Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information for

Effects of crystal deformation on spin-valley interplay and topological phase transition: A case study in VSi_2X_4 (X = N or P) monolayers

Zhenning Sun, Xinru Li*, Zhuojun Zhao, Yaojie Zeng, Yadong Wei* and Jian Wang

Section I

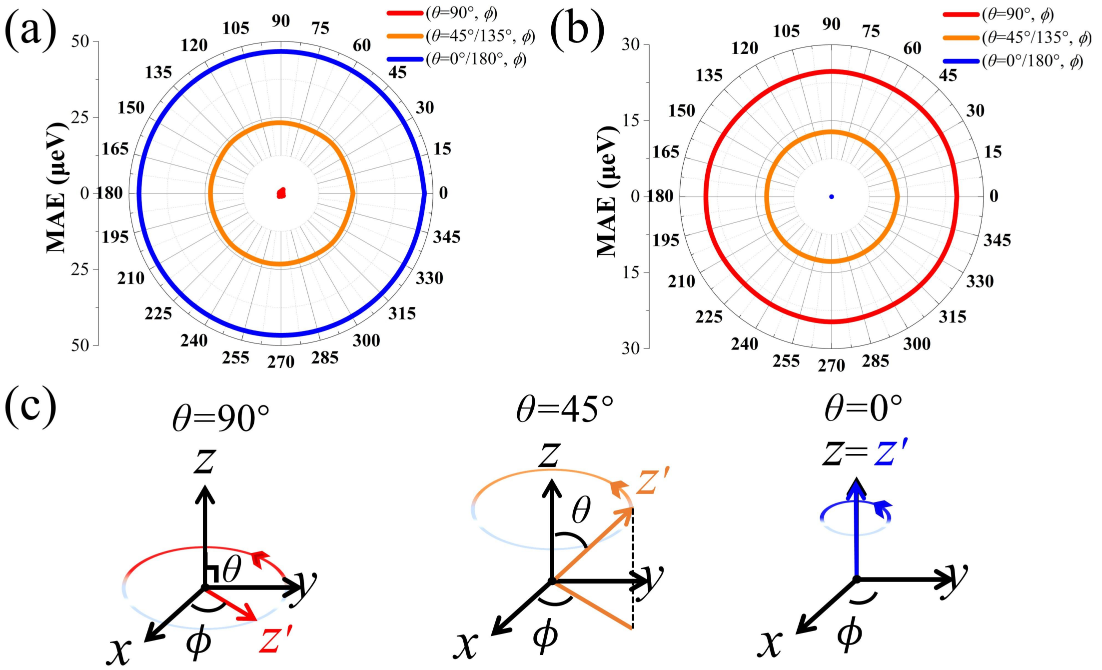

Figure S1 Angular dependence of magnetic anisotropy energy (MAE) arising from rotating the spin axis of (a) VSi_2N_4 and (b) VSi_2P_4 by scanning ϕ with θ fixed. (c) The reference cases for MAE calculation. The red, orange, and blue curves represent the different spinning surfaces of the spin.

