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Magnetic Structure and Origin of Insulating Behavior in the $\text{Ba}_2\text{CuOsO}_6$ System, and the Role of A-Site Ionic Size in Its Bandgap Opening: Density Functional Theory Approaches

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Abstract: The magnetic structure and the origin of band gap opening for $\text{Ba}_2\text{CuOsO}_6$ were investigated by exploring the spin exchange interactions and employing the spin–orbit coupling effect. It revealed that the double-perovskite $\text{Ba}_2\text{CuOsO}_6$, composed of the 3d (Cu^{2+}) and 5d (Os^{6+}) transition metal magnetic ions is magnetic insulator. The magnetic susceptibilities of $\text{Ba}_2\text{CuOsO}_6$ obey the Curie–Weiss law, with an estimated Weiss temperature of -13.3 K, indicating AFM ordering. From the density functional theory approach, it is demonstrated that the spin exchange interaction between Cu ions plays a major role in exhibiting an antiferromagnetic behavior in the $\text{Ba}_2\text{CuOsO}_6$ system. An important factor to understand regarding the insulating behavior on $\text{Ba}_2\text{CuOsO}_6$ is the structural distortion shape of OsO_6 octahedron, which should be closely connected with the ionic size of the A-site ion. Since the d-block of Os^{6+} (d^2) ions of $\text{Ba}_2\text{CuOsO}_6$ is split into four states ($xy < xz, yz < x^2-y^2 < z^2$), the crucial key is separation of doubly degenerated xz and yz levels to describe the magnetic insulating states of $\text{Ba}_2\text{CuOsO}_6$. By orbital symmetry breaking, caused by the spin–orbit coupling, the t_{2g} level of Os^{6+} (d^2) ions is separated into three sublevels. Two electrons of Os^{6+} (d^2) ions occupy two levels of the three spin–orbit-coupled levels. Since $\text{Ba}_2\text{CuOsO}_6$ is a strongly correlated system, and the Os atom belongs to the heavy element group, one speculates that it is necessary to take into account both electron correlation and the spin–orbit coupling effect in describing the magnetic insulating states of $\text{Ba}_2\text{CuOsO}_6$.

Keywords: magnetic structure; BaOsCuO_6 ; SOC effect; magnetic insulating behavior; orbital interaction

Citation: Park, T.; Lee, W.R.; Son, W.-J.; Shim, J.-H.; Lee, C. Magnetic Structure and Origin of Insulating Behavior in the $\text{Ba}_2\text{CuOsO}_6$ System, and the Role of A-Site Ionic Size in Its Bandgap Opening: Density Functional Theory Approaches. *Nanomaterials* **2022**, *12*, 144. <https://doi.org/10.3390/nano12010144>

Academic Editor: Zhidong Zhang

Received: 2 December 2021

Accepted: 29 December 2021

Published: 31 December 2021

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1. Introduction

Various osmium oxide compounds exhibit attractive magnetic and electronic phenomena developed from their electron correlation effects, such as the ferromagnetic gapped state in $\text{Ba}_2\text{NiOsO}_6$ [1], the singlet ground-state excitonic magnetism in Y_2OsO_7 [2–4], the spin-driven metal to insulator transition in $\text{Pb}_2\text{CaOsO}_6$ [5], and the unusual superconductivity in AOsO_6 ($A = \text{Cs, Rb, and K}$) [6].

The solid-state osmium oxides are noteworthy for the following two reasons. One lies in understanding the origin of the band gap inducing of the metal to insulator transition. So far, various mechanisms for explaining the band gap opening for solid-state osmium oxide compounds have been extensively considered, such as the Mott-type mechanism, the d-level splitting pattern caused by the electron correlation effect, the Slater-type mechanism, and the orbital symmetry breaking mechanism, driven by the spin–orbit coupling (SOC)

effect. As an example, the band gap opening for $\text{Cd}_2\text{Os}_2\text{O}_7$ and NaOsO_3 is explained by Slater-type insulators, which are associated with magnetic ordering [7–9].

For $\text{Ba}_2\text{NaOsO}_6$, there has been a debate on whether it is a Mott-type insulator or a SOC effect-driven insulator. In a study by Erickson et al., the nature of the insulating phase for $\text{Ba}_2\text{NaOsO}_6$ is represented as a Mott-type insulator [10,11]. Xiang et al. suggest that the insulating behavior of $\text{Ba}_2\text{NaOsO}_6$ should be developed by the simultaneous effects of electron correlation and SOC [12]. Although it is well known that the 5d-block element has considerably extended valence orbitals, resulting in weak on-site Coulomb repulsion, the magnetic insulating features of Sr_2MOsO_6 ($M = \text{Cu}$ and Ni) are reproduced with a significantly large on-site repulsion at the Os atom site [13]. Thus, it is of great importance to explore the origin of the band gap opening in solid-state osmium oxide compounds.

The other issue on solid-state osmium oxide is related to the various oxidation states of the Os ion. Osmium forms compounds with oxidation states, ranging from -2 to $+8$. As an example, the oxidation states of the Os ion in $\text{Na}_2[\text{Os}(\text{CO})]$, $\text{Na}_2[\text{Os}_4(\text{CO})_{13}]$, $\text{Os}_3(\text{CO})_{12}$, OsI , OsI_2 , OsBr_3 , OsO_2 , OsF_5 , OsF_6 , OsOF_5 , and OsO_4 are -2 , -1 , 0 , $+1$, $+2$, $+3$, $+4$, $+5$, $+6$, $+7$, and $+8$, respectively. A large spatial extension of Os at the 5d level is a main reason for the wide spectrum of oxidation states of the Os atom in osmium compounds. In general, the nd orbital of metal in the zero-oxidation state shows a spatial extension that increases in the order $3d < 4d < 5d$, so that the widths of the d-block bands should increase in the order $3d < 4d < 5d$. For this reason, 5d oxides show various valence states with the wide band widths of d-blocks. The electron correlation effects for 4d and 5d systems are weak while the effects of SOC are strong [14].

