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Bulk inversion asymmetry effect on band structure and optical transition of a new class all-inorganic cubic perovskite nanoplatelet

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The band structures at near the \( R \) point of all-inorganic cubic \( \text{CsSnBr}_3 \) perovskite nanoplatelets (NPLs) are investigated by using an 8-band \( k \cdot p \) method. The Luttinger parameters are given by fitting the first-principles results, the \( E-K \) curves and optical transition rule at near the \( R \) point are obtained. The bulk invasion asymmetry is taken into consideration in the method. The splitting of energy subbands is observed at non-\( R \) point due to the bulk invasion asymmetry effect, however they are still two-fold degenerated at the \( R \) point. The optical transition rule follows the \( \Delta n=0 \) for the thin NPLs, however, for the thicker NPLs, the optical transition rule of \( \Delta n=0 \) does not hold. The results are helpful to understand the cubic perovskite nanoplatelet based spintronics and optoelectronics. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5048349

I. INTRODUCTION

Since Miyasaka\(^1\) and co-workers open the door of the hybrid organic-inorganic halide perovskite \( \text{AMX}_3 \) (where A is an organic cation, M = Pb, Sn, or Ge, and X = I, Br, or Cl), it has attracted the increasing attention from the photovoltaic community. Such craze arises from the early successes in improving the conversion efficiency in solar cell, from 3.8% to more than 20% in only a few years, combined with the low-cost of production.\(^2\)\(^-\)\(^5\) Not only the application research is done, more physical phenomena are investigated and some mechanisms also are explored. The rapid progresses in experiments include the magnetic field effect phenomena,\(^6\)\(^,\)\(^7\) the direct measurement of the exciton binding energy and effective mass,\(^8\) ultrafast transient pump-probe measurement\(^9\) and so on. In addition, the related theory also provides model to understand these interesting phenomena. Recently, a new class all-inorganic perovskite quantum dot with the cubic structure was reported in Refs. 10 and 11. More information about this kind of new material has been revealed through the calculation of densities functional theory (DFT). However, DFT method is too time consumption to simulate the low-dimensional perovskite, such as the nanoplatelets (NPLs) and quantum dots. In this project, we will develop an 8-band \( k \cdot p \) model including the spin-orbit coupling (SOC) to investigate a new class all-inorganic perovskite NPLs. With the 8-band \( k \cdot p \) model, the band structure and optical transition matrix elements of the cubic \( \text{CsSnBr}_3 \) perovskite NPLs are investigated.

II. METHODS

Because the \( \text{CsSnBr}_3 \) perovskite has a cubic structure and the direct band gap is at the \( R \) point,\(^7\) one can take the basis functions as following.

\[
\varphi_V(+) = \left| S \uparrow \right> \\
\varphi_C\left(\frac{\sqrt{3}}{2}, \frac{\sqrt{3}}{2}\right) = -\frac{i}{\sqrt{2}}\left( (X+iY) \uparrow \right)
\]

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\[ \varphi_C\left(\frac{1}{2}, \frac{1}{2}\right) = -\frac{i}{\sqrt{6}} \left[\sigma_y \downarrow \downarrow - 2Z \uparrow\right] \]  
\[ \varphi_C\left(\frac{1}{2}, \frac{1}{2}\right) = \frac{i}{\sqrt{3}} \left[\sigma_y \downarrow \downarrow + Z \uparrow\right] \]  
\[ \varphi_C\left(\frac{1}{2}, -\frac{1}{2}\right) = \frac{i}{\sqrt{2}} \left[\sigma_y \downarrow \downarrow \right] \]  
\[ \varphi_C\left(\frac{3}{2}, -\frac{1}{2}\right) = \frac{i}{\sqrt{6}} \left[\sigma_y \downarrow \downarrow + 2Z \downarrow\right] \]  
\[ \varphi_C\left(\frac{3}{2}, -\frac{1}{2}\right) = \frac{i}{\sqrt{3}} \left[\sigma_y \downarrow \downarrow - Z \downarrow\right] \]  

Under the above-mentioned basis, the Hamiltonian can be written as:

\[
H = -\begin{bmatrix}
V_B & c.c. & c.c. & c.c. & c.c. & c.c. & c.c. \\
0 & V_B & c.c. & c.c. & c.c. & c.c. & c.c. \\
\frac{1}{\sqrt{2}} P_- & 0 & CH & c.c. & c.c. & c.c. & c.c. \\
-\frac{1}{\sqrt{3}} P_z & \frac{1}{\sqrt{6}} P_- & S^z & CL & c.c. & c.c. & c.c. \\
0 & -\frac{1}{\sqrt{2}} P_+ & -R^z & 0 & CL & c.c. & c.c. \\
-\frac{1}{\sqrt{3}} P_z & -\frac{1}{\sqrt{3}} P_- & -S^z & -D & -\sqrt{\frac{3}{2}} S & \sqrt{2} R & CS & c.c. \\
-\frac{1}{\sqrt{3}} P_+ & -\frac{1}{\sqrt{3}} P_+ & -\sqrt{2} R^z & -\sqrt{\frac{3}{2}} S & D & \frac{S}{\sqrt{2}} & 0 & CS
\end{bmatrix}
\]  

