Supporting Information for

Layer Hall effect in multiferroic two-dimensional materials

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Note 1: Calculation methods

Our first-principles calculations are performed based on density functional theory (DFT) [1] as implemented in the Vienna *ab initio* simulation package (VASP) [2]. The exchange-correlation interaction is described by generalized gradient approximation (GGA) [3] in the form of Perdew, Burke, and Ernzerhof (PBE) functional. All atoms and structures are fully optimized during structure relaxation with the convergence criteria of 10^{-6} eV and 0.01 eVÅ^{-1} for energy and force, respectively. The cutoff energy is set to 600 eV. Considering the strong correlations, the effective Hubbard U_{eff} = 2.0 eV is introduced for *d* electrons of Co atom according to previous work [4]. A Monkhorst-Pack k-point mesh of $15 \times 15 \times 1$ is used to sample the Brillouin zone. To avoid spurious interlayer interaction, a vacuum space of at least 20 Å is included. DFT-D3 method is adopted to describe the van der Waals interactions between individual layers [5]. The phonon dispersion is calculated using the PHONOPY code [6]. The ferroelectric polarization is evaluated using the Berry phase approach [7], and ferroelectric switching pathway is obtained by nudged elastic band (NEB) method [8]. We employ VASPBERRY to calculate the Berry curvature [9]. Anomalous Hall conductivity is calculated using the maximally localized Wannier functions (MLWFs) as implemented in WANNIER90 package [10].

Note 2: The low energy *k*·*p* model

This model only focuses on the energy near the K and K' valleys of the conduction and valence bands around the Fermi level. As the corresponding bands are mainly contributed by the *d* orbitals of transition metal (TM) atoms, the basis functions are usually composed of a linear combination of them. Under C_{3v} symmetry, the *d* orbitals of TM atom split into $A_1(d_{z^2})$ and $E(d_{xy}, d_{x^2-y^2}; d_{xz}, d_{yz})$. The bottom of the conduction band and the top of the valance band dominantly consist from the hybridization between d_{xz} and d_{yz} orbitals on the TM atom, involving with a inappreciable contribution from the $d_{x^2-y^2}$ and d_{xy} states. To describe the conduction and valence bands, the linear combinations of d_{xz} and d_{yz} orbitals are chosen as basis functions, then, symmetry adapted basis functions are chosen as:

$$\left|\varphi_{c}^{\tau}\right\rangle = \frac{1}{\sqrt{2}}\left(\left|d_{xz}\right\rangle - i\tau\left|d_{yz}\right\rangle\right), \left|\varphi_{v}^{\tau}\right\rangle = \frac{1}{\sqrt{2}}\left(\left|d_{xz}\right\rangle + i\tau\left|d_{yz}\right\rangle\right).$$

Under the above basis functions, the Hamiltonian is a 2×2 matrix:

$$H_0 = \begin{bmatrix} H_{cc} & H_{cv} \\ H_{vc} & H_{vv} \end{bmatrix}.$$

The expansion to second order approximation near K and K' valleys is given as:

$$H_{0}^{u}(\mathbf{k}) = \begin{bmatrix} \frac{\Delta}{2} + \varepsilon + t_{11}'(q_{x}^{2} + q_{y}^{2}) & t_{12}(\tau q_{x} - iq_{y}) + t_{12}'(\tau q_{x} + iq_{y})^{2} \\ t_{12}(\tau q_{x} + iq_{y}) + t_{12}'(\tau q_{x} - iq_{y})^{2} & -\frac{\Delta}{2} + \varepsilon + t_{22}'(q_{x}^{2} + q_{y}^{2}) \end{bmatrix},$$

where superscript *u* denotes upper layer of the bilayer lattice, Δ is the band gap of single layer at the valleys, ε is a correction energy bound up with the Fermi energy, t_{12} is the effective nearest-neighbor intralayer hopping integral, t_{11}' , t_{12}' , and t_{22}' are parameters related to the second-nearest-neighbor intralayer hopping and $\mathbf{q} = \mathbf{k} - \mathbf{K}$ is the momentum vector. The index $\tau = +1$ (-1) represents the K (K') valley.

The multiferroic bilayer lattice has A-type AFM coupling and FE bilayer stacking pattern. Considering SOC effect and exchange interaction of localized d electrons, the total Hamiltonian of the bilayer system for the case of 0° rotation is expressed as follows:

$$H(\mathbf{k}) = \begin{bmatrix} H_0^u(\mathbf{k}) + H_{\text{SOC}} + H_{ex} - H_P & H_{\perp} \\ H_{\perp} & H_0^l(\mathbf{k}) + H_{\text{SOC}} - H_{ex} + H_P \end{bmatrix}$$

