

## 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<sup>1</sup> as implemented in the Vienna *ab initio* simulation package (VASP).<sup>2</sup> The exchange-correlation interaction was treated by the generalized gradient approximation (GGA) in form of Perdew-Burke-Ernzerhof (PBE) functional.<sup>3</sup> 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.<sup>4</sup> 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,<sup>5</sup> 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  $r_{n\mu} = R_n + r_\mu$ , 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  $\varphi_\gamma(r - r_{n\mu})$ , where  $\gamma$  refers to  $p_x$  and  $p_y$ . Then, the TB model is represented as

$$H_0 = \sum_{n,\mu} \varepsilon_{n\mu} c_{n\mu}^\dagger c_{n\mu} + \sum_{n,\alpha,\beta} t_n^{\alpha\beta} c_{n\alpha}^\dagger c_{n\beta} + h.c. \#(1)$$

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

$$H_0(k) = H_+(k) + H_-(k) \#(2)$$

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

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

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

$$h_{\alpha x} = \varepsilon_\alpha + \alpha_1 \cos(k_x a) + \alpha_1' \cos(k_y a) \#(5)$$

$$h_{\beta x} = \varepsilon_\beta + \beta_1 \cos(k_x a) + \beta_1' \cos(k_y a) \#(6)$$

$$h_{\alpha y} = \varepsilon_\alpha + \alpha_1' \cos(k_x a) + \alpha_1 \cos(k_y a) \#(7)$$

$$h_{\beta y} = \varepsilon_\beta + \beta_1' \cos(k_x a) + \beta_1 \cos(k_y a) \#(8)$$

$$h_1 = 2\cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right)(\gamma_1 + \gamma_2) \quad (9)$$

$$h_2 = -2\sin\left(\frac{k_x a}{2}\right)\sin\left(\frac{k_y a}{2}\right)(\gamma_1 + \gamma_2) \quad (10)$$

The parameters we used to obtain the energy dispersion shown in Fig. 1 are  $\varepsilon_\alpha = 1.2$ ,  $\varepsilon_\alpha = -1.1$ ,  $\alpha_1 = 0.6$ ,  $\alpha_1' = 0.1$ ,  $\beta_1 = -0.5$ ,  $\beta_1' = -0.1$ ,  $\gamma_1 = 0.49$ ,  $\gamma_2 = -0.1$  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  $H = I_{2 \times 2} \otimes H_0 + H_{so} + H'$ , and the perturbation of crystalline asymmetry can be written as  $H' = \Delta(I_{4 \times 4} \otimes \hat{\sigma}_z)$ . 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) –

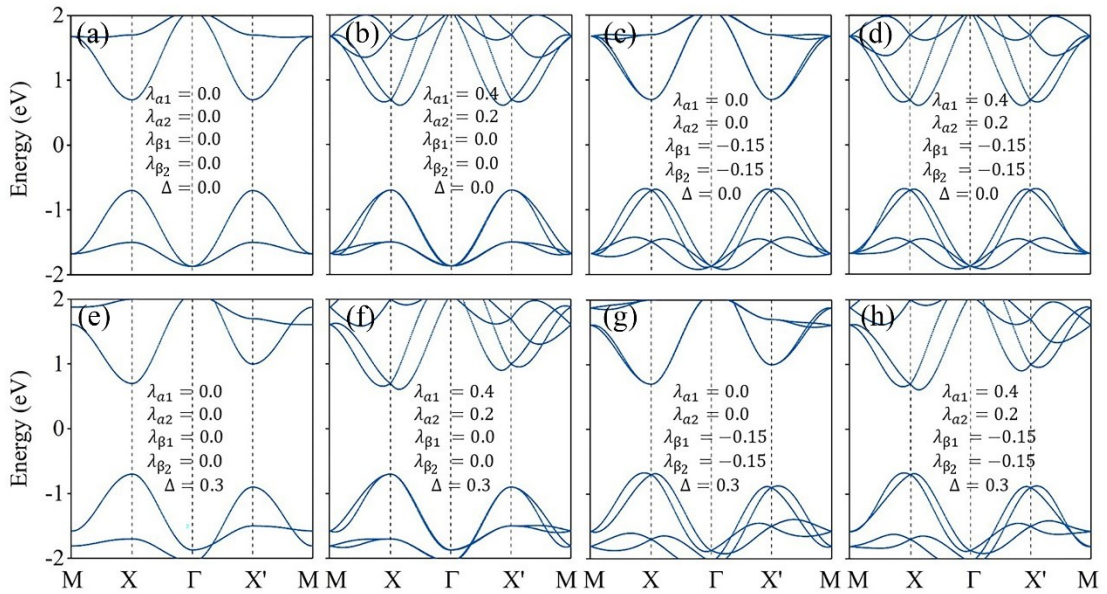
(h).

