

The Role of Favoured Orientations of Organic Cation on The Electronic Properties and Spin Textures of Hybrid Organic-Inorganic

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ABSTRACT

The electronic structure of bulk Hybrid Organic-Inorganic Perovskite (HOIP) $CH_3NH_3PbX_3$ ($X = Br$ and Cl) has been investigated by using a computational method based on Density Functional Theory (DFT). The investigation demonstrates that spin splitting is found when a favoured orientation of organic cation align along the $[111]$, the $[101]$ and the $[011]$ directions. We show that Rashba splitting is induced with the anisotropical character of spin polarization in $[111]$ directions, whereas the unidirectional out-of-plane of spin polarizations are achieved in $[011]$ and $[101]$ directions. By employing $\vec{k} \cdot \vec{p}$ perturbation theory based on symmetry consideration, we find a large spin-orbit strength from these splitting. These findings show that the bulk HOIP $CH_3NH_3PbX_3$ is a promising material for the development of perovskite-based spintronic devices.

Keywords : *first-principles calculations; spin-orbit interaction; spintronics; condensed matter and materials physics*

A. Introduction

Contemporary development of energy-saving spintronics hinges on the new approach for harnessing spin in semiconductor materials by exploiting the effect of spin-orbit interaction (SOI). In a crystal structures lacking spatial inversion symmetry, the SOI leads to a spin-momentum coupling that breaks Kramer's degeneracy in electronic bands. Accordingly, the SOI plays an important role for manipulation of electron spin, inducing to numerous novel effects such as spin Hall effect and spin interference [1]. Specifically, Rashba SOI draws much attention caused by its electrical controllability, which is useful for spintronic devices, e.g spin-field effect transistor (S-FET) [2]. For spintronics device operation, materials having strong Rashba SOI are inevitably required, which allows for operating at room temperatures. Therefore, it is crucially important to find a new material that exhibit strong Rashba SOI combined with stable spin-polarized states. One of the

new class of materials possessing strong SOI is Hybrid Organic-Inorganic Perovskite (HOIP) [3-4].

Recently, Hybrid Organic-Inorganic Perovskites $\text{CH}_3\text{NH}_3\text{PbX}_3$ has emerged as a new class of semiconductor materials that demonstrate excellent performance in photovoltaic solar cells [4]. These compounds have been reported to exhibit large and tunable SOI, spin-dependent optical selection rules and the existence of Rashba splitting [3]. In addition, at room temperature, the role of organic cation in crystal structures could directly affect electronic properties and unique spin texture [5]. Furthermore, the intrinsic mechanisms for long carrier lifetime have been proposed in $\text{CH}_3\text{NH}_3\text{PbI}_3$ [6]. Also, the long spin time has been observed experimentally in polycrystalline films of the HOIP [3]. Therefore, based on such materials, it is possible to extend the functionality of material by exploiting the role of cation and substituting halogen atoms in crystal systems.

Here, we propose to use a substitution of halogen atom for investigating the electronic properties of bulk HOIP $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($X = \text{Br}, \text{Cl}$). This paper is focused on the impact of special orientations of organic cation to the characteristic of spin splitting. By using first-principles density functional theory (DFT) calculations, we show that the preferential orientation of organic cation induces the Rashba splitting with anisotropic character of spin polarizations. Interestingly, the unidirectional spin textures are realized in [011] and [101] directions. Our analysis using $\vec{k} \cdot \vec{p}$ perturbation combined with the symmetry consideration found the large spin-orbit strength from these splitting. Finally, the potential applications of the present systems for perovskite spintronics are discussed.

B. Methods

In this paper, we consider $\text{CH}_3\text{NH}_3\text{PbBr}_3$ as a prototypical example of the bulk HOIP systems based on cubic crystal structure with a preferential orientation of cation align along the [111], [101] and [011] directions. We performed first-principles electronic structures calculations on the bulk $\text{CH}_3\text{NH}_3\text{PbX}_3$ based on density functional theory (DFT) within the generalized gradient approximation (GGA) realized in OpenMX code [7]. We used norm-conserving pseudopotential [8] with an energy cutoff at 300 Ry for charge density. The wavefunctions were generated by the linear combination of multiple pseudoatomic orbitals (LCPAOs) using a confinement scheme [10]. Here, each atom used in the calculation were C6.0- $s^3p^3d^2$, H5.0- $s^2p^2d^2$, N6.0- $s^2p^2d^2$, Pb8.0- $s^2p^2d^2$, Br7.0- $s^3p^2d^1$ and Cl8.0- $s^3p^3d^2$. Crystal structures were fully relaxed until the force acting

