Supplementary Information

Valley Polarization Caused by Crystalline Symmetry Breaking

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Computation methods

All calculations were performed on the basis of density functional theory\(^1\) as implemented in the Vienna \textit{ab initio} simulation package (VASP).\(^2\) The exchange-correlation interaction was treated by the generalized gradient approximation (GGA) in form of Perdew-Burke-Ernzerhof (PBE) functional.\(^3\) The cutoff energy was set to 500 eV. The lattice constant and atom position were relaxed until the force on each atom was less than 0.01 eV/Å, and the electronic iterations convergence criterion was set to \(1 \times 10^{-5}\) eV. A Monkhorst–Pack (MP) grid of \(15 \times 15 \times 1\) was used to sample the Brillouin zone.\(^4\) To avoid the interactions between adjacent layers, a vacuum space of 20 Å was applied. The spin–orbit coupling (SOC) was considered in the calculations. The vibrational properties were obtained with PHONOPY code,\(^5\) in which the force constants were calculated with the finite-displacement method.

Tight-binding model
In this section, we show the details of the tight-binding (TB) model for the checkboard lattice, and two $p$ orbitals were considered in our TB model. There are two sublattices in a unit cell, e.g., $\alpha$ and $\beta$ sublattices, and we denote them as $\mu = \alpha, \beta$. The atom positions are denoted as $r_{\mu} = R_n + r_\mu$, where $R_n$ is the lattice vector and $r_\mu$ is the relative positions of the atoms in unit cell. The atomic orbital wave function is $\psi_\gamma(r - r_\mu)$, where $\gamma$ refers to $p_x$ and $p_y$. Then, the TB model is represented as

$$H_0 = \sum_{\mu} \varepsilon_{n\mu} c_{n\mu}^+ c_{n\mu} + \sum_{\alpha, \beta} t_{n\alpha\beta}^\mu c_{n\alpha}^+ c_{n\beta} + h.c. \tag{1}$$

Under the Fourier Transformation, the TB Hamiltonian in the momentum space can be written as

$$H_0(k) = H_+(k) + H_-(k) \tag{2}$$

$$H_0(k) = \sum_{\alpha, \beta} \varepsilon_{n\alpha\beta}^\mu c_{n\alpha}^\mu(k) + \sum_{\alpha, \beta, \delta} t_{n\alpha\beta\delta}^\mu e^{-ik \cdot (r_{n\alpha} - r_{n\beta})}c_{n\alpha}^+ c_{n\beta} + h.c. \tag{3}$$

with basis being $(|p_x, \alpha, k\rangle, |p_y, \alpha, k\rangle, |p_x, \beta, k\rangle, |p_y, \beta, k\rangle)^T$, thus the matrix form of the Hamiltonian is

$$H_0 = \begin{pmatrix}
  h_{\alpha x} & 0 & h_1 & h_2 \\
  0 & h_{\alpha y} & h_2 & h_1 \\
  h_1 & h_2 & h_{\beta x} & 0 \\
  h_2 & h_1 & 0 & h_{\beta y}
\end{pmatrix} \tag{4}$$

$$h_{\alpha x} = \varepsilon_{\alpha} + \alpha_1 \cos(k_x a) + \alpha_1^\prime \cos(k_y a) \tag{5}$$

$$h_{\beta x} = \varepsilon_{\beta} + \beta_1 \cos(k_x a) + \beta_1^\prime \cos(k_y a) \tag{6}$$

$$h_{\alpha y} = \varepsilon_{\alpha} + \alpha_1 \cos(k_x a) + \alpha_1^\prime \cos(k_y a) \tag{7}$$

$$h_{\beta y} = \varepsilon_{\beta} + \beta_1 \cos(k_x a) + \beta_1^\prime \cos(k_y a) \tag{8}$$
\[ h_1 = 2\cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right)(\gamma_1 + \gamma_2) \text{#(9)} \]

\[ h_2 = -2\sin\left(\frac{k_x a}{2}\right)\sin\left(\frac{k_y a}{2}\right)(\gamma_1 + \gamma_2) \text{#(10)} \]

