Out-of-plane polarization and topological magnetic vortices in multiferroic CrPSe$_3$

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Two-dimensional (2D) multiferroic materials are ideal systems for exploring new coupling mechanisms between different ferroic orders and producing novel quantum phenomena with potential applications. We employed first-principles density functional theory calculations to discover intrinsic ferroelectric and anti-ferroelectric phases of CrPSe$_3$, which show ferromagnetic order and compete with the centrosymmetric phase with an antiferromagnetic order. Our analysis show that the electrical dipoles of such type-I multiferroic phases come from the out-of-plane displacements of phosphorus ions due to the stereochemically active lone pairs. The coupling between polar and magnetic orders creates the opportunity for tunning the magnetic ground state by switching from the centrosymmetric to the ferroelectric phase using an out-of-plane electric field. In ferroelectric and antiferroelectric phases, the combination of easy-plane anisotropy and Dzyaloshinskii-Moriya interactions (DMI) indicate they can host topological magnetic vortices like meron pairs.

Multiferroic systems concomitantly host two or more ferroic orders and promise novel applications by coupling different order parameters and supporting exotic quantum states [1]. In particular, intrinsic magnetoelectric multiferroics, such as BiFeO$_3$ and YMnO$_3$, are of special interest not only because they are model systems for understanding magnetoelectric coupling, but also because they have unusual features like conductive domain walls [2–4] and photostriction [5, 6]. As different ferroic ordering [7–11] have recently been found in 2D materials, researchers are devoting more attention to 2D multiferroic systems [12]. However, intrinsic bulk magnetoelectrics, let alone 2D magnetoelectrics, are difficult to find owing to the contradicting requirements for chemical conditions supporting ferroelectricity and magnetism [13].

Recently, artificial 2D multiferroic systems have been proposed, which involve combining materials with diverse ferroic orders to generate heterostructures [14], doping magnetic ions into ferroelectrics [15], or creating bilayer structures with customized stacking orders [16]. Theoretically, a few intrinsic 2D magnetoelectrics have also been predicted. For example, Zhang et al. proposed a type-II multiferroic MXene with weak electric dipole moments induced by the helical magnetic order [17]. Qi et al. discovered that a class of monolayer quaternary compounds has an anti-ferroelectric ground-state structure combined with long-range magnetism [18]. Several groups predicted that monolayer VOX$_2$ (X = Cl, Br, I) will have magnetic ordering as well as in-plane ferroelectricity [19, 20]. In monolayer VOI$_2$, the combination of iodine’s strong spin-orbital coupling and breaking inversion symmetry causes large DMI [21, 22] and topological magnetic vortices [19]. Meanwhile, there are still debates in the literature about the metallicity of VOI$_2$, which hinders its in-plane ferroelectricity [23]. Experiments have yet to corroborate these pioneering predictions of intrinsic 2D multiferroics.

In this Letter, we revisit the layered Van der Waals material CrPSe$_3$ using first-principles calculations and Monte-Carlo simulations. Our study reveals unexpected ferroelectric and anti-ferroelectric phases which has ferromagnetic orders and compete with the centrosymmetric phase, which is antiferromagnetic. The coupling between magnetic ground states and polar orders sheds light on tunning magnetism using electric field. In addition, the polar and anti-polar phases also display sizable DMI and easy-plane anisotropy, which support the formation of topological magnetic vortices such as merons [24].

CrPSe$_3$ belongs to the MPX$_3$ family of metal thio- and selenophosphites, where M stands for transition metal elements and X for sulfur or selenium [25]. Most MPX$_3$, including CrPSe$_3$, have layered structures stabilized by Van der Waals interactions, but they appear in various stacking orders. To investigate the structure and magnetic order of CrPSe$_3$, we performed density functional theory (DFT) calculations based on a plane-wave pseudopotential framework [26, 27]. When comparing various exchange-correlation functionals [28, 29], we found PBEsol and local-density approximation functionals provide a better overall description of the structural properties of bulk CrPSe$_3$ (as shown in Supplementary materials [30][31–33]). Here all results presented were calculated with the PBEsol functional.