Recently, a new double perovskite osmium oxide $\text{Ba}_2\text{CuOsO}_6$ was synthesized under somewhat extreme conditions (~ 6 GPa and ~ 1800 K). The crystal structure and magnetic properties of $\text{Ba}_2\text{CuOsO}_6$ were characterized with synchrotron X-ray diffraction, thermogravimetric analysis, magnetic susceptibility, isothermal magnetization, and specific heat measurements [15]. The temperature dependence of the specific heat showed an electrically insulating behavior at all measured temperatures [15]. They also found that the $\text{Ba}_2\text{CuOsO}_6$ obeys the Curie–Weiss law with the estimated Weiss temperature -13.3 K [15]. Interestingly, a magnetic susceptibility measurement shows two T_{max} at ~ 55 K and ~ 70 K. This would be associated with two different magnetic ions in $\text{Ba}_2\text{CuOsO}_6$, which lead to more than two types of magnetic sublattice.

The $\text{Ba}_2\text{CuOsO}_6$ crystallizes in a tetragonal space group, $I4/m$, in which the valence states of the Os and Cu atoms are Os^{6+} (d^2 , $S = 1$) and Cu^{2+} (d^9 , $S = 1/2$), respectively. The Cu^{2+} and Os^{6+} ions are located on the perovskite B-site, and they form the CuO_6 and OsO_6 octahedrons, respectively. They share their corners in all crystallographic directions, such that alternating CuO_6 and OsO_6 run in all three crystallographic directions, as shown in Figure 1. The Ba^{2+} ion is located on the center of the Cu_4Os_4 cube (see Figure 1). With the structural distortion of CuO_6 and OsO_6 octahedrons from the ideal MO_6 octahedron, the Cu–O–Os bridges in the ab plane are bent, whereas those along the c direction are linear, which should be closely related with the orbital splitting and the orbital occupancy.

One can easily predict that the axial Cu–O bond is elongated by a strong Jahn–Teller distortion, associated with the electron configuration of the Cu^{2+} (d^9) ion in each CuO_6 octahedron, with two long Cu– O_{ax} bonds along the z^2 orbital direction (crystallographic c direction) and four short equatorial Cu–O bonds in the x^2-y^2 orbital locating plane (the crystallographic ab plane). Besides, in each OsO_6 octahedron, the $(t_{2g})^2$ electron configuration of the Os^{6+} ion exhibits a weak Jahn–Teller distortion, associated with spatial extension of 5d orbital (see Scheme 1). As a consequence, unlike CuO_6 octahedrons, each OsO_6 octahedron is weakly compressed in the axial direction with two short Os– O_{ax} bonds along the c direction and four elongated Os– O_{eq} bonds in the ab plane.

Figure 1. Crystal structure of $\text{Ba}_2\text{CuOsO}_6$, where blue polyhedra and yellow polyhedra and blue, yellow, pink, red, and white circles represent CuO_6 and OsO_6 units and Cu, Os, Ba, O_{eq} , and O_{ax} atoms, respectively. Perspective view of (a) ac plane and (b) ab plane. (c) Arrangement of the Ba-centered Cu_4Os_4 cube in which the Ba ion is connected by 4 O_{ax} and 8 O_{eq} atoms.

Scheme 1. The t_{2g} level splitting of Os^{6+} by the Jahn–Teller instability. It shows different types of octahedral distortion in $\text{Ba}_2\text{CuOsO}_6$ and $\text{Sr}_2\text{CuOsO}_6$.

Here, we examined the causes of several interesting and seemingly puzzling phenomena, such as the magnetic structures and the origin of the insulating phase in $\text{Ba}_2\text{CuOsO}_6$, by performing the DFT, the DFT + U, and the DFT + U + SOC electronic band structure calculations. Then, we studied the spin exchange interactions of $\text{Ba}_2\text{CuOsO}_6$ by a relative energy-mapping analysis. The magnetic properties of $\text{Ba}_2\text{CuOsO}_6$ were explained by the aspect of their orbital interactions and their spin exchange interactions. The double antiferromagnetic (AFM) anomaly at ~ 55 K and ~ 70 K of the susceptibility curve was investigated by analyzing its spin exchange interaction. Finally, we examined the reason for the insulating phase on the basis of the DFT studies and a perturbation theory analysis using $\hat{H}_{\text{SOC}}$ as perturbation.

2. Computational Details

In our DFT calculations, we employed the frozen-core, projector-augmented wave method [16,17], encoded in the Vienna ab initio simulation package (VASP) [18], and the generalized-gradient approximation of Perdew, Burke, and Ernzerhof [19], for the exchange

correlation functional, with the plane-wave cut-off energy of 450 eV and a set of 48 k-points for the irreducible Brillouin zone.

In general, the orbitals of the 5d element are much more diffuse than 3d orbitals, so the U_{Os} value is expected to be smaller than the U value of Cu. However, in Ba_2CuOsO_6 , the oxidation state of Os ion is +6, so that 5d state of Os^{6+} ion is strongly contracted. Note that the ionic size of six coordinated Cu^{2+} ions (0.870 Å) is larger than that of six coordinated Os^{6+} ions (0.685 Å) [20]. Moreover, the electronegativity of six coordinated Os^{6+} and Cu^{2+} ions are 2.362 and 1.372, respectively [21]. Thus, we use the larger U values on the Os^{6+} ion than on the Cu^{2+} ion. In our DFT calculation, we employed U value sets of $U_{Cu} = 2$, $U_{Os} = 3$ eV and $U_{Cu} = 4$, $U_{Os} = 5$ eV, respectively [22].