## References

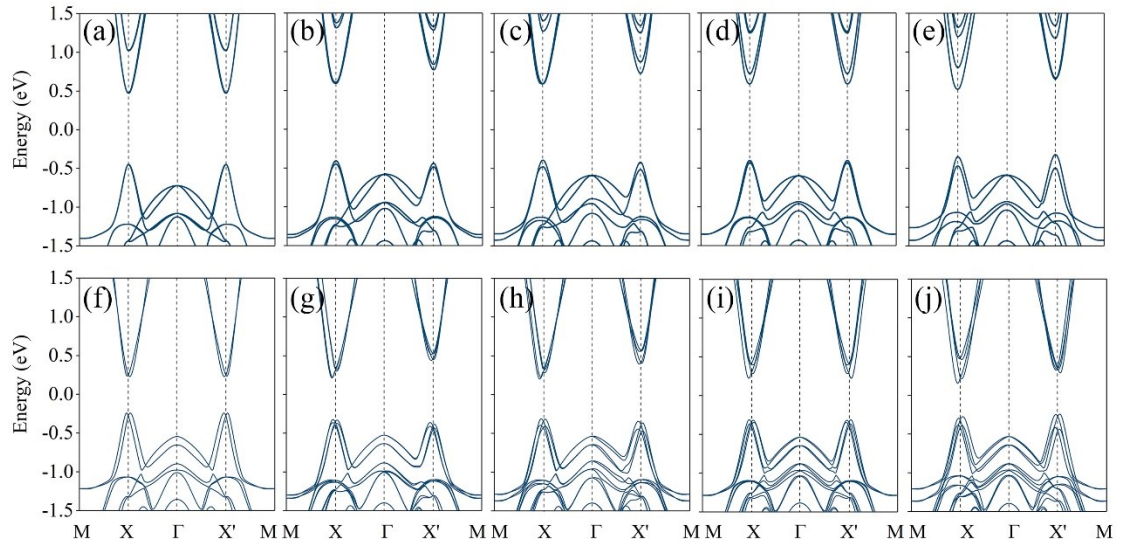
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**Table S1** Total energy per atom, Bi–S bond length, and lattice parameters of TL LaOBiS<sub>2</sub>. The total energy of the pristine structures (DS<sub>0</sub>) is set to zero as a reference.

	DS <sub>0</sub>	DS <sub>1</sub>	DS <sub>2</sub>	DS <sub>3</sub>
Energy (meV)	0	−2.227	−2.232	−2.226
Bi–S bond (Å)	2.879/2.879	2.735/3.040	2.736/3.038	2.726/3.048
<i>a</i> (Å)	4.036	4.036	4.036	4.036
<i>b</i> (Å)	4.036	4.036	4.036	4.036



**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<sub>0</sub> (b) DS<sub>1</sub>, (c) DS<sub>2</sub>, (d) DS<sub>3</sub> and (e) DS<sub>3</sub> with electric field applied, and the SOC is unconsidered. Lower panel exhibits the corresponding energy structures of (f) pristine DS<sub>0</sub> (g) DS<sub>1</sub>, (h) DS<sub>2</sub>, (i) DS<sub>3</sub> and (j) DS<sub>3</sub> with electric field applied, and take SOC into account. The Fermi level is set as zero.