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Magnetic Structure and Origin of Insulating Behavior in the Ba$_2$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 Ba$_2$CuOsO$_6$ were investigated by exploring the spin exchange interactions and employing the spin–orbit coupling effect. It revealed that the double-perovskite Ba$_2$CuOsO$_6$, composed of the 3d (Cu$^{2+}$) and 5d (Os$^{6+}$) transition metal magnetic ions is magnetic insulator. The magnetic susceptibilities of Ba$_2$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 Ba$_2$CuOsO$_6$ system. An important factor to understand regarding the insulating behavior on Ba$_2$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$^{6+}$ ($d^3$) ions of Ba$_2$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 Ba$_2$CuOsO$_6$. By orbital symmetry breaking, caused by the spin–orbit coupling, the $t_{2g}$ level of Os$^{6+}$ ($d^3$) is separated into three sublevels. Two electrons of Os$^{6+}$ ($d^3$) occupy two levels of the three spin-orbit-coupled levels. Since Ba$_2$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 Ba$_2$CuOsO$_6$.

Keywords: magnetic structure; BaOsCuO$_6$; SOC effect; magnetic insulating behavior; orbital interaction

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 Ba$_3$NiOsO$_6$ [1], the singlet ground-state excitonic magnetism in Y$_2$OsO$_7$ [2–4], the spin-driven metal to insulator transition in Pb$_2$CaOsO$_6$ [5], and the unusual superconductivity in AOsO$_5$ (A = 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 Cd₂Os₂O₇ and NaOsO₃ is explained by Slater-type insulators, which are associated with magnetic ordering [7–9].

For Ba₂NaOsO₆, 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 Ba₂NaOsO₆ is represented as a Mott-type insulator [10,11]. Xiang et al. suggest that the insulating behavior of Ba₂NaOsO₆ 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 Sr₂MOsO₆ (M = 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 Na₂[Os(CO)]₆, Na₂[Os₄(CO)₁₃], Os₅₃(CO)₁₂, OsI, OsI₂, OsBr₃, OsO₂, OsF₅, OsF₆, OsOF₅, and OsO₄ 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 Ba₂CuOsO₆ was synthesized under somewhat extreme conditions (~6 GPa and ~1800 K). The crystal structure and magnetic properties of Ba₂CuOsO₆ 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 Ba₂CuOsO₆ obeys the Curie–Weiss law with the estimated Weiss temperature −13.3 K [15]. Interestingly, a magnetic susceptibility measurement shows two Tₘₐₓ at ~55 K and ~70 K. This would be associated with two different magnetic ions in Ba₂CuOsO₆, which lead to more than two types of magnetic sublattice.

The Ba₂CuOsO₆ crystallizes in a tetragonal space group, I₄/m, in which the valence states of the Os and Cu atoms are Os⁶⁺ (d⁶, S = 1) and Cu²⁺ (d⁹, S = 1/2), respectively. The Cu²⁺ and Os⁶⁺ ions are located on the perovskite B-site, and they form the CuO₆ and OsO₆ octahedrons, respectively. They share their corners in all crystallographic directions, such that alternating CuO₆ and OsO₆ run in all three crystallographic directions, as shown in Figure 1. The Ba²⁺ ion is located on the center of the CuO₄Os₄ cube (see Figure 1). With the structural distortion of CuO₆ and OsO₆ octahedrons from the ideal MO₆ 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 Cu²⁺ (d⁹) ion in each CuO₆ octahedron, with two long Cu-Oₐx bonds along the z² orbital direction (crystallographic c direction) and four short equatorial Cu-O bonds in the x²−y² orbital locating plane (the crystallographic ab plane). Besides, in each OsO₆ octahedron, the (t₂g)² electron configuration of the Os⁶⁺ ion exhibits a weak Jahn–Teller distortion, associated with spatial extension of 5d orbital (see Scheme 1). As a consequence, unlike CuO₆ octahedrons, each OsO₆ octahedron is weakly compressed in the axial direction with two short Os-Oₐx bonds along the c direction and four elongated Os-Oeq bonds in the ab plane.
In understanding the magnetic structure of Ba$_2$CuOsO$_6$, it is important to inspect its local structure and its following spin exchange paths. Figure 2 shows eight possible spin configurations of the Cu$^{2+}$ ions, which are connected by Os$^{6+}$ ions.

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 Ba$_2$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 Ba$_2$CuOsO$_6$ by a relative energy-mapping analysis. The magnetic properties of Ba$_2$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 $H_{soc}$ 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

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**Figure 1.** Crystal structure of Ba$_2$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$_4$Os$_4$ 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 Ba$_2$CuOsO$_6$ and Sr$_2$CuOsO$_6$.