We carried out DFT+U calculations [34] with effective parameters $U_{\text{eff}}$ to optimize the structure and determine the energy of monolayer and bulk CrPSe$_3$ [25]. Interestingly, in addition to the centrosymmetric phase similar to other MPX$_3$, we found an unexpected polar phase with phosphorus ions tilting along the out-of-plane direction.
“FE-FM”, for example, denotes the phase with the polar (i.e., paraelectric or PE) structures with the FM and three 1 (c), the energies of 12 configurations are compared with the energy of the FE-FM phase, which is set as the reference point. Overall, the energies of the PE phases change with $U_{\text{eff}}$ at a different rate compared to the AFE and FE phases. The difference is attributed to different electron occupations of the Cr 3d-orbitals (i.e., different oxidation states of Cr atoms) in polar and non-polar structures. For a reasonable range of $U_{\text{eff}} \in [2.0, 3.0]$ eV of Cr [36], the FE-FM, AFE-FM, and PE-ST phases are competing phases with similar energies. The competition between AFE-FM, FE-FM, and PE-ST phases of CrPSe$_3$ suggest the possibility of the coexistence of these three phases. Similar competitions between various phases has also been observed in ferroelectrics such as In$_2$Se$_3$ [37], CuInP$_2$Se$_6$ [38], and so on [39–41].

Among different multiferroic configurations, the AFE-FM phase has the lowest energy when $U_{\text{eff}} < 2.5$ eV, while PE-ST is the lowest when $U_{\text{eff}} > 2.5$ eV, as shown in Fig. 1 (c). The AFE-FM and FE-FM phases have small energy differences within 12 meV/f.u. As $U_{\text{eff}}$ rises over 3.2 eV, the energy of FE-FM phase falls below that of AFE-FM phase. Examining the magnetic orders, we find FM order remains the lowest-energy magnetic order for both the FE and AFE structures. When $U_{\text{eff}} > 1.5$ eV, the PE phase has the ST magnetic order, which changes to the FM order when $U_{\text{eff}}$ is lower than 1.5 eV. When $U_{\text{eff}}$ is set to 0, which is an improper value for Cr, the predicted magnetic order of the PE structure is the FM order, which matches prior work [42] utilizing the PBE+D2 method [43]. We also conducted PBE+D2 [29] computations, which quantitatively agree with earlier results for these magnetic ordering [42], reinforcing the reproducibility of our work.

Using a frozen-phonon method [44], we computed the phonon spectra of the polar (as shown in Fig. 2 (a)), centrosymmetric, and antipolar structures. Their phonon dispersions show no imaginary frequency modes and demonstrate dynamical stability. Our Berry-phase calculations [45] show the polar phase has an electric polarization density of 3.98 pC/m, which is larger than the predicted type-II multiferroic Hf$_2$VC$_2$F$_2$ (1.98 pC/m) [17]. The nudged-elastic band (NEB) approach is adopted to determine the energy barrier $E^{P \rightarrow \text{AFE}}$ of collectively reversing the electric polarization direction [46]. The switching energy barrier $E^{P \rightarrow \text{AFE}}$ changes from 0.05 to 0.13 eV/f.u when $U_{\text{eff}}$ varies from 3.0 eV to 2.0 eV. When the $U_{\text{eff}}$ is set to a value greater than 2.4 eV, a local minimum similar to the PE phase appears in the middle of the transition path, as shown in Fig. 2 (b). The energy barrier to leave the potential well around the local minimum structure, however, is reasonably low (less than 100 meV/f.u. for $U_{\text{eff}} < 3.0$ eV) to permit a switching of polarization under suitable electric field, as it is comparable to other out-of-plane 2D ferroelectrics [47, 48]. Notably, the interdependence between the polar and magnetic order in CrPSe$_3$ is uncommon and offers an opportunity for altering magnetic ground-states by inducing a transition from the centrosymmetric structure to the polar structure.