The measured electrical resistivity (ρ) vs. temperature of Ba_2CuOsO_6 , given in the previous study [15], shows an insulating behavior for all temperature ranges, which means that the insulating behavior of Ba_2CuOsO_6 is an intrinsic nature, not a phenomenon coupled with magnetic ordering. Additionally, Khaliullin et al. suggest that the band gap is developed from excitonic transition from singlet to triplet in the $Y_2Os_2O_7$ system [4]. The $Y_2Os_2O_7$ (Os^{4+} , d^4) belongs to the van Vleck-type Mott system, showing non-magnetic ground state, due to SOC and weak temperature dependence, such as uniform magnetic susceptibility above Neel temperature. However, magnetic susceptibility curve in Ba_2CuOsO_6 showed Curie–Weiss behavior over a broad temperature range [15], implying that it is not a case of suppressed effective magnetic moment by SOC. Thus, we considered the ferromagnetic (FM) state of Ba_2CuOsO_6 in our DFT + U + SOC calculation, even though this system undergoes the antiferromagnetic ordering. In order to find proper U value set for reproducing the insulating state of Ba_2CuOsO_6 , we perform systematic DFT + U + SOC calculations with various U value sets. However, all U sets failed to reproduce the insulating state of Ba_2CuOsO_6 except U value set of $U_{Cu} = 4$ and $U_{Os} = 5$ eV (see Table S1 and Figure S1). Thereby, we carried out the DFT + U + SOC calculation with the U value set of $U_{Os} = 5$ and $U_{Cu} = 4$ eV for understanding the origin of the insulating behavior on Ba_2CuOsO_6 .

3. Spin Exchange Interaction and Spin Lattice

In understanding the magnetic structure of Ba_2CuOsO_6 , it is important to inspect its local structure and its following spin exchange paths. Figure 2 shows eight possible spin exchange paths of Ba_2CuOsO_6 . There are three spin exchanges between Cu ions, three spin exchanges between Os ions, and two Cu–Os spin exchanges. The J_1 and J_2 are the superexchange (SE) type, involving the Cu–O–Os path, while the J_3 – J_8 are super-superexchange (SSE), involving M–O···M–O exchange path (M = Cu or Os). The J_1 , J_3 , J_4 , J_7 , and J_8 exchanges are ab plane interactions and the J_2 , J_5 , and J_6 exchanges are interactions between ab planes. The geometrical parameters associated with these paths are listed in Table 1.

Figure 2. The considered spin exchange paths J_1 – J_8 of the Ba_2CuOsO_6 : (a) projection view of an isolated $\parallel ab$ layer of corner-sharing CuO_6 and OsO_6 octahedrons, in which the Cu–O–Os linkage is bent. (b) Perspective view of two $\parallel ab$ layers of corner-sharing CuO_6 and OsO_6 octahedrons. The blue, yellow, red, and white circles represent the Cu, Os, O_{eq} , and O_{ax} atoms, respectively. Red arrows with 1–8 numbering refer to spin exchange paths of J_1 – J_8 , respectively.

Table 1. Geometrical parameters associated with the exchange paths J_1 – J_8 in $\text{Ba}_2\text{CuOsO}_6$; distance (Å); angle ($^\circ$).

			M-M	Cu-O	Os-O	O-O	$\angle\text{Cu-O-Os}$	$\angle\text{M-O-O-M}$
J_1	Cu-Os	ab plane	3.937	1.986	1.960		172.6	
J_2	Cu-Os	c-axis	4.256	2.31	1.946		180	
J_3	Cu-Cu	ab plane	5.568	1.986 ($\times 2$)		2.771 ($\times 2$)		127.6142.4
J_4	Os-Os	ab plane	5.568		1.960	2.808		127.6142.4
J_5	Cu-Cu	ac	5.798	1.986 2.310		2.762 ($\times 2$)		134.7134.8
J_6	Os-Os	ac	5.798			3.047 ($\times 2$)		
J_7	Cu-Cu	ab plane	7.874					
J_8	Os-Os	ab plane	7.874					

Let us examine the relationship between the spin exchange interactions J_1 – J_8 and the structural parameters associated with their exchange pathways and the spin exchange interactions in a viewpoint of orbital interaction. As mentioned, the CuO_6 and OsO_6 octahedrons are distorted from regular MO_6 octahedrons. The nature of distortion should be explained by the crystal field effect, the Jahn–Teller instability, and the different magnitude of interaction between the Ba^{2+} ion and the MO_6 ($\text{M} = \text{Os}$, and Cu) octahedron. The distortion of the CuO_6 and OsO_6 octahedrons plays an important role in the nature and the strength of the spin exchanges. The CuO_6 octahedron is axially elongated and the OsO_6 octahedron is axially shrunk by the Jahn–Teller instability. Thus, the d-orbital sequence of Cu^{2+} ion is $xz, yz < xy < z^2 < x^2-y^2$ and the d-orbital splitting of Os^{6+} ion is $xy < xz, yz < x^2-y^2 < z^2$. As depicted in Figure 3a,b, the magnetic orbitals of Cu^{2+} ion and Os^{6+} are singly occupied x^2-y^2 orbital and two orbitals of three t_{2g} orbitals, respectively. The structural parameters are listed in Table 1. The $\angle\text{Cu-O-Os}$ angle in J_1 path is close to 180° (172.6°), so the J_1 exchange should be strong FM, because of orthogonality between $\text{Cu } x^2-y^2$ and $\text{Os } t_{2g}$ orbitals, according to Goodenough’s rule [23]. In the J_2 exchange, the Cu-O and Os-O bonds of the Cu-O-Os linkage does not contain magnetic orbitals and the $\angle\text{Cu-O-Os}$ angle is 180° . Thus, the Cu^{2+} ion and the Os^{6+} ion in the J_2 exchange do not interact. The J_2 exchange interaction should be a very weak interaction. The J_3 exchange is unsymmetrical and the $\angle\text{Cu-O}\cdots\text{O-Cu}$ angles are 127.6 and 142.4° , which contain magnetic orbitals, indicating possible good orbital overlap between Cu^{2+} ions (see Figure 3d). Thus, we expect that J_3 should be AFM. The geometrical structure of J_4 exchange is almost identical to that of the J_3 exchange. However, the J_4 exchange contains two magnetic orbitals, indicating multiple channel spin exchange interactions, suggesting a presence of a strong orbital overlap via the $\text{Os-O}\cdots\text{O-Os}$ linkage (Figure 2a). The J_4 spin exchange should have strong AFM because the two magnetic orbitals of the t_{2g} orbitals can overlap across their $\text{O}\cdots\text{O}$ contacts, as shown in Figure 3e. The J_5 and J_6 exchanges are the interactions between the adjacent ab layers, and the $\text{O}\cdots\text{O}$ contact distances of the SSE path J_5 and J_6 are $4.264 \text{ \AA}$. The M-O bonds of the $\text{M-O}\cdots\text{O-M}$ linkage are not located in the magnetic orbital plane. One can predict that the magnetic interaction of J_5 and J_6 exchange path is negligibly weak.