Here, $H_0^l(\mathbf{k})$ has the same form as $H_0^u(\mathbf{k})$. The SOC term can be written as a 2 × 2 matrix:

$$H_{\rm SOC} = \begin{bmatrix} \tau s \lambda_c & 0 \\ 0 & \tau s \lambda_v \end{bmatrix},$$

where the index s = +1 (-1) represents spin-up (-down) state. $2 \lambda_{c(v)}$ is defined as the spin splitting at the bottom of the conduction band (the top of the valance band) in single-layer lattice. The exchange interaction is given by:

$$H_{ex} = \begin{bmatrix} -sm_c & 0\\ 0 & -sm_v \end{bmatrix},$$

where $m_{c(v)}$ represents the effective exchange splitting at the band edge of conduction band (valance

band) for single-layer lattice. H_{\perp} is the interlayer hopping term, which can be written as:

$$H_{\perp} = \begin{bmatrix} t_{cc} & 0 \\ 0 & t_{vv} \end{bmatrix}.$$

Note that the minor interlayer hopping between conduction band and valence band is neglected. t_{cc} and t_{vv} are the interlayer hopping energies for the conduction and valence bands, respectively.

 H_P represents the effect of out-of-plane electric polarization, which is given by:

$$H_P = I_2 \otimes \frac{U}{2}.$$

 I_2 here is the 2 × 2 identity matrix. As a result, there is an energy shift of +U/2 for lower layer and the one of -U/2 for upper layer.

For the case of 180° rotation, the total Hamiltonian is expressed as follows:

$$H'(\mathbf{k}) = \begin{bmatrix} H_0^u(\mathbf{k}) - H_{\text{SOC}} + H_{ex} - H_p' & H_{\perp}' \\ H_{\perp}' & H_0^l(\mathbf{k}) + H_{\text{SOC}} - H_{ex} + H_p' \end{bmatrix}.$$

Here, $H_0^u(\mathbf{k})$ is the complex conjugate of $H_0^l(\mathbf{k})$. H_{\perp}' term is given by:

$$H_{\perp}' = \begin{bmatrix} t_{cc} & 0 \\ 0 & t_{vv} \end{bmatrix}.$$

 H_{P}' term is given by:

$$H_{P}'=I_2\otimes\frac{U'}{2}.$$

Note that other terms are invariable since the parameters describing intralayer effects are based on the single-layer lattice.





Figure S1. Schematic diagrams of low-energy conduction band near the K and K' valleys for (a) multiferroic hexagonal lattice with opposite magnetization orientations and (b) multiferroic bilayer lattice with 180° rotation under state-I (solid line in the top) and state-II (bold dashed line in the bottom). In (a, b), dark blue (brown) and light blue (orange) curves correspond to spin-down (up) bands from lower layer and upper layer, respectively. (c) Low-energy conduction bands around the K and K' valleys and the schematic representations of the Berry curvature for state-I and state-II. Blue and red cones in (c) correspond to the spin-down bands from lower layer and spin-up bands from upper layer, respectively.



Note 4: Low-energy band dispersions around the K and K' valleys obtained from the *k*·*p* model

Figure S2. Low-energy (a,b) conduction band and (c,d) valence band dispersions around the K and K' valleys for the case of 0° rotation in (a,c) state-I and (b,d) state-II obtained from the *k*·*p* model. Upward-pointing (downward-pointing) triangles correspond to electronic states from lower (upper) layer.



Figure S3. Low-energy (a,b) conduction band and (c,d) valence band dispersions around the K and K' valleys for the case of 180° rotation in (a,c) state-I and (b,d) state-II obtained from the $k \cdot p$ model. Upward-pointing (downward-pointing) triangles correspond to electronic states from lower (upper) layer.



Figure S4. Phonon spectra of (a) single-layer Co_2CF_2 , and -P phase of (b) AC and (c) AB' patterns of bilayer Co_2CF_2 .



Note 6: Electronic properties of single-layer Co₂CF₂

Figure S5. Spin-resolved band structures of single-layer Co_2CF_2 (a) without SOC; (b) and (c) with SOC for magnetic moment of Co along the positive and negative *z* direction (out of plane), respectively. (d) Orbital-resolved band structures of single-layer Co_2CF_2 . The Fermi level is set to 0 eV.

Note 7: Stacking patterns and calculation details of bilayer Co₂CF₂.



Figure S6. Crystal structures for different stacking patterns of bilayer Co₂CF₂.



Figure S7. Stacking energies under the magnetic ground state with respect to the -P phase of AC pattern. The circular symbols represent the -P phases, and the triangular symbols represent the antiferroelectric stacking.

Table S1. Lattice constant (Å), interlayer distance (Å), energy difference between FM and AFM coupling (meV), band gap (eV), valley polarization (meV), electric polarization (pC m⁻¹) and FE switching barriers (eV/f.u.) for the -/+ P phase of AC/AB and AB'/AC' patterns in the 0° and 180° rotation cases, respectively.