on each atom was less than $0.1 \text{ meV/\text{Å}}$. The SOI is also included with non-collinear spin polarization with the $8 \times 8 \times 8$ k-point mesh. By using the spin density matrix of spinor wavefunctions obtained from the DFT calculations, the spin textures can be calculated [9]. Here, the orientation of crystal structure was considered at [001] direction for the preferential orientations in order to map the oriented spin texture in the momentum space.

C. Results and Discussion

Figure 1(a)-1(c) shows the optimized crystal structure of bulk HOIP $\text{CH}_3\text{NH}_3\text{PbX}_3$ and it was consistent with the model. The calculated values of lattice parameter are summarized in Table 1. Overall, we find that these lattice parameters are in a good agreement with previous calculation. The electronic band structure is performed at high symmetry points of the cubic structures in the Brillouin zone. The chosen k-path is configured by the order of Γ -X-M- Γ -R-X shown in figure 1(d). The band dispersion of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ is calculated with and without SOI as shown in Figure 2.

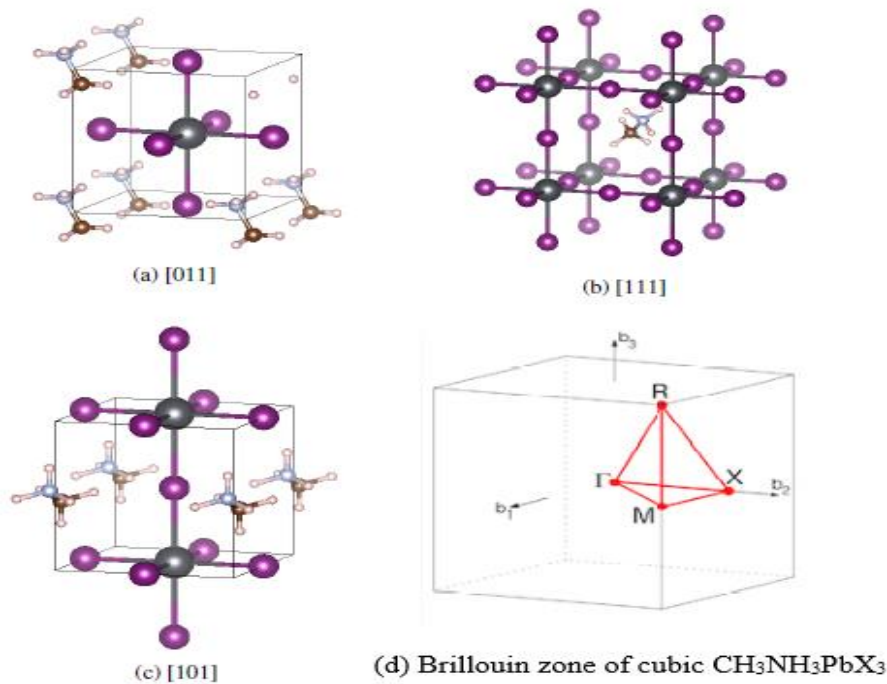


Figure 1. Crystal structure of HOIP oriented along (a) [011], (b) [111], (c) [101] and (d) First Brillouin zone of the bulk crystal structure $\text{CH}_3\text{NH}_3\text{PbX}_3$ in the k-space is shown.

Without SOI, it was found that the characteristic of indirect band gap is emerged between Γ and R points in the conduction band minimum (CBM) for cation oriented along [011] direction. Accordingly, this such properties have been

Table 1. The optimized structural-related parameters for the preferential orientation of organic cation in the bulk HOIP $\text{CH}_3\text{NH}_3\text{PbX}_3$