The $\angle\text{M-O}\cdots\text{O-M}$ angles of the SE paths J_7 and J_8 are close to 180° (172.6°) and the M-O bond of $\text{M-O}\cdots\text{M-O}$ linkage contains a magnetic orbital. Thus, the spin exchange interaction J_7 and J_8 should have strong AFM. However, the magnitude of the J_7 spin exchange is much stronger than that of J_8 . It is due to the fact that the orbital interaction in the J_7 exchange is a π -type orbital interaction, while the orbital interaction in J_8 is a σ -type orbital interaction, as shown in Figure 3f,g.

Figure 3. (a) The $d_{x^2-y^2}$ magnetic orbitals of the Cu^{2+} ion; (b) the t_{2g} -type magnetic orbitals of the Os^{6+} ion; (c–g) the magnetic orbital interaction of J_1 , J_3 , J_4 , J_7 , and J_8 exchange paths in $\text{Ba}_2\text{CuOsO}_6$.

We extracted the spin exchange interactions using the DFT + U + SOC calculation to elucidate our analysis of the spin exchange interactions in terms of the local geometrical structure and the orbital interaction analysis. To extract the values for the J_1 – J_8 exchanges, we carried out a total energy calculation of the nine ordered spin configurations of $\text{Ba}_2\text{CuOsO}_6$, shown in Figure 4. To obtain the values of J_1 – J_8 , we determined the relative energies of the abovementioned cases obtained from the DFT + U + SOC calculations with $U_{\text{Cu}} = 2$, $U_{\text{Os}} = 3$ eV and $U_{\text{Cu}} = 4$, $U_{\text{Os}} = 5$ eV. The relative energies of various AFM cases obtained are summarized in Figure 4. In terms of the spin Hamiltonian $\hat{H} = -\sum_{i<j} J_{ij} \hat{S}_i \cdot \hat{S}_j$, where $J_{ij} = J_1$ – J_8 , the total spin exchange energies of these states per formula units (FUs) are expressed as follows:

$$E_{\text{spin}} = (n_1 J_1)(MN/4) + n_2 J_2(MN/4) + n_3 J_3(M^2/4) + n_4 J_4(N^2/4) + n_5 J_5(M^2/4) + n_6 J_6(N^2/4) + n_7 J_7(M^2/4) + n_8 J_8(N^2/4) \quad (1)$$

by using the energy expressions obtained for spin dimers with M and N unpaired spins per spin site (here, $M(\text{Cu}^{2+}) = 1$ and $N(\text{Os}^{6+}) = 2$) [24]. The values of n_1 – n_8 for the eight ordered spin states, FM, and AF1–AF8, are described in Table S2.

Thus, by mapping the relative energies of the nine spin arrangements presented in Figure 2 onto corresponding energies expected from Equation (1), we obtain J_1 – J_8 , as summarized in Table 2.

Figure 4. Spin arrangements in the FM and AF1–AF8 states of $\text{Ba}_2\text{CuOsO}_6$ to evaluate the J_1 – J_8 values where the filled yellow, empty yellow, filled blue, and empty blue circles refer to spin-up Os^{6+} , and spin-down Os^{6+} , spin-up Cu^{2+} , and spin-down Cu^{2+} sites, respectively. In each state, the two //ab layers with the given ordered spin arrangements alternate along the c direction. The numbers in the parentheses refers to the relative energies associated with their FM state (in meV/FU), which was obtained from the DFT + U + SOC calculations with $U_{\text{Cu}} = 2$, $U_{\text{Os}} = 3$ eV and $U_{\text{Cu}} = 4$, $U_{\text{Os}} = 5$ eV.

Table 2. Values of the spin exchanges J_1 – J_8 (in k_BK) of $\text{Ba}_2\text{CuOsO}_6$ obtained from the DFT + U + SOC calculations with $U_{\text{Cu}} = 2$, $U_{\text{Os}} = 3$ eV and $U_{\text{Cu}} = 4$, $U_{\text{Os}} = 5$ eV.