Similarly, we estimated the energy barrier $E^{\text{FE} \rightarrow \text{AFE}}$ between the FE-FM and AFE-FM phases. The energy profile of transitioning from the FE-FM phase to the AFE-FM phase is shown in Fig. 2 (c). There are two energy barriers along the transition path. The crystal structure transforms into an intermediate configuration close to the PE phase after passing through the first energy barrier. The intermediate configuration corresponds to the dip on energy curve of the switching process, as shown in Fig. 2 (c). After overcoming the second barrier, the structure turns into the AFE structure. Overall, the heights of these two barriers are on the order of 40 meV/f.u., which is in the same order-of-magnitude as the energy barrier $E^{P \rightarrow \text{AFE}}$ of switching the polarization of the FE
phase. Although the FE-FM phase is metastable, the energy ordering of the FE-FM and AFE-FM phases can be reversed with moderate electric fields or strain (see the supplementary materials), suggesting the possibility of inducing a phase transition from the AFE-FM phase to the FE-FM phase using electric field or strain.

For bulk CrPSe$_3$ phases, we considered additional interlayer antiferroelectric and interlayer antiferromagnetic orders (see Supplementary Material for details of these two orders), and constructed 20 different multiferroic configurations. The dependence of ground-state phases on $U_{\text{eff}}$ is similar to the situation of monolayer CrPSe$_3$. As the Hubbard $U_{\text{eff}}$ parameter changes, the lowest-energy configuration is the PE-ST phase when $U_{\text{eff}}$ parameter is between around 2.6 to 3.6 eV, but changes to the AFE-FM phase when $U_{\text{eff}}$ drops to below 2.6 eV. With $U_{\text{eff}}$ larger than 2.0 eV, our calculation results show that the ground-state magnetic order of the centrosymmetric phase is anti-ferromagnetic ST ordering. Recently, a theoretical study shows that monolayer and bulk PE phase of CrPSe$_3$ have NL order, while the ST order has an energy slightly higher than the NL order [49]. The discrepancy between this work and our study likely originates from different types of pseudopotentials (see Supplementary materials for more details). Experiments show that bulk CrPSe$_3$ has an anti-ferromagnetic order [50], while its detailed anti-ferromagnetic spin arrangement is not determined.

Because phosphorous contributes polarization and chromium contributes magnetism, the coexistence of polar and magnetic order does not violate the $d^9$-rule [13] and the FE-FM and AFE-FM phases are type-I multiferroic phases. The out-of-plane displacements of phosphorus ions in polar and anti-polar structures are related to the oxidation states of Cr ions. In the centrosymmetric phase, the oxidation state of chromium ions are Cr$^{2+}$, similar as the transition metal ions M$^{2+}$ in most MPSe$_3$ systems [25]. However, in the anti-polar and polar phases, it becomes Cr$^{3+}$. Compared to the centrosymmetric structure with Cr$^{2+}$, a pair of Cr$^{3+}$ ions in the polar structures give up two electrons, generating a lone pair located nearby phosphorus atoms. As a result, analogous to BiFeO$_3$ [1], lone-pair electrons result in an asymmetric charge distribution that pushes the phosphorus atoms out of plane. The isosurface map of the electron-localization function (ELF) visualizes the position of lone pairs and the consequent structural change, as illustrated in Fig. 2 (d).