Axially elongated OsO$_6$  
Axially shrank OsO$_6$  

SOC

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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$_2$CuOsO$_6$, 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$_2$CuOsO$_6$, given in the previous study [15], shows an insulating behavior for all temperature ranges, which means that the insulating behavior of Ba$_2$CuOsO$_6$ is an intrinsic nature, not a phenomenon coupled with magnetic ordering. Additionally, Khalilullin et al. suggest that the band gap is developed from excitonic transition from singlet to triplet in the Y$_2$Os$_2$O$_7$ system [4]. The Y$_2$Os$_2$O$_7$ (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$_2$CuOsO$_6$ 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$_2$CuOsO$_6$ 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$_2$CuOsO$_6$, we perform systematic DFT + U + SOC calculations with various U value sets. However, all U sets failed to reproduce the insulating state of Ba$_2$CuOsO$_6$ 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$_2$CuOsO$_6$.

3. Spin Exchange Interaction and Spin Lattice

In understanding the magnetic structure of Ba$_2$CuOsO$_6$, it is important to inspect its local structure and its following spin exchange paths. Figure 2 shows eight possible spin exchange paths of Ba$_2$CuOsO$_6$. 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](image-url)  
Figure 2. The considered spin exchange paths J$_1$–J$_8$ of the Ba$_2$CuOsO$_6$: (a) projection view of an isolated ||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 ||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.
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$_6$ (M = 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 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 Os-O···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 O···O contacts, as shown in Figure 3e. The $J_5$ and $J_6$ exchanges are the interactions between the adjacent ab layers, and the O···O contact distances of the SSE path $J_5$ and $J_6$ are 4.264 Å. The M-O bonds of the M-O···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 $\angle$M-O···O-M angles of the SE paths $J_5$ and $J_6$ are close to 180° (172.6°) and the M-O bond of M-O···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.
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:

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

(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.

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**Figure 3.** (a) The \( d_{x^2-y^2} \) magnetic orbitals of the \( \text{Cu}^{2+} \) 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 \( \text{Ba}_2\text{CuOsO}_6 \).
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 \( |J_7| \approx 0.385 \), \( |J_8| \approx 0.025 \), \( |J_1| \approx 0.005 \), \( |J_2| \approx 0.283 \), \( |J_3| \approx 0.850 \), \( |J_4| \approx 0.015 \), \( |J_5| \approx 0.025 \), \( |J_6| \approx 0.339 \), respectively. This suggests that the magnetic property of \( \text{Ba}_2\text{CuOsO}_6 \) is mainly governed by \( J_1, J_3, J_4, J_5, J_6, J_7, \) and \( J_8 \) exchanges, in which all of them are AFM except \( J_7 \). 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 $T_{\text{max}}$ at $\sim$55 K and $\sim$70 K in susceptibility measurement would support such a possibility of magnetic sublattice [15]. The presence of two different magnetic ions in Ba$_2$CuOsO$_6$ system should be related with the double AFM-like anomaly at $\sim$55 K and $\sim$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 $(J_1,J_1,J_7)$, $(J_1,J_3,J_8)$, $(J_1,J_3,J_3)$, $(J_3,J_3,J_7)$, 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 $(f = |T_N|/|T_{\text{max}}|)$ is just $\sim$0.24, and there is no divergence between the zero-field and field susceptibility curves in Ba$_2$CuOsO$_6$ indicating the absence of spin frustration [15]. For a spin frustrated magnetic system, it is generally expected that the ratio, $f = |T_N|/|T_{\text{max}}|$, is greater than 6 [29–31]. The spin frustration factor $f$-value for Ba$_2$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 Ba$_2$CuOsO$_6$, despite its similar system (Sr$_2$CuOsO$_6$, Sr$_2$CuIrO$_6$) [32,33] showing strong spin frustration.

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

4. Describing the Magnetic Insulating Behavior of Ba$_2$CuOsO$_6$

As mentioned in the introduction section, the Ba$_2$CuOsO$_6$ system is a magnetic insulator. Feng et al. [15] measured the temperature dependence of resistivity $\rho$ of polycrystalline Ba$_2$CuOsO$_6$, in which it showed an insulating behavior at all measured temperature ranges. This reveals that the insulating behavior of Ba$_2$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 Ba$_2$CuOsO$_6$. The calculated electronic structures for Ba$_2$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 Ba$_2$CuOsO$_6$ (see Figure 5b,c).