Where,

\[ P_\pm = P(k_x \pm i k_y) \]  
\[ P_z = Pk_z + i \delta \]  
\[ V_B = E_G + \frac{\hbar^2}{2m_0} \gamma_V(k_x^2 + k_y^2 + k_z^2) \]  
\[ \gamma_V = \frac{1}{m_V} \left( \frac{E_p}{3} \right) \frac{2}{E_G + \Delta} \]  
\[ C_H = -\frac{\hbar^2}{2m_0} \left[ (\gamma_1 + \gamma_2)(k_x^2 + k_y^2) + (\gamma_1 - 2\gamma_2)k_z^2 \right] \]  
\[ C_L = -\frac{\hbar^2}{2m_0} \left[ (\gamma_1 - \gamma_2)(k_x^2 + k_y^2) + (\gamma_1 + 2\gamma_2)k_z^2 \right] \]  
\[ C_S = -\frac{\hbar^2}{2m_0} \left[ \gamma_1 (k_x^2 + k_y^2 + k_z^2) \right] - \Delta \]  
\[ S = \frac{\hbar^2}{2m_0} 2\sqrt{3} \gamma_3 (-k_x + ik_y)k_z \]  
\[ R = -\frac{\hbar^2}{2m_0} \sqrt{3} \gamma_2 (k_x^2 - k_y^2) - 2\gamma_3 i k_y k_z \]  
\[ D = \frac{\hbar^2}{2m_0} \sqrt{2} \gamma_3 (k_x^2 + k_y^2 - 2k_z^2) \]
$E_G$ is the band gap. $A$ is the spin-orbit splitting energy. $h$ is the reduced Planck constant. $P$ is the Kane matrix element and is normally expressed in term of energy units as:

$$E_P = \frac{2m_0}{\hbar^2}P^2 = \frac{2}{m_0}P_0^2$$  \hspace{1cm} (4)

$\delta$ describes the inversion asymmetry. $\gamma_1, \gamma_2, \gamma_3$ are the normalized Luttinger parameters.

$$\gamma_1 = \gamma_1^L - \frac{1}{3} \frac{E_P}{E_G}$$  \hspace{1cm} (5a)

$$\gamma_2 = \gamma_2^L - \frac{1}{6} \frac{E_P}{E_G}$$  \hspace{1cm} (5b)

$$\gamma_3 = \gamma_3^L - \frac{1}{6} \frac{E_P}{E_G}$$  \hspace{1cm} (5c)

$\gamma_1^L, \gamma_2^L, \gamma_3^L$ are the Luttinger parameters, $k_x, k_y, k_z$ are the wave vector operators away from the $R$ point.

The squared optical transition matrix elements are written as

$$Q_{i}^{n,c} = \frac{2}{m_0} |\langle \Psi_n | \hat{\epsilon} \cdot \mathbf{p} | \Psi_c \rangle|^2, \hspace{0.5cm} i=x, y, z,$$  \hspace{1cm} (6)

where $\hat{\epsilon}$ is the unit vector in the direction of the electric field, $\mathbf{p}$ is the momentum operator, and $\Psi_n$ and $\Psi_c$ are the real electron and hole wave functions, respectively. The real wave function is the product of the envelope wave functions and the Bloch wave functions.

### III. RESULTS AND DISCUSSIONS

The band parameters of CsSnBr$_3$ are extracted from the first-principles calculations in Ref. 15. The Luttinger parameters are obtained by using the following method.

$$m_{he}^{*}[100] = \frac{1}{\gamma_1^L - 2\gamma_2^L}$$  \hspace{1cm} (7a)

$$m_{he}^{*}[100] = \frac{1}{\gamma_1^L + 2\gamma_2^L}$$  \hspace{1cm} (7b)

$$m_{he}^{*}[111] = \frac{1}{\gamma_1^L - 2\gamma_3^L}$$  \hspace{1cm} (7c)

$$m_{he}^{*}[111] = \frac{1}{\gamma_1^L + 2\gamma_3^L}$$  \hspace{1cm} (7d)