$\text{CH}_3\text{NH}_3\text{PbX}_3$ (X = Br, Cl)	Orientation of Cation	Calculation of lattice parameter (\AA)	Reference
	[011]	6.044	Ref. [11]
$\text{CH}_3\text{NH}_3\text{PbBr}_3$	[101]	6.237	This work
	[111]	6.135	Ref. [12]
$\text{CH}_3\text{NH}_3\text{PbCl}_3$	[011]	5.871	Ref. [13]
	[101]	6.162	This work
	[111]	6.020	Ref. [13]

reported which is responsible for the emergence of Rashba splitting [14]. Turning to SOI, a pronounced spin splitting of the band structure in $\text{CH}_3\text{NH}_3\text{PbX}_3$ confirmed the lack of inversion symmetry, which is previously reported due to the structural distortion induced by organic cation [4,5,14]. Firstly, large spin splitting is found at both R and M points when the orientation of cation aligned along [011] and [101] direction. Moreover, a substantial spin splitting also emerged when the cation is oriented along [111] direction. In addition, the emergence of anisotropical character of Rashba-type splitting is identified in the CBM of bulk HOIP $\text{CH}_3\text{NH}_3\text{PbX}_3$ for these preferential orientations. Furthermore, the indirect band gap at CBM of R point is preserved for the cation oriented along [011] direction whereas the direct band gap is found both along [111] and [101] direction. It is noted here that depending on the Z number of halogen atoms, enhancement of spin splitting is observed for each orientation from $\text{CH}_3\text{NH}_3\text{PbCl}_3$ to $\text{CH}_3\text{NH}_3\text{PbBr}_3$.

Since the electronic properties of bulk HOIP $\text{CH}_3\text{NH}_3\text{PbX}_3$ are significantly modified by special orientation of organic cation, it is expected that the distinct characteristic of spin polarization for each orientation of organic cation can be achieved. To demonstrate the properties of spin-split bands at Fermi

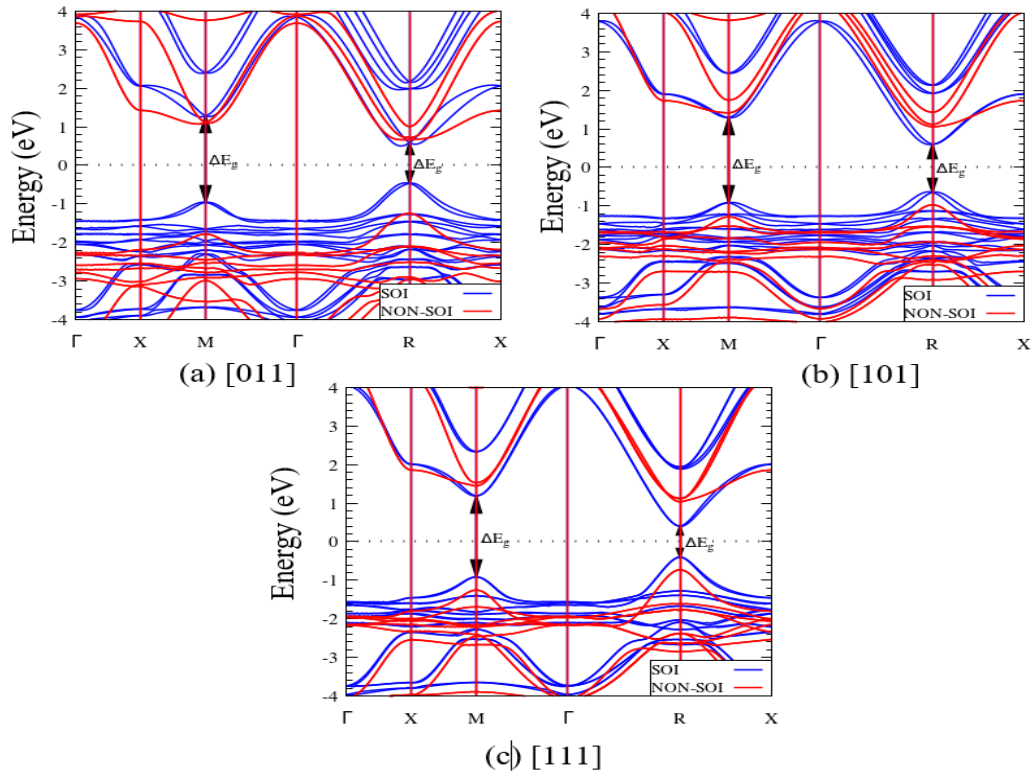


Figure 2. Electronic band structures with SOI (blue) and without SOI (red) of bulk HOIP $\text{CH}_3\text{NH}_3\text{PbBr}_3$ oriented along (a) [011], (b) [101], (c) [111]