			M-M (Å)	$U_{\text{Cu}} = 2$, $U_{\text{Os}} = 3$	$U_{\text{Cu}} = 4$, $U_{\text{Os}} = 5$
J_1	Cu-Os	ab plane	3.937	92.1	112.0
J_2	Cu-Os	c-axis	4.256	−20.0	1.4
J_3	Cu-Cu	ab plane	5.568	−81.0	−79.4
J_4	Os-Os	ab plane	5.568	−120.9	−247.5
J_5	Cu-Cu	ac	5.798	3.3	−4.2
J_6	Os-Os	ac	5.798	18.7	7.4
J_7	Cu-Cu	ab plane	7.874	−190.8	−291.2
J_8	Os-Os	ab plane	7.874	−24.4	−98.7

The determined spin exchange interactions, based on the DFT + U + SOC calculation ($U = 4$ and 5 eV for Cu and Os), show that the relative strength of the spin exchange interactions associated with their strongest interaction, J_7 , are $|J_1| \approx 0.385 |J_7|$, $|J_2| \approx 0.005 |J_7|$, $|J_3| \approx 0.283 |J_7|$, $|J_4| \approx 0.850 |J_7|$, $|J_5| \approx 0.015 |J_7|$, $|J_6| \approx 0.025 |J_7|$, and $|J_8| \approx 0.339 |J_7|$, respectively. This suggests that the magnetic property of $\text{Ba}_2\text{CuOsO}_6$ is mainly governed by J_1 , J_3 , J_4 , J_7 , and J_8 exchanges, in which all of them are AFM except J_1 . The J_1 exchange is an FM interaction, as expected in the previous section. The J_4 and J_7 spin exchanges are much stronger than others. As a consequence, the magnetic property of the $\text{Ba}_2\text{CuOsO}_6$ system mainly comes from the J_4 and J_7 spin exchange interactions, which would deduce the existence of magnetic sublattice. In addition, the observed phenomena

of two $T_{\max}$ at ~55 K and ~70 K in susceptibility measurement would support such a possibility of magnetic sublattice [15]. The presence of two different magnetic ions in $\text{Ba}_2\text{CuOsO}_6$ system should be related with the double AFM-like anomaly at ~55 K and ~70 K. We roughly obtained Neel temperature T_N using a mean field approximation with the extracted spin exchange interactions, based on the DFT + U + SOC calculation ($U_{\text{Cu}} = 4$ and $U_{\text{Os}} = 5$ eV). The calculated Neel temperatures for the Cu^{2+} ion and Os^{6+} ion sublattices are 256 K and 297 K, respectively. The expected T_N for the Cu and Os sublattices is largely overestimated. The overestimation of the calculated T_N is comprehensible because it is well known that the DFT calculations generally overestimate the magnitude of spin exchange interactions by a factor of, approximately, up to four [25–28].

Although there is a possibility of spin frustration occurred by (J_1, J_1, J_7) , (J_1, J_1, J_8) , (J_1, J_1, J_3) , (J_1, J_1, J_4) , (J_3, J_3, J_7) , and (J_4, J_4, J_8) triangles, it does not occur due to the fact that the strong J_4 and J_7 exchanges are forced to avoid spin frustration. This is in good agreement with the experimental result, in which the spin frustration factor ($f = |\theta| / |T_N|$) is just ~0.24, and there is no divergence between the zero-field and field susceptibility curves in $\text{Ba}_2\text{CuOsO}_6$ indicating the absence of spin frustration [15]. For a spin frustrated magnetic system, it is generally expected that the ratio, $f = |\theta| / |T_N|$, is greater than 6 [29–31]. The spin frustration factor f -value for $\text{Ba}_2\text{CuOsO}_6$ system is much lower than this critical value. Thus, the low f -value suggests that the spin frustration is very weak or does not occur in $\text{Ba}_2\text{CuOsO}_6$, despite its similar system ($\text{Sr}_2\text{CuOsO}_6$, $\text{Sr}_2\text{CuIrO}_6$) [32,33] showing strong spin frustration.

In summary, the overall magnetic property of the $\text{Ba}_2\text{CuOsO}_6$ system should be explained by AFM, and it does not show spin frustration.

4. Describing the Magnetic Insulating Behavior of $\text{Ba}_2\text{CuOsO}_6$

As mentioned in the introduction section, the $\text{Ba}_2\text{CuOsO}_6$ system is a magnetic insulator. Feng et al. [15] measured the temperature dependence of resistivity ρ of polycrystalline $\text{Ba}_2\text{CuOsO}_6$, in which it showed an insulating behavior at all measured temperature ranges. This reveals that the insulating behavior of $\text{Ba}_2\text{CuOsO}_6$ is an intrinsic nature, not a phenomenon coupled with magnetic ordering.

Although they mentioned the origin of the band gap in terms of a theoretical approach, they did not show evidence as well as a discussion for opening the band gap. Here, we discuss the origin of the insulating state of $\text{Ba}_2\text{CuOsO}_6$. The calculated electronic structures for $\text{Ba}_2\text{CuOsO}_6$ are presented in Figures 5 and 6. The main distribution near the Fermi level comes from the Os^{6+} ion rather than the Cu^{2+} ion, which connotes that the Os^{6+} 5d states are mainly concerned with the insulating behavior of $\text{Ba}_2\text{CuOsO}_6$ (see Figure 5b,c).