The parameters used in our calculations are listed in Table I. The electronic structures of the 4, 6, 7 and 8 ML CsSnBr$_3$ NPLs are calculated and shown in Fig. 1. Like the hole subbands of traditional semiconductor NPLs, we can name the CsSnBr$_3$ NPLs’ electron subbands as spin-orbit electron (SE), heavy electron (HE) and light electron (LE). For the 4 ML and 6 ML NPLs, the electron subbands

<table>
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<td>Valence band effective mass ($m_0$)</td>
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<tr>
<td>Luttinger parameter $\gamma_1^L$</td>
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<tr>
<td>Luttinger parameter $\gamma_2^L$</td>
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<tr>
<td>Luttinger parameter $\gamma_3^L$</td>
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<tr>
<td>Band gap (eV) $E_G$</td>
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<tr>
<td>Spin-orbit splitting energy (eV)</td>
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<tr>
<td>Kane matrix element const. (eV)</td>
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<tr>
<td>Inversion asymmetry parameter (eV)</td>
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<tr>
<td>Lattice constant (Å)</td>
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from bottom to top are named as SE1, HE1, LE1, SE2 and HE2 according to the state components at the $R$ point ($k=0$ point). However, for the 7 ML and 8 ML NPLs, the electron subbands from bottom to top are changed as SE1, HE1, SE2, LE1 and HE2. The SE2 is below LE1 for the thicker NPLs.
We can see the two-fold degeneracy of electron and hole subbands are broken at the non-$R$ point because of the bulk inversion asymmetry, i.e. the $\delta$ term in eq. (3b). On the other hand, at the $k=0$ point, the subbands are still two-fold degenerated. In order to observe the subband splitting more clearly, we plot the SE1 and valance subband 1 (V1) splitting in Fig. 2. The bulk inversion asymmetry induced energy band splitting for the electron SE1 subband is larger than the hole V1 subband along [110] direction because of the stronger SE and LE band mixing. The conduction subband 1 (C1, i.e. SE1) splitting is increased when increasing the ML number, and it can reach about 170 meV for the 8 ML NPL, which is much larger than the Rashba spin-splitting in the InNbSb/InSb quantum wells.\textsuperscript{17} Fig. 3 shows the band gap of the CsSnBr$_3$ NPLs versus the number of ML. The bulk CsSnBr$_3$ band gap is inserted in the graph for comparison. One can see that when the number of
ML reducing, the bandgap of NPL is increasing because of the quantum confinement effect. And, the band gap of NPL is greater than that of bulk material, which indicates our calculation results are reasonable.
The squared wavefunctions at the $R$ point of the four NPLs are shown in Fig. 4. The barrier width is fixed at 20 nm and band offset is fixed at 3 eV in the calculations. We can see that the V2 wavefunction are almost symmetry for the 4 and 6 ML NPLs, however it show asymmetry clearly for the 7 and 8 ML, especially for the 8 ML NPL, see the inserted graph in Fig. 4. The results are consistent with the energy band splitting results in Fig. 3. The influence of bulk inversion asymmetry on the band structure and wavefunction is stronger when increasing the thickness of NPL.

The optical transition matrix elements at near $R$ point for the 6 and 7 ML CsSnBr$_3$ NPLs are shown in Fig. 5 and Fig. 6, respectively. The TE and TM mode optical transitions from the first 5 electron subbands to the first 2 hole subbands are investigated. The averaged subband transition curves are calculated and shown in the figures because of the energy band splitting. From Fig. 5, one can see that the optical transition rule $\Delta n=0$ is hold for the 6 ML NPL. The $n$ is the subband index. However, the optical transition rule $\Delta n=0$ is broken for the 7 ML NPL, see the SE2-V1 and LE1-V2 optical transitions in Fig. 6. The 4 ML and 8 ML NPLs have the similar results as the 6 ML and 7 ML NPLs, respectively, not shown here.

IV. CONCLUSIONS

A new simple 8-band k.p method is developed to calculate the band structure and optical properties of cubic CsSnBr$_3$ perovskite NPLs. The Luttinger band parameters are given. And, the $E$-$K$ curves, wavefunctions and polarization dependent optical transition at near $R$ point are calculated. The bulk inversion asymmetry effect is taken into consideration in the model. The very large bulk inversion asymmetry induced energy splitting is observed at non-$R$ point. And, the energy splitting is increased with the ML number of NPL, it can reach at about 170 meV for the 8 ML NPL. The optical transition rule follows $\Delta n=0$ for the thinner NPL (ML No. $<6$), however for the thicker NPL (ML No. $>7$), the $\Delta n=0$ rule does not hold.

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