	а	d	E_{FM} - E_{AFM}	Gap	ΔE_c	Polarization	Barrier
0° rotation	2.85	2.46	0.10	0.131	58.9/-58.9	-15.12/15.12	0.144
180° rotation	2.85	2.43	0.11	0.128	59.4/59.4	-15.03/15.03	0.142



Note 8: Electronic properties for -P phase of AB' pattern and +P phase of AC' pattern

Figure S8. Crystal structures of bilayer Co_2CF_2 for (a) -P phase of AB' pattern and (d) +P phase of AC' pattern. Layer-resolved and spin-resolved band structures of bilayer Co_2CF_2 for (b, c) -P phase of AB' pattern and (e, f) +P phase of AC' pattern. The Fermi level is set to 0 eV.

Figure S8 displays the corresponding results for -P phase of AB' pattern and +P phase of AC' pattern, which exhibit an indirect band gap of 0.128 eV. Similar to the case of AC and AB patterns, AB' and AC' patterns also have a pair of valleys in the conduction band. However, because of the 180° rotation operation on one layer, the valley index is exchanged. In this regard, the CBM of -P and +P phases are both located at the K point and the spontaneous valley polarization are found to be $\Delta E_c = 59.4$ meV, as shown in **Figure S8(c, f)**. For -P phase of AB' pattern and +P phase of AC' pattern, the CBM is from spin-down channel of lower layer and spin-up channel of upper layer, respectively (**Figure S8**). Therefore, similar to AC and AB patterns, the layer degree of freedom is also coupled with the band edge, spin and valley physics for AB' and AC' patterns.





Figure S9. Comparison of enlarged low-energy band dispersions around the K and K' valleys from the $k \cdot p$ model (open triangles) and the corresponding results from first-principles calculations (solid lines). Conduction band for -P phase of (a) AC and (c) AB' patterns, and +P phase of (b) AB and (d) AC' patterns of bilayer Co₂CF₂.

Table S2. The low energy $k \cdot p$ model parameters obtained by fitting to first-principles calculations. The parameters describing intralayer effects are obtained from the single-layer band structures directly. All of the parameters are in units of eV.

Δ	ϵ	t_{11}'	<i>t</i> ₁₂	t_{12}'	<i>t</i> ₂₂ ′	λ_c	λ_v	m_c	m_v	t_{cc}/t_{cc}'	t_{vv} / t_{vv} '	U / U'	
1.95	0.278	0.006	0.525	0.076	0.031	0.029	0.021	0.871	0.29	0.147/0.16	0.01/0.007	0.619/0.613	

Note 10: The feasibility of realizing and manipulating LP-AHE.



Figure S10. Anomalous Hall conductance for -P phase of (a) AC and (b) AB' patterns of bilayer Co_2CF_2 .



Figure S11. Energy barriers of FE switching from (a) -P phase of AC pattern to +P phase of AB pattern and (c) -P phase of AB' pattern to +P phase of AC' pattern. Variation of out-of-plane electric polarization of bilayer Co_2CF_2 under FE switching from (b) -P phase of AC pattern to +P phase of AB pattern and (d) -P phase of AB' pattern to +P phase of AC' pattern.

References:

- 1. W. Kohn, L. Sham, Self-Consistent Equations Including Exchange and Correlation Effects. Phys. Rev. 140, A1133 (1965).
- 2. G. G. Kresse, J. J. Furthmuller, Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. Phys. Rev. B: Condens. Matter Mater. Phys. 54, 11169 (1996).
- 3. J. P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 77, 3865 (1996).
- 4. C. Huang, J. Zhou, H. Sun, F. Wu, Y. Hou, E. Kan, Toward Room-Temperature Electrical Control of Magnetic Order in Multiferroic van der Waals Materials. Nano Lett. 22, 5191 (2022).
- 5. S. Grimme, S. Ehrlich, L. Goerigk, Effect of the Damping Function in Dispersion Corrected Density Functional Theory. J. Comput. Chem. 32, 1456 (2011).
- 6. X. Gonze, C. Lee, Dynamical Matrices, Born Effective Charges, Dielectric Permittivity Tensors, and Interatomic Force Constants from Density-Functional Perturbation Theory. Phys. Rev. B 55, 10355 (1997).
- R. D. King-Smith, D. Vanderbilt, Theory of Polarization of Crystalline Solids. Phys. Rev. B 47, 1651 (1993).
- 8. G. Henkelman, B. P. Uberuaga, H. Jónsson, A Climbing Image Nudged Elastic Band Method for Finding Saddle Points and Minimum Energy Paths. J. Chem. Phys. 113, 9901 (2000).
- 9. T. Fukui, Y. Hatsugai, H. Suzuki, Chern Numbers in Discretized Brillouin Zone: Efficient Method of Computing (Spin) Hall Conductances. J. Phys. Soc. Jap. 74, 1674 (2005).
- A. A. Mostofi, J. R. Yates, G. Pizzi, Y.-S. Lee, I. Souza, D. Vanderbilt, N. Marzari, An Updated Version of Wannier90: A Tool for Obtaining Maximally-Localised Wannier Functions. Comput. Phys. Commun. 185, 2309 (2014).