For Sr$_2$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 Os$_6$ octahedron with axially elongated Os$_6$ octahedron (i.e., Os-O$_{2\text{eq}}$ = 1.928 (×2) Å, Os-O$_{\text{ax}}$ = 1.888 (×4) Å) appears slightly distorted, compared with the Cu$_6$ octahedron, caused by a weak Jahn–Teller instability. Therefore, the Os 5d state of axially elongated Os$_6$ octahedron is split into four states (xz, yz, $xy < x^2 < x^2-y^2$) 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 Sr$_2$CuOsO$_6$. On the other hand, each Os$_6$ of Ba$_2$CuOsO$_6$ has an axially shrunk octahedron, indicating the different types of Os 5d state splitting with Sr$_2$CuOsO$_6$. The Os 5d state of Ba$_2$CuOsO$_6$ is split into four states ($xy < xz, yz < x^2-y^2 < z^2$). However, the Os 5d state splitting of Ba$_2$CuOsO$_6$ is very weak compared to that of Sr$_2$CuOsO$_6$, as shown in the Scheme 1 and Figure 5c. Split Os 5d state of Ba$_2$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 Ba$_2$CuOsO$_6$. The crucial key to describing the insulating behavior of Ba$_2$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 Ba$_2$CuOsO$_6$, thereby it is necessary to consider the SOC effect.

![Energy Bands](image)

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

DFT+U ($U_{Cu}=4.0, U_{Os}=5.0$ eV)

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

![Band Structures](image)
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 Ba$_2$CuOsO$_6$.

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

$$\hat{H}_{SOC} = \lambda \vec{S} \cdot \hat{L}$$

where the SOC constant $\lambda > 0$ for the Os$^{6+}$ ($d^2$) ion, with less than half-filled $t_{2g}$ levels. With $\theta$ and $\varphi$ as the azimuthal and polar angles of the magnetization in the rectangular crystal coordinate system, respectively, the $\hat{L}$ and $\vec{S}$ terms are rewritten $[34,35]$ as follows:

$$\hat{H}_{soc} = \lambda \mathbf{S} \cdot \mathbf{L} = \frac{\lambda}{2} \left( L_z \cos \theta + \frac{1}{2} L_+ e^{-i\varphi} \sin \theta + \frac{1}{2} L_- e^{i\varphi} \sin \theta \right)$$

$$+ \frac{\lambda}{2} \left( \frac{1}{\sqrt{2}} \left( -L_z \sin \theta - L_+ e^{-i\varphi} \sin^2 \frac{\theta}{2} + L_- e^{i\varphi} \cos^2 \frac{\theta}{2} \right) \right)$$

$$+ \frac{\lambda}{2} \left( \frac{1}{\sqrt{2}} \left( -L_z \sin \theta + L_+ e^{-i\varphi} \cos^2 \frac{\theta}{2} - L_- e^{i\varphi} \sin^2 \frac{\theta}{2} \right) \right)$$

(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:

$$d_{xy} = \frac{1}{\sqrt{2}} (Y_1^2 - Y_2^2)$$

$$d_{yz} = \frac{1}{\sqrt{2}} (Y_1^2 + Y_2^{-1})$$

$$d_{xz} = \frac{1}{\sqrt{2}} (Y_1^2 - Y_2^{-1})$$

(4)

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

$$i \hbar \lambda = \frac{\hbar}{2} \left( \begin{array}{ccc} 0 & \sin \theta \sin \varphi & -\sin \theta \sin \varphi \\ -\sin \theta \sin \varphi & 0 & \cos \theta \\ \sin \theta \cos \varphi & -\cos \theta & 0 \end{array} \right)$$

(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 $\psi_1$, $\psi_2$, and $\psi_3$ are given $[12,34,35]$ by the following:

$$\psi_1 = \frac{\sqrt{2}}{\lambda} \left[ \sin \theta d_{xy} + (\sin \varphi - \cos \theta \cos \varphi) d_{yz} - (i \cos \varphi + \cos \theta \sin \varphi) d_{xz} \right]$$

$$\psi_2 = \frac{\sqrt{2}}{\lambda} \left[ \sin \theta d_{xy} - (i \sin \varphi + \cos \theta \cos \varphi) d_{yz} + (i \cos \varphi - \cos \theta \sin \varphi) d_{xz} \right]$$

$$\psi_3 = \cos \theta d_{xy} + \sin \theta \cos \varphi d_{yz} + \sin \theta \sin \varphi d_{xz}$$

(6)

The above analysis indicates that the SOC effect splits the $t_{2g}$ states into three substates by orbital symmetry breaking. For the Os$^{6+}$ ($d^2$) ion, two electrons of $t_{2g}$ state should occupy $\psi_1$ and $\psi_2$. Therefore, the band gap around the Fermi level should be developed in between the occupied $\psi_2$ and the unoccupied $\psi_3$ state.