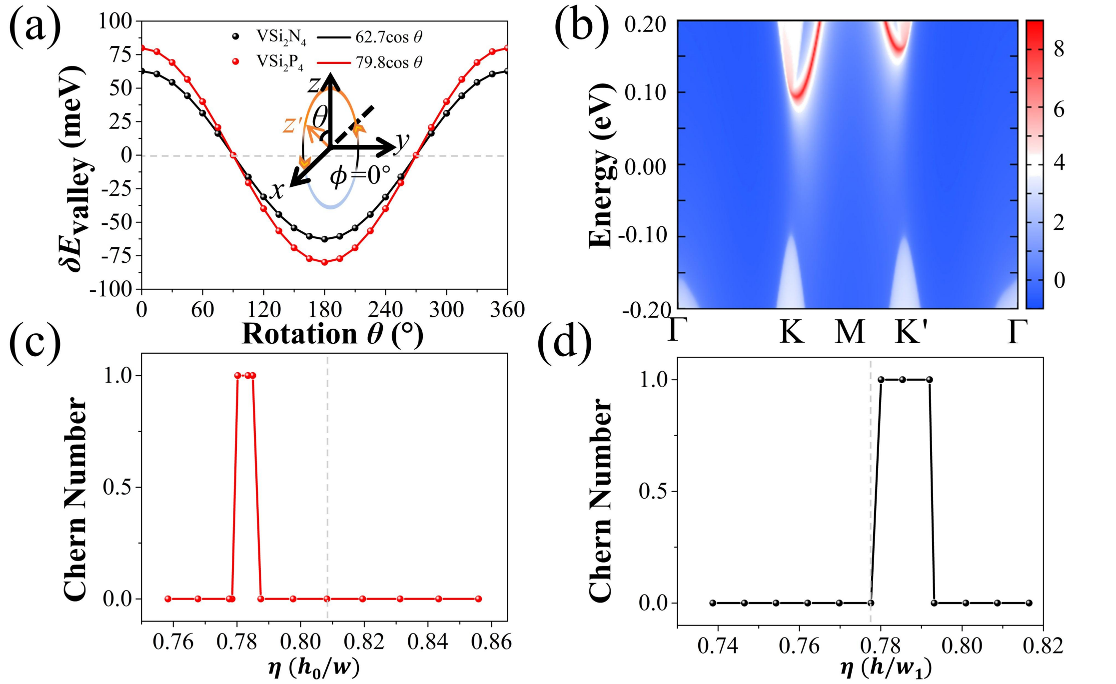

Figure S2 (a) A function between the polar angle (θ) and the valley polarization energies ($\delta E_{\text{valley}} = E^{\mathrm{K}} - E^{\mathrm{K'}}$) with azimuth angle $\phi = 0°$ for both VSi_2X_4 monolayers. The illustration shows the reference orientation of the spin. (b) Edge state of FM VSi_2N_4 monolayer with $C = 0$ at $\eta = 0.768$. (c) The Chern number C as a function of index η (by elongating or shortening w) for VSi_2N_4. (d) The Chern number C as a function of index η (by elongating or shortening h) for VSi_2N_4. The range display remains the same as in Fig. 4(c) and 4(d).

Section II

A. The SOC Hamiltonian

The magnetic moment of each spin site results from the spin moment interacting with the unquenched orbital moment under the spin-orbital coupling (SOC) $\hat{H}_{\mathrm{SOC}} = \lambda\hat{\boldsymbol{L}}\cdot\hat{\mathbf{S}}$. λ is the SOC constant. Let the magnetization direction be $\hat{n}(\theta,\phi)$, where θ and ϕ are the polar and azimuthal angles of the magnetization direction with respect to the un-rotated (x, y, z) coordinate system. The SOC term as can be writen as [1]

$$\begin{aligned}\hat{H}_{\mathrm{SOC}} &= \lambda(\hat{L}_z\hat{S}_z + \frac{1}{2}\hat{L}_+\hat{S}_- + \frac{1}{2}\hat{L}_-\hat{S}_+) \\ &= \hat{H}_{\mathrm{p}} + \hat{H}_{\mathrm{a}}\end{aligned} \tag{1}$$

$$\hat{H}_{\mathrm{p}} = \lambda\hat{S}_n\left(\hat{L}_z\cos\theta + \hat{L}_x\cos\phi\sin\theta + \hat{L}_y\sin\phi\sin\theta\right) \tag{2}$$

$$\begin{aligned}\hat{H}_{\mathrm{a}} =& \frac{1}{2}\lambda\Big[(\hat{S}_+ + \hat{S}_-)(-\hat{L}_z\sin\theta + \hat{L}_x\cos\phi\cos\theta + \hat{L}_y\sin\phi\cos\theta) \\ &+ i(\hat{S}_+ - \hat{S}_-)(\hat{L}_x\sin\phi - \hat{L}_y\cos\phi)\Big]\end{aligned} \tag{3}$$

where $\hat{S}_n = \hat{S}_{z'}$, $\hat{S}_+ = \hat{S}_{x'} + i\hat{S}_{y'}$, $\hat{S}_- = \hat{S}_{x'} - i\hat{S}_{y'}$, $\hat{L}_+ = \hat{L}_x + i\hat{L}_y$, $\hat{L}_- = \hat{L}_x - i\hat{L}_y$. See **Fig. 1(g)** for (x, y, z) and (x', y', z').

For ferromagnetic (FM) system, $\hat{H}_{\mathrm{a}}$ can be neglected. First principles calculations in the section *3.2. Magnetic ground states* shows that the two-dimensional $\mathrm{VSi_2X_4}$ systems possess properties of FM semiconductor, thus the systems can only consider the $\hat{H}_{\mathrm{p}}$.

