323, 1329 (2009).
9 X. Liu, V. M. Katukuri, L. Hozoi, W.-G. Yin, M. P. M. Dean, M. H. Upton, J. Kim, D. Casa, A. Said, T. Gog, T. F. Qi, G. Cao, A. M. Tselik, J. van den Brink, and J. P. Hill, Phys. Rev. Lett. 109, 157401 (2012).
10 G. Khaliullin, Phys. Rev. Lett. 111, 197201 (2013).
11 O. N. Meetee, W. S. Cole, M. Randera, and N. Trivedi, arXiv:1311.2823 (2013).
12 M. Bremholm, S. E. Dutton, P. W. Stephens, and R. J. Cava, J. Solid State Chem. 184, 601 (2011).
13 R. F. Sarkozy and B. L. Chamberland, Mat. Res. Bull. 8, 1351 (1973).
14 B. L. Chamberland, Mat. Res. Bull. 13, 1273 (1978).
15 Y. Shi, Y. Guo, Y. Shirako, W. Yi, X. Wang, A. A. Belik, Y. Matsushita, H. L. Feng, Y. Tsujimoto, M. Arai, N. Wang, M. Akao, and K. Yamaura, J. Am. Chem. Soc. 135, 16507 (2013).
16 C.-Q. Jin, J.-S. Zhou, J. B. Goodenough, Q. Q. Liu, J. G. Zhao, L. X. Yang, Y. Yu, R. C. Yu, T. Katsura, A. Shatskiy, and E. Ito, P. Natl. Acad. Sci. USA 105, 7115 (2008).
17 K. Koepernik and H. Eschrig, Phys. Rev. B 59, 1743 (1999).
18 K. Schwarz and P. Blaha, Comp. Mat. Sci. 28, 259 (2003).
19 J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
20 P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dubo, A. Dal Corso, S. Fabris, G. Fratesi, S. de Gironcoli, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, L. Lazzi, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, J. Phys.:Condens. Matter 21, 395502 (2009).
21 I. I. Mazin and D. J. Singh, Phys. Rev. B 56, 2556 (1997).
22 Y.-J. Song and K.-W. Lee, J. Kor. Phys. Soc. 62, 1869 (2013).
23 H. Rosner, R. Weht, M. D. Johannes, W. E. Pickett, and E. Tosatti, Phys. Rev. Lett. 88, 027001 (2001).
24 Our LSDA+SOC calculations show the same results, indicating that these results are insensitive to a selection of the exchange-correlation functional.
25 G. Rahman, J. M. Morbec, R. Ferradás, and V. M. García-Suárez, arXiv:1310.3502 (2013).
26 S. Amisi, E. Bousquet, K. Katcho, and Ph. Ghosez, Phys. Rev. B 85, 064112 (2012).
27 R. A. Cowley, Phys. Rev. 134, A981 (1964).
28 J. He and C. Franchini, Phys. Rev. B 89, 045104 (2014).
29 A. Podlesnyak, G. Ehlers, H. Cao, M. Matsuda, M. Frontzek, O. Zaharko, V. A. Kazantsev, A. F. Gubkin, and N. V. Baranov, Phys. Rev. B 88, 024117 (2013).
30 W. Zhong and D. Vanderbilt, Phys. Rev. Lett. 74, 2587 (1995); Phys. Rev. B 53, 5047 (1996).
31 R. Kagimura, M. Suewattana, and D. J. Singh, Phys. Rev. B 78, 012103 (2008).
32 G. Cao, T. F. Qi, L. Li, J. Terzic, S. J. Yuan, L. E. DeLong, G. Murthy, and R. K. Kaul, Phys. Rev. Lett. 112, 056402 (2014).