To elucidate the above discussion, we carried out calculations to reproduce the insulating state of Ba$_2$CuOsO$_6$ 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 Ba$_2$CuOsO$_6$ (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 Ba$_2$CuOsO$_6$. However, the electronic structure obtained from the DFT + SOC still failed to reproduce the insulating behavior for Ba$_2$CuOsO$_6$ (See Figure 5a). Presented in Figure 3a, the spin-up and spin-down bands are overlapped, which leads to a metallic state for Ba$_2$CuOsO$_6$. 
We imagine the hypothetical compounds of $A_2$ (see Figure 1c). In $A_2$ (spin-down) by increasing exchange splitting, should be required to describe the insulating state of $\text{Ba}_2\text{CuO}_6$. 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 $\text{Ba}_2\text{CuO}_6$.

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 $\text{Ba}_2\text{CuO}_6$ 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 $\text{Ba}_2\text{CuO}_6$.

Meanwhile, there remains one question about the origin of the band gap opening in $\text{Ba}_2\text{CuO}_6$. The insulating behavior of $\text{Ba}_2\text{CuO}_6$ is intimately linked with the structural distortion of the OsO$_6$ octahedron. We remind that the OsO$_6$ octahedron for $\text{Ba}_2\text{CuO}_6$ is an axially compressed octahedral shape, while the OsO$_6$ octahedron of $\text{Sr}_2\text{CuO}_6$ 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 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 $\text{Sr}_2\text{CuO}_6$ and $\text{Ba}_2\text{CuO}_6$ 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 $\text{A}_2\text{CuO}_6$ (A = Sr and Ba), the A-site ion is located in the center of CuO$_4$ distorted cubes and distorted (Os$^{4+}$)$_4$ 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 $\text{A}_2\text{CuO}_6$, 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 $\text{Ba}_2\text{CuO}_6$, 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 $\text{Ba}_2\text{CuO}_6$ and $\text{Sr}_2\text{CuO}_6$ are 1.960 and 1.888 Å, respectively, while the Os-O$_{ax}$ distances in $\text{Ba}_2\text{CuO}_6$ and $\text{Sr}_2\text{CuO}_6$ 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 $\text{A}_2\text{CuO}_6$.

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 $\text{Ba}_2\text{CuO}_6$. We imagine the hypothetical compounds of $\text{A}_2\text{CuO}_6$ (A = Sr, Ca) by replacing the Ba atoms of $\text{Ba}_2\text{CuO}_6$ with other alkali earth atoms—Sr and Ca. $\text{A}_2\text{CuO}_6$ (A = 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 $\text{Ba}_2\text{CuO}_6$ but also for the axial elongation of OsO$_6$ octahedrons in

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

5. Concluding Remarks

The magnetic structure and the origin of the band gap opening for Ba$_2$CuOsO$_6$ are investigated by exploring the spin exchange interactions and analyzing the spin–orbit coupling effect. The magnetic property of Ba$_2$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 Ba$_2$CuOsO$_6$. Each OsO$_6$ octahedron of Sr$_2$CuOsO$_6$ displays an axially elongated octahedral shape, while each OsO$_6$ octahedron of Ba$_2$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$^{5+}$ ions of Ba$_2$CuOsO$_6$ and Sr$_2$CuOsO$_6$ by the Jahn–Teller instability is differently depicted in Scheme 1. Consequently, to explain the magnetic insulating states of Sr$_2$CuOsO$_6$, which are isostructural and isoelectronic in Ba$_2$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 Ba$_2$CuOsO$_6$, which is highly related with the t$_{2g}$ orbital splitting of the Os$^{5+}$ 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 n1–n8 of Equation (1) for the nine ordered spin states (FM and AF1–AF8) to extract spin exchange interaction J1–J8, Table S3: The optimized structural parameters of A$_2$CuOsO$_6$ (A = Ba, Sr, and Ca) obtained from the DFT + U + SOC (UCu = 4, UOs = 5 eV). Space group I4$_1$/m (#87). A is at site (0, 0, 0.5), 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 Sr$_2$CuOsO$_6$ calculated by DFT+U+SOC. U values for Cu and Os in this DOS calculation are chosen as (a) UCu = 4 eV, UOs = 5 eV, (b) UCu = 5 eV, UOs = 4 eV, (c) UCu = 3 eV, UOs = 4 eV, and (d) UCu = 2 eV, UOs = 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. 2020R1A5A1019141, 2021R1F1A1063478). 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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