The parameters we used to obtain the energy dispersion shown in Fig. 1 are \( \varepsilon_a = 1.2 \), \( \varepsilon_a' = -1.1 \), \( \alpha_1 = 0.6 \), \( \alpha_1' = 0.1 \), \( \beta_1 = -0.5 \), \( \beta_1' = -0.1 \), \( \gamma_1 = 0.49 \), \( \gamma_2 = -0.1 \) and \( a = 4.03 \).

Then we consider the atomic spin-orbit interaction, the basis is \((|\uparrow\rangle, |\downarrow\rangle)^T \otimes (|p_x\alpha,k\rangle, |p_y\alpha,k\rangle, |p_x\beta,k\rangle, |p_y\beta,k\rangle)^T\), the spin-orbit coupling term is

\[ H_{so} = \begin{pmatrix} 0 & r_{so} \\ r_{so}^* & 0 \end{pmatrix} \]

\[ r_{so} = \begin{pmatrix} r_{ax} & 0 & 0 & 0 \\ 0 & r_{ay} & 0 & 0 \\ 0 & 0 & r_{\beta x} & 0 \\ 0 & 0 & 0 & r_{\beta y} \end{pmatrix} \]

\[ r_{ax} = i\lambda_{a1}\sin(k_x a) + \lambda_{a2}\sin(k_y a) \]

\[ r_{ay} = i\lambda_{a2}\sin(k_x a) + \lambda_{a1}\sin(k_y a) \]

\[ r_{\beta x} = i\lambda_{\beta 1}\sin(k_x a) + \lambda_{\beta 2}\sin(k_y a) \]

\[ r_{\beta y} = i\lambda_{\beta 2}\sin(k_x a) + \lambda_{\beta 1}\sin(k_y a) \]

The total Hamiltonian is given by \( H = I_2 \otimes H_0 + H_{so} + H' \), and the perturbation of crystalline asymmetry can be written as \( H' = \Delta(I_4 \otimes \sigma_z) \). The model gives a pair of valleys with energy degeneracy at X and X' points as shown Figs. S1(a)–(d), and the perturbation lifts energy degeneracy between X and X' points as shown in Figs. S1(e)–
(h).

References


**Table S1** Total energy per atom, Bi–S bond length, and lattice parameters of TL LaOBiS$_2$. The total energy of the pristine structures (DS$_0$) is set to zero as a reference.

<table>
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<th>DS$_0$</th>
<th>DS$_1$</th>
<th>DS$_2$</th>
<th>DS$_3$</th>
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<tr>
<td>Energy (meV)</td>
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<td>−2.232</td>
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<td>2.736/3.038</td>
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<td>$a$ (Å)</td>
<td>4.036</td>
<td>4.036</td>
<td>4.036</td>
<td>4.036</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>4.036</td>
<td>4.036</td>
<td>4.036</td>
<td>4.036</td>
</tr>
</tbody>
</table>
**Fig. S1** Band structures calculated by tight-binding model, in which different SOC strength and perturbation of crystalline asymmetry are applied. The parameters are exhibited in corresponding dispersions.

**Fig. S2** Upper panel, energy dispersion of (a) pristine DS\textsubscript{0} (b) DS\textsubscript{1}, (c) DS\textsubscript{2}, (d) DS\textsubscript{3} and (e) DS\textsubscript{3} with electric field applied, and the SOC is unconsidered. Lower panel exhibits the corresponding energy structures of (f) pristine DS\textsubscript{0} (g) DS\textsubscript{1}, (h) DS\textsubscript{2}, (i) DS\textsubscript{3} and (j) DS\textsubscript{3} with electric field applied, and take SOC into account. The Fermi level is set as zero.