level around the R point, we calculate spin texture by using the spin-density matrix of spinor wavefunctions obtained from the DFT calculations [9]. In this case, the orientation of crystal structure is evaluated at [001] direction in order to pinpoint the R point at the center of Brillouin zone (\vec{k}) relative to the Γ point. The calculated result of spin textures is shown in Figure 3. For cation aligned along [111] direction [Fig 3(b)], we find that the constant-energy intersection exhibit outer and inner circles representing clockwise and counterclockwise rotating spin polarizations, which is compatible with the Rashba splitting. However, we also identify anisotropical character of Rashba splitting shown by variation of spin polarization along z-direction, revealing predominant out-of-plane spin components. In the case of cation oriented along [011] and [101] direction, we find that the Fermi surface is distinguished by the shifted of two

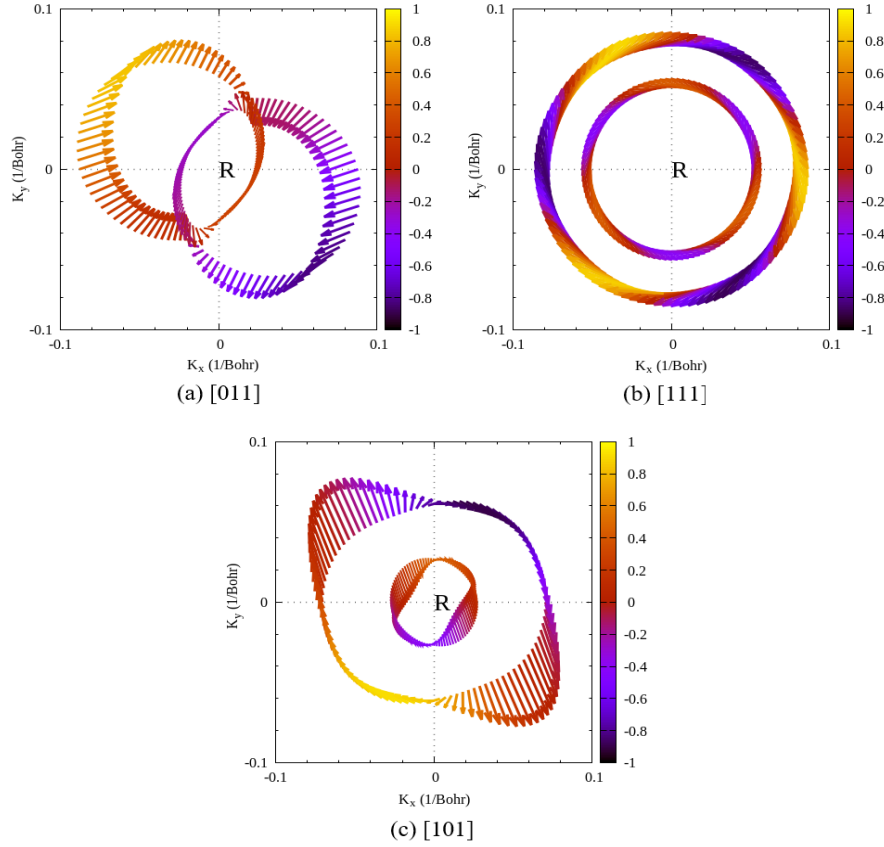


Figure 3. The spin textures of the CBM in the bulk HOIP $\text{CH}_3\text{NH}_3\text{PbBr}_3$ for three preferential orientation of cation aligned along [011], [111] and [101] direction calculated close to the R point. The arrow represents the spin polarizations in the $k_x - k_y$ plane while the color palette specify the out-of-plane directions of spin polarization.

circles [Fig(3a) and Fig(3c)], dominated by the out-of-plane spin orientations. These characteristic Fermi surface and spin textures indicate that the unidirectional out-of-plane of spin polarizations are achieved, which is similar to the observed properties on the ZnO (10-10) surface [15]. The observed anisotropic Rashba splitting in these system cannot be suitably described by conventional Rashba Hamiltonian.