For $\text{Sr}_2\text{CuOsO}_6$, it should be required to use larger Hubbard value on the Os atom than usual in realizing the magnetic insulating state [13]. Each OsO_6 octahedron with axially elongated OsO_6 octahedron (i.e., $\text{Os-O}_{\text{ax}} = 1.928 (\times 2) \text{ \AA}$, $\text{Os-O}_{\text{eq}} = 1.888 (\times 4) \text{ \AA}$) appears slightly distorted, compared with the CuO_6 octahedron, caused by a weak Jahn–Teller instability. Therefore, the Os 5d state of axially elongated OsO_6 octahedron is split into four states ($xz, yz < xy < z^2 < x^2 - y^2$) by the Jahn–Teller distortion. Two t_{2g} electrons in the Os^{6+} ion are now occupied to the degeneracy-lifted xz and yz states (see Scheme 1). The band gap is then created by the energy difference between occupied (xz, yz) and unoccupied states (xy). The large Hubbard U value, which enhances the electron correlation effect, is enough to describe the insulating behavior of $\text{Sr}_2\text{CuOsO}_6$. On the other hand, each OsO_6 of $\text{Ba}_2\text{CuOsO}_6$ has an axially shrunk octahedron, indicating the different types of Os 5d state splitting with $\text{Sr}_2\text{CuOsO}_6$. The Os 5d state of $\text{Ba}_2\text{CuOsO}_6$ is split into four states ($xy < xz, yz < x^2 - y^2 < z^2$). However, the Os 5d state splitting of $\text{Ba}_2\text{CuOsO}_6$ is very weak compared to that of $\text{Sr}_2\text{CuOsO}_6$, as shown in the Scheme 1 and Figure 5c. Split Os 5d state of $\text{Ba}_2\text{CuOsO}_6$ is presented in Figure 5c, in terms of the projected DOS, which shows that the t_{2g} level of the Os 5d state is very weakly separated into the two states. In the $(t_{2g})^2$ electron of the Os^{6+} , one electron is occupied in the lowest xy state, and the remaining electron is occupied in doubly degenerated xz and yz states, as depicted in Scheme 1. Thus, one can predict

that the simple DFT and DFT + U approaches are insufficient to describe the magnetic insulating behavior of $\text{Ba}_2\text{CuOsO}_6$. The crucial key to describing the insulating behavior of $\text{Ba}_2\text{CuOsO}_6$ is in splitting the degenerate xz and yz states of the Os^{6+} ion. The SOC effect splits the t_{2g} state into three substates by the orbital symmetry breaking. Thus, one can speculate that the SOC effect should play an important role in describing the insulating behavior of $\text{Ba}_2\text{CuOsO}_6$, thereby it is necessary to consider the SOC effect.

Figure 5. (a) Total density of states calculated for FM state of $\text{Ba}_2\text{CuOsO}_6$ obtained from DFT, DFT + U, and DFT + SOC calculations with $U_{\text{Cu}} = 4$ eV, $U_{\text{Os}} = 5$ eV. Projected density of state plots for (b) Cu 3d orbitals and (c) Os 5d orbitals obtained from DFT + U calculation with $U_{\text{Cu}} = 4$ eV, $U_{\text{Os}} = 5$ eV for the FM state of $\text{Ba}_2\text{CuOsO}_6$. The spin-up and spin-down states are presented by positive and negative sign in the y-axis, respectively.

Figure 6. Band structures calculated for $\text{Ba}_2\text{CuOsO}_6$ using different methods with U value set of $U_{\text{Cu}} = 4$ eV, $U_{\text{Os}} = 5$ eV. (a) DFT + SOC, (b) DFT + U + SOC. In (a), red and blue colors refer to the spin-up and spin-down bands, respectively.

Moreover, since the Os atom belongs to a heavy element group, the SOC effect should be expected to have a dramatically strong effect on the electronic structure of Ba₂CuOsO₆.

The spin–orbital part of the Hamiltonian in the Os sphere is then given by the following:

$$\hat{H}_{SOC} = \lambda \hat{S} \cdot \hat{L} \quad (2)$$

where the SOC constant $\lambda > 0$ for the Os⁶⁺ (d²) ion, with less than half-filled t_{2g} levels. With θ and φ as the azimuthal and polar angles of the magnetization in the rectangular crystal coordinate system, respectively, the $\hat{L}$ and $\hat{S}$ terms are rewritten [34,35] as follows:

$$\begin{aligned} \hat{H}_{soc} = & \lambda \hat{S}_z' \left(\hat{L}_z \cos \theta + \frac{1}{2} \hat{L}_+ e^{-i\varphi} \sin \theta + \frac{1}{2} \hat{L}_- e^{i\varphi} \sin \theta \right) \\ & + \frac{\lambda}{2} \hat{S}_+' \left(-\hat{L}_z \sin \theta - \hat{L}_+ e^{-i\varphi} \sin^2 \frac{\theta}{2} + \hat{L}_- e^{i\varphi} \cos^2 \frac{\theta}{2} \right) \\ & + \frac{\lambda}{2} \hat{S}_-' \left(-\hat{L}_z \sin \theta + \hat{L}_+ e^{-i\varphi} \cos^2 \frac{\theta}{2} - \hat{L}_- e^{i\varphi} \sin^2 \frac{\theta}{2} \right) \end{aligned} \quad (3)$$

Since the spin-up and spin-down t_{2g} states are separated by the exchange splitting in the first order approximation, there is no need to consider interactions between different spin-up and -down states in SOC. Thus, one simply needs to consider only spin-up parts of t_{2g} states in using the degenerate perturbation theory, which requires calculation of the matrix elements $i|\hat{H}_{so}|j$ ($i, j = xy, yz, xz$) [6]. For that reason, only the S_z operator term, as in the first line of Equation (3), brings about non-zero matrix elements. In evaluating these matrix elements, it is convenient to rewrite the angular parts of the xy , yz , and xz orbitals in terms of the spherical harmonics [12], as follows:

$$\begin{aligned} d_{xy} &= \frac{-i}{\sqrt{2}} (Y_2^2 - Y_2^{-2}) \\ d_{yz} &= \frac{i}{\sqrt{2}} (Y_2^1 + Y_2^{-1}) \\ d_{xz} &= \frac{-1}{\sqrt{2}} (Y_2^1 - Y_2^{-1}) \end{aligned} \quad (4)$$