With the spin-orbit coupling effects contributed by Se atoms and the breaking local inversion symmetry, the AFE-FM and FE-FM phases can potentially show significant DMI, which can lead to topological spin textures. Here an extended Heisenberg model describing the magnetic interactions in a 2D spin-lattice is considered:

$$H = \sum_{i,j} J_1 \mathbf{n}_i \cdot \mathbf{n}_j + \sum_{i,j} J_2 \mathbf{n}_i \cdot \mathbf{n}_j + \sum_{i,j} \mathbf{D}_1 \cdot (\mathbf{n}_i \times \mathbf{n}_j) + \sum_i A_{\alpha} n_{\alpha}^2$$

where $\mathbf{n}_i$ are unit vectors; $<>$ and $<<>$ stand for nearest and next-nearest neighbors, respectively; $J_{1,2}$ are the symmetric exchange coupling and $\mathbf{D}_1$ is the DMI coupling; $A_{\alpha}$ describes the single-ion magnetic anisotropy. The exchange parameters are calculated using a four-states mapping method for FE-FM and AFE-FM phases [51]. Table I contains the magnetic parameters of the FE-FM phase. Details on the magnetic parameters of the AFE-FM phase are presented in the Supplementary Material. Both FE-FM and AFE-FM phase have easy-plane magnetic anisotropy and large nearest-neighbor DMI interaction $\mathbf{D}_1$. The FE-FM phase retains the $C_3$ symmetry of the PE phases and its easy-plane anisotropy is close to the XY model. According to the Mermin-Wagner theorem [52], the FE phase does not allow long-range FM order in a perfect infinite-size crystal. In a finite-size sample of the FE-FM phase, however, weak ferromagnetism can arise. In its easy plane, the AFE-FM phase has an easy axis along $y$-direction, which violates the continuous $O(2)$ symmetry and allows for long-range ferromagnetic order.

| $J_1$  | $J_2$  | $A_x$  | $A_y$  | $\mathbf{D}_1$ |
|--------|--------|--------|--------|----------------|
| -21.7  | -0.75  | -0.27  | -0.27  | [0.3, 0.0, -1.9] |

Because the electric polarization for the FE-FM phase...
According to Moriya’s rules \[22\], the DMI vector \(D\) has a mirror plane passing through two nearest-neighbour Cr ions. The FE-FM structure has a mirror plane passing through \(\text{Cr}_1\text{Cr}_2\), as well as the middle point \(M\) of the line \(\text{Cr}_1\text{Cr}_2\) connecting them. Fig. 3 (a) depicts the local structure of two nearest-neighbour Cr ions. The FE-FM structure has a mirror plane passing through \(M\) and is perpendicular to \(\text{Cr}_1\text{Cr}_2\). According to Moriya’s rules \[22\], the DMI vector \(D_1\) should also be perpendicular to \(\text{Cr}_1\text{Cr}_2\). Our computational results agree with these rules. The distortion of Se ions, which mediates the indirect exchange contacts between nearby Cr ions, accounts for the large out-of-plane component of \(D_1\). In the PE phase, atoms \(\text{Cr}_1\), \(\text{Cr}_2\), \(\text{Se}_1\), and \(\text{Se}_2\) are coplanar and form a parallelogram in the PE phase. In contrast, in the FE phase, the displacements of selenium ions make the dihedral angle \(\angle\text{Se}_1\text{Cr}_1\text{Cr}_2\text{Se}_2 = 168^\circ\) and bond lengths \(d_{\text{Cr}_1\text{Se}_1} \neq d_{\text{Cr}_1\text{Se}_2}\), shown in Fig. 3 (a). This local environment breaks the inversion symmetry and results in large out-of-plane components of \(D_1\). The modest dipole field induced by the shifted phosphorous ions, on the other hand, creates a significantly smaller in-plane DMI component.