B. Valley splitting in single layer [on valence band as an example]

The SOC Hamiltonian in FM systems is

$$\begin{aligned}\hat{H}_{\mathrm{SOC}} &= \lambda\hat{S}_{z'}\left(\hat{L}_z\cos\theta + \hat{L}_x\cos\phi\sin\theta + \hat{L}_y\sin\phi\sin\theta\right) \\ &= \lambda\hat{S}_{z'}\left(\hat{L}_z\cos\theta + \frac{1}{2}\hat{L}_+e^{-i\phi}\sin\theta + \frac{1}{2}\hat{L}_-e^{i\phi}\sin\theta\right)\end{aligned} \tag{4}$$

When the wavefunctions can be written as

$$|\psi_c\rangle = |d_{z^2}\rangle \tag{5}$$

$$|\psi_v^\tau\rangle = \sqrt{\frac{1}{2}}(|d_{x^2-y^2}\rangle + i\tau\,|d_{xy}\rangle) \tag{6}$$

where τ = ±1 represents the valley index. The energy difference between valleys at the K and K' points is given by

$$E_v^{\mathrm{K}} - E_v^{\mathrm{K}'} = i\,\langle d_{x^2-y^2}|\,\hat{H}_{\mathrm{SOC}}\,|d_{xy}\rangle - i\,\langle d_{xy}|\,\hat{H}_{\mathrm{SOC}}\,|d_{x^2-y^2}\rangle \tag{7}$$

$$E_c^{\mathrm{K}} - E_c^{\mathrm{K}'} = 0 \tag{8}$$

For ease of solution, spherical harmonic function is used for the basis vector conversion. The basis functions $|d_{xy}\rangle$ and $|d_{x^2-y^2}\rangle$ have the form

$$|d_{xy}\rangle = \sqrt{\frac{1}{2}}[-i(|Y_{2,+2}\rangle - |Y_{2,-2}\rangle)] \tag{9}$$

$$|d_{x^2-y^2}\rangle = \sqrt{\frac{1}{2}}\,(|Y_{2,+2}\rangle + |Y_{2,-2}\rangle) \tag{10}$$

By considering of

$$\begin{gathered}\hat{L}_z\,|Y_{l,m}\rangle = m\hbar\,|Y_{l,m}\rangle \\ \hat{L}_\pm\,|Y_{l,m}\rangle = \sqrt{(l \pm m + 1)(l \mp m)}\hbar\,|Y_{l,m\pm 1}\rangle\end{gathered} \tag{11}$$

we will have

$$\begin{aligned}\hat{H}_{\mathrm{SOC}}\,|d_{xy}\rangle &= -2i\hbar\lambda\hat{S}_{z'}\cos\theta\,|d_{x^2+y^2}\rangle + \hbar\lambda\hat{S}_{z'}\frac{i\sin\theta}{\sqrt{2}}(|Y_{2,-1}\rangle e^{-i\phi} - |Y_{2,+1}\rangle e^{i\phi}) \\ &\propto -2i\cos\theta\,|d_{x^2+y^2}\rangle + \frac{i\sin\theta}{\sqrt{2}}(|Y_{2,-1}\rangle e^{-i\phi} - |Y_{2,+1}\rangle e^{i\phi})\end{aligned} \tag{12}$$

$$\begin{aligned}\hat{H}_{\mathrm{SOC}}\,|d_{x^2-y^2}\rangle &= 2i\hbar\lambda\hat{S}_{z'}\left[\sqrt{\frac{1}{2}}(-i)(|Y_{2,+2}\rangle + |Y_{2,-2}\rangle)\cos\theta\right] + \hbar\lambda\hat{S}_{z'}\frac{\sin\theta}{\sqrt{2}}(|Y_{2,-1}\rangle e^{-i\phi} + |Y_{2,+1}\rangle e^{i\phi}) \\ &\propto 2i\cos\theta\,|d_{xy}\rangle + \frac{\sin\theta}{\sqrt{2}}(|Y_{2,-1}\rangle e^{-i\phi} + |Y_{2,+1}\rangle e^{i\phi})\end{aligned} \tag{13}$$

which results in

$$\langle d_{x^2-y^2}|\,\hat{H}_{\mathrm{SOC}}\,|d_{xy}\rangle = -2i\cos\theta \tag{14}$$

$$\langle d_{xy}|\,\hat{H}_{\mathrm{SOC}}\,|d_{x^2-y^2}\rangle = 2i\cos\theta \tag{15}$$

Inserting above relationship into $E_v^{\mathrm{K}} - E_v^{\mathrm{K}'}$, we obtain

$$\begin{aligned} E_v^{\mathrm{K}} - E_v^{\mathrm{K}'} &= i \langle d_{x^2-y^2} | \hat{H}_{\mathrm{SOC}} | d_{xy} \rangle - i \langle d_{xy} | \hat{H}_{\mathrm{SOC}} | d_{x^2-y^2} \rangle \\ &\propto \cos\theta \end{aligned} \tag{16}$$

which means that the valley splitting will gradually disappear when spin rotates from out-of-plane to in-plane as shown in **Fig. S2**.

REFERENCES

[1] D. Dai, H. Xiang, and M.-H. Whangbo, J. Comput. Chem. **29**, 2187 (2008).