Using these functions, the matrix representation elements $i|\hat{H}_{so}|j$ ($i, j = xy, yz, xz$) are found as follows:

$$\frac{i\hbar\lambda}{2} \begin{pmatrix} 0 & \sin\theta\sin\varphi & -\sin\theta\sin\varphi \\ -\sin\theta\sin\varphi & 0 & \cos\theta \\ \sin\theta\cos\varphi & -\cos\theta & 0 \end{pmatrix} \quad (5)$$

By the diagonalization of Equation (5), we obtain eigenvalues of the three spin–orbit coupled states, $E_1 = -\hbar\lambda/2$, $E_2 = 0$, and $E_3 = \hbar\lambda/2$. The associated eigenfunctions ψ_1 , ψ_2 , and ψ_3 are given [12,34,35] by the following:

$$\begin{aligned} \psi_1 &= \frac{\sqrt{2}}{2} [\sin\theta d_{xy} + (i\sin\varphi - \cos\theta\cos\varphi)d_{yz} - (i\cos\varphi + \cos\theta\sin\varphi)d_{xz}] \\ \psi_2 &= \frac{\sqrt{2}}{2} [\sin\theta d_{xy} - (i\sin\varphi + \cos\theta\cos\varphi)d_{yz} + (i\cos\varphi - \cos\theta\sin\varphi)d_{xz}] \\ \psi_3 &= \cos\theta d_{xy} + \sin\theta\cos\varphi d_{yz} + \sin\theta\sin\varphi d_{xz} \end{aligned} \quad (6)$$

The above analysis indicates that the SOC effect splits the t_{2g} states into three substates by orbital symmetry breaking. For the Os⁶⁺ (d²) ion, two electrons of t_{2g} state should occupy ψ_1 and ψ_2 . Therefore, the band gap around the Fermi level should be developed in between the occupied ψ_2 and the unoccupied ψ_3 state.

To elucidate the above discussion, we carried out calculations to reproduce the insulating state of Ba₂CuOsO₆ by employing different theoretical methods, namely, simple DFT, DFT + U ($U_{Cu} = 4$, $U_{Os} = 5$ eV), and DFT + SOC methods, but all of them failed to reproduce the insulating behavior for Ba₂CuOsO₆ (see Figure 5a). Metallic electronic structures obtained from the DFT and the DFT + U calculations are already expected because the exchange splitting is not enough condition to open the band gap in Ba₂CuOsO₆. However, the electronic structure obtained from the DFT + SOC still failed to reproduce the insulating behavior for Ba₂CuOsO₆ (See Figure 5a). Presented in Figure 3a, the spin-up and spin-down bands are overlapped, which leads to a metallic state for Ba₂CuOsO₆.

This means that not only the breaking of orbital symmetry by adapting the SOC effect, but also the separation of energy between the filled level (spin-up) and the empty level (spin-down) by increasing exchange splitting, should be required to describe the insulating state of $\text{Ba}_2\text{CuOsO}_6$. On-site repulsion, which properly describes the electron correlation effect, gives help to enhance the exchange splitting; thereby, the energy separation between the filled and the unfilled states within each spin channel is increased. Thus, the on-site repulsion should be also a crucial key to be considered in explaining the insulating state of $\text{Ba}_2\text{CuOsO}_6$.

To gain insight into this analysis, we carried out the band structure calculation, considering the electron correlation and the SOC effect simultaneously. The band structure calculated for the FM state of $\text{Ba}_2\text{CuOsO}_6$ using the DFT + U + SOC ($U_{\text{eff}} = 4$ and 5 eV on Cu and Os) is shown in Figure 6b. Indeed, the calculated electronic structure clearly shows an insulating band gap. In consequence, the interplay between the electron correlation and the SOC effect plays an essential role in opening a band gap for $\text{Ba}_2\text{CuOsO}_6$.

Meanwhile, there remains one question about the origin of the band gap opening in $\text{Ba}_2\text{CuOsO}_6$. The insulating behavior of $\text{Ba}_2\text{CuOsO}_6$ is intimately linked with the structural distortion of the OsO_6 octahedron. We remind that the OsO_6 octahedron for $\text{Ba}_2\text{CuOsO}_6$ is an axially compressed octahedral shape, while the OsO_6 octahedron of $\text{Sr}_2\text{CuOsO}_6$ is an axially elongated octahedral shape. This implies that they undergo different types of structural distortion by the Jahn–Teller instability, which leads to different orbital splitting at the $\text{Os}^{6+} t_{2g}$ level. Thus, they show different chemical and physical properties, especially in explaining the mechanism of band gap opening. The only difference between $\text{Sr}_2\text{CuOsO}_6$ and $\text{Ba}_2\text{CuOsO}_6$ is an ionic size of the A-site ion, namely, the ionic size of the Ba^{2+} ion is larger than that of the Sr^{2+} ion. In A_2CuOsO_6 ($\text{A} = \text{Sr}$ and Ba), the A-site ion is located in the center of Cu_4Os_4 distorted cubes and distorted $(\text{O}_{\text{ax}})_4$ squares, presented in Figure 1c. It is connected with 8 O_{eq} and 4 O_{ax} atoms to form a 12-coordinate AO_{12} (see Figure 1c). In A_2CuOsO_6 , a change in the A– O_{eq} distance affects a, b, and c lattice parameters symmetrically; whereas, a change of A– O_{ax} distance affects the lattice parameter a (=b). Assuming that the increase of the A– O_{ax} distance leads to structural distortion forming axially shrunk type- OsO_6 octahedrons, by increasing the Os– O_{eq} distance in the ab plane, while the decrease of the A– O_{ax} distance causes structural distortion to have axially elongated OsO_6 octahedrons by decreasing the Os– O_{eq} distance. The A– O_{ax} distance should be mainly dominated by the ionic size of the A-site ion. Since the ionic size of the Ba^{2+} ion is larger than that of the Sr^{2+} ion, the Ba– O_{ax} distance is longer than the Sr– O_{ax} distance, which gives rise to a much longer Os– O_{eq} distance on $\text{Ba}_2\text{CuOsO}_6$, associated with the expansion of its lattice parameter a (=b). On the other hand, the effect of ionic size of the A-site on the change of the Os– O_{ax} distance is relatively insignificant. Indeed, the Os– O_{eq} distances in $\text{Ba}_2\text{CuOsO}_6$ and $\text{Sr}_2\text{CuOsO}_6$ are 1.960 and 1.888 Å, respectively, while the Os– O_{ax} distances in $\text{Ba}_2\text{CuOsO}_6$ and $\text{Sr}_2\text{CuOsO}_6$ are 1.928 Å and 1.946 Å, respectively [15,33]. Hence, the ionic size of the A-site ion should play an important role in determining the shape of the OsO_6 octahedron in A_2CuOsO_6 .