Table 2. The fitting results of Rashba parameter α_R for bulk HOIP $\text{CH}_3\text{NH}_3\text{PbBr}_3$ from the analysis of $\vec{k} \cdot \vec{p}$ model based on perturbation theory

Systems	α_R (eV.Å)	Reference
[011]- $\text{CH}_3\text{NH}_3\text{PbBr}_3$ bulk cubic	1.71	This work

[101]-CH ₃ NH ₃ PbBr ₃ bulk cubic	0.70	This work
[111]-CH ₃ NH ₃ PbBr ₃ bulk cubic	0.67	This work
[011]-CH ₃ NH ₃ PbCl ₃ bulk cubic	1.01	This work
[101]-CH ₃ NH ₃ PbCl ₃ bulk cubic	0.72	This work
[111]-CH ₃ NH ₃ PbCl ₃ bulk cubic	0.42	This work
CH ₃ NH ₃ PbI ₃ bulk (Tetragonal)	1.50	Ref [15]
ZnO(10-10) surface	34.78 x 10 ⁻³	Ref [16]

To confirm the observed anisotropic Rashba splitting and spin textures around the R point, we consider our system based on $\vec{k} \cdot \vec{p}$ model regarding the effective low-energy Hamiltonian, which is obtained by symmetry analysis of crystal structure. For instance, the crystal symmetry of both [011] and [101] orientation of cation is considered for C_s point group while symmetry of [101] orientations of cation is evaluated for C_{3v} point group. The spin splitting energy for both C_s and C_{3v} point group is expressed in the form, respectively:

$$[\Delta\varepsilon(k)]^2 = (\alpha_1^1 k_x + \alpha_3^1 k_x^3)^2 + (\alpha_1^2 k_x + \alpha_1^2 k_x k_y^2)^2 + (\alpha_1^3 k_y + \alpha_3^3 k_y k_x^2 + \alpha_3^4 k_y^3)^2 \quad (1)$$

$$[\Delta\varepsilon(k)]^2 = [\alpha_1^1 k_x + \alpha_3^1 (k_x^3 + k_x k_y^2)]^2 + [\alpha_3^2 (k_x^3 - 3k_x k_y^2)]^2 + [-\alpha_1^1 k_y - \alpha_3^1 (k_y^3 + k_y k_x^2)]^2 \quad (2)$$

where α is fitting parameter of spin splitting energy, $k_x = |k| \cos \theta$ and $k_y = |k| \sin \theta$ is wave number for x-axis and y-axis in Brillouin zone, respectively. These equation is used to find the fitting Rashba parameter for each orientation of cation in the bulk CH₃NH₃PbX₃. The calculated results of the α_R are summarized in Table (2) and compared with the result of few selected materials from previously reported data. The calculated values of Rashba parameter for bulk CH₃NH₃PbX₃ is much larger than that ZnO(10-10) surface [16], the strained interface LaAlO₃/SrTiO₃ [17] and comparable with bulk tetragonal CH₃NH₃PbI₃ [15]. Moreover, the larger value of α_R means that the spin-split states are dominated by the out-of-plane spin component, which is also confirmed with the calculated spin texture in figure 3(a) and 3(c).

Specifically, the typical spin textures for the cation oriented along [011] and [101] directions could indicate an emergence of novel effect, which exhibits fully unidirectional out-of-plane called as Persistent Spin Helix (PSH) states [16-17]. Since it is suggested that PSH could provide a long spin lifetime, the performance of potential spintronics devices could be enhanced based on HOIP materials. Furthermore, it is also reported experimentally that the HOIP materials hosted a long spin lifetime [3]. In addition, bulk $\text{CH}_3\text{NH}_3\text{PbX}_3$ of cubic structure has several advantages, such as it exists at high temperature phase and low-cost processable, which is useful for the development of spintronics devices operating at room temperature [4]. It is noted here that this method can be extended to other halogen atom, such as atom I and another typical cation that could be responsible to the structural distortion of cubic structure. Therefore, this work provides a shed light on the possible way to induce the distinctive spin splitting in the bulk HOIP $\text{CH}_3\text{NH}_3\text{PbX}_3$ of cubic structure, which is favorable for future spintronics devices.

D. Conclusion

In summary, we have investigated the effect of preferential orientations of organic cation on the electronic properties of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ by using the first-principles DFT calculations. We found that the special orientations of organic cation oriented along [011] and [101] can induce the unidirectional out-of-plane spin polarizations, which is expected hosting a long spin lifetime. We clarified the properties of spin splitting by using $\vec{k} \cdot \vec{p}$ model based on perturbation theory. Finally, we anticipate that our theoretical model will inspire another theoretical predictions and experimental attempt in the exploration of the Rashba splitting in the HOIP materials, which could be useful for future development of spintronic applications.

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