The synergy of out-of-plane DMI components and in-plane magnetic anisotropy favors the formation of meron and anti-meron pairs \[19, 53\] in both FE-FM and AFE-FM phases.. Monte-Carlo (MC) simulations \[54\] of the magnetic Hamiltonian were conducted for the FE-FM and AFE-FM phases. We initialized the spin-lattice with random spin vectors and examine its evolution in MC simulations. Typically, after a few thousand MC steps, small in-plane ferromagnetic domains emerge and topologically non-trivial spin vortices and anti-vortices form on the domain boundaries. Such topologically non-trivial magnetic excitations have a topological charge of one half or negative one half, suggesting they are anti-merons or merons. Notably, merons appear even under \(T = 30\) K, which is higher than the allowed temperature range for merons to emerge in CrCl\(_3\) \[55\] and VOI\(_2\) \[19\]. Furthermore, the formation of merons is robust to the variation of DMI parameters and Heisenberg exchange parameters. Merons and antimerons are still observed at around \(T = 5\) K even when the magnitude of DMI vector decreases by 50%. In MC simulations, merons with winding numbers \(w = 1\) and \(w = -1\), which are known as vortex and anti-vortex merons, emerge in pairs, similar as in prior investigations \[56, 57\]. Fig. 3 (b) is a typical snapshot of MC simulations for the FE-FM phase, showing real-space spin textures and the distribution of topological charge in the spin-lattice. Clearly, the topological charge density is concentrated near merons or antimerons. As the MC simulation progresses, vortex (anti)meron tend to attract nearby antivortex (anti)merons. Such annihilation phenomenon is also observed in Landau-Lifshitz-Gilbert simulations for CrCl\(_3\) \[55, 56\] and kagome magnets \[58\]. In the FE-FM phase, merons and anti-merons will all be annihilated after a long enough MC simulation (typically after \(5 \times 10^5\) steps). In the AFE-FM phase, unusual long-lived vortex and anti-vortex meron pairs appears. Even after \(2 \times 10^6\) MC steps, these topological excitation pairs stabilize on the boundaries of adjacent ferromagnetic domains and exhibit no tendency to annihilate each other. Three long-lived vortex-antivortex pairs are shown in Fig. 3 (c). Such long-lived merons are typically located on the domain boundaries parallel to the \(y\) or \(x\)-axis.

In all, we comprehensively investigated the structures and magnetic orders of different phases in bulk and monolayer CrPSe\(_3\). We identify two multiferroic phases of CrPSe\(_3\), namely a ferroelectric and an anti-ferroelectric phase with ferromagnetic orders, while the experimentally
studied centrosymmetric phases is antiferromagnetic. The multiferroic phases are both dynamically stable and compete with the centrosymmetric phase. The metastable ferroelectric phase carries an out-of-plane electric polarization and is separated from the centrosymmetric and anti-ferroelectric phase by smantorable energy barriers. The coupling between the polar order and magnetic ground state provide new opportunities for tuning magnetism through electric field. Moreover, with significant out-of-plane DMI interaction and in-plane anisotropy, the ferroelectric and anti-ferroelectric phases can potentially host magnetic topological excitations including merons and antimerons under suitable conditions. Our work suggests CrPSe$_3$ is a promising material for exploring intrinsic low-dimensional multiferroicity and topological magnetic excitations.

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[1] N. A. Spaldin and R. Ramesh, “Advances in magnetoelectric multiferroics,” Nature Materials 18, 203–212 (2019).
[2] S. Ghara, K. Geirhos, L. Kuerten, P. Lunkenheimer, V. Tsurkan, M. Fiebig, and I. Kézsmárki, “Giant conductivity of mobile non-oxide domain walls,” Nature Communications 12, 3975 (2021).
[3] J. Seidel, L. W. Martin, Q. He, Q. Zhan, Y.-H. Chu, A. Rother, M. E. Hawkridge, P. Maksymovych, P. Yu, M. Gajek, N. Balke, S. V. Kalinin, S. Gemming, F. Wang, G. Catalan, J. F. Scott, N. A. Spaldin, J. Orenstein, and R. Ramesh, “Conduction at domain walls in oxide multiferroics,” Nature Materials 8, 229–234 (2009).
[4] Dennis Meier, “Functional domain walls in multiferroics,” Journal of Physics: Condensed Matter 27, 463003