To verify the importance of the ionic size effect, we examine the aforementioned questions with the DFT + U + SOC ($U_{\text{Cu}} = 4$, $U_{\text{Os}} = 5$ eV) calculation for $\text{Ba}_2\text{CuOsO}_6$. We imagine the hypothetical compounds of A_2CuOsO_6 ($\text{A} = \text{Sr}$, Ca) by replacing the Ba atoms of $\text{Ba}_2\text{CuOsO}_6$ with other alkali earth atoms—Sr and Ca. A_2CuOsO_6 ($\text{A} = \text{Ba}$, Sr , and Ca) are fully optimized with the DFT + U + SOC ($U_{\text{Cu}} = 4$, $U_{\text{Os}} = 5$ eV) calculation. The optimized atomic positions and cell parameters are presented in the Supplementary Materials, Table S3. Results show that the lattice parameters decrease gradually with the decreasing ionic size of the A-site ion, but the decreasing of the a lattice parameter is greater than that of the c lattice parameter, which means that each Os– O_{eq} distance is increased as the A-site ionic size increases. Therefore, the cooperative effect of the A-site ionic size and the Jahn–Teller distortion, is responsible not only for the axially compressed OsO_6 octahedrons in $\text{Ba}_2\text{CuOsO}_6$ but also for the axial elongation of OsO_6 octahedrons in

$\text{Sr}_2\text{CuOsO}_6$; this is closely related to the description of the insulating behavior of A_2CuOsO_6 ($\text{A} = \text{Ba}, \text{Sr}, \text{and Ca}$).

5. Concluding Remarks

The magnetic structure and the origin of the band gap opening for $\text{Ba}_2\text{CuOsO}_6$ are investigated by exploring the spin exchange interactions and analyzing the spin–orbit coupling effect. The magnetic property of $\text{Ba}_2\text{CuOsO}_6$ is explained by AFM, and it does not show spin frustration caused by the strong AFM interactions of J_4 and J_7 . The structural distortion shape of the OsO_6 octahedron, which should be closely connected with the ionic size of the A-site ion, is an important factor in understanding the insulating behavior of $\text{Ba}_2\text{CuOsO}_6$. Each OsO_6 octahedron of $\text{Sr}_2\text{CuOsO}_6$ displays an axially elongated octahedral shape, while each OsO_6 octahedron of $\text{Ba}_2\text{CuOsO}_6$ exhibits an axially compressed octahedral shape, which is caused by an ionic size effect of the A-site ion. Therefore, the t_{2g} level splitting of the Os^{6+} ions of $\text{Ba}_2\text{CuOsO}_6$ and $\text{Sr}_2\text{CuOsO}_6$ by the Jahn–Teller instability is differently depicted in Scheme 1. Consequently, to explain the magnetic insulating states of $\text{Sr}_2\text{CuOsO}_6$, which are isostructural and isoelectronic in $\text{Ba}_2\text{CuOsO}_6$, it is necessary to properly employ an electron correlation effect. On the other hand, a cooperative effect of electron correlation and spin–orbit coupling is essential in describing the insulating behavior of $\text{Ba}_2\text{CuOsO}_6$, which is highly related with the t_{2g} orbital splitting of the Os^{6+} ion.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/nano12010144/s1>, Table S1: The expected electronic properties for various U sets obtained from DFT+U+SOC calculation, Table S2: Values of the coefficients n_1 – n_8 of Equation (1) for the nine ordered spin states (FM and AF1–AF8) to extract spin exchange interaction J_1 – J_8 , Table S3: The optimized structural parameters of A_2CuOsO_6 ($\text{A} = \text{Ba}, \text{Sr}, \text{and Ca}$) obtained from the DFT + U + SOC ($U_{\text{Cu}} = 4$, $U_{\text{Os}} = 5$ eV). Space group $I4/m$ (#87). A is at site (0, 0.5, 0.25), Cu at (0, 0, 0), Os at (0, 0, 0.5), Oab at (x, y, 0) and Oc at (0, 0, z), Figure S1: Total density of states in $\text{Ba}_2\text{CuOsO}_6$ calculated by DFT+U+SOC. U values for Cu and Os in this DOS calculation are chosen as (a) $U_{\text{Cu}} = 4$ eV, $U_{\text{Os}} = 5$ eV, (b) $U_{\text{Cu}} = 5$ eV, $U_{\text{Os}} = 4$ eV, (c) $U_{\text{Cu}} = 3$ eV, $U_{\text{Os}} = 4$ eV, and (d) $U_{\text{Cu}} = 2$ eV, $U_{\text{Os}} = 3$ eV.

Author Contributions: T.P. and C.L. conceived the overall idea. T.P. and C.L. performed the electronic structure calculations and the analysis. All authors discussed the results and co-wrote the manuscript and commented on the paper. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2017R1D1A1B03036257, 2020R1A5A1019141, 2021R1F1A1063478), the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (No. 2020R1F1A1052898, 2020M3H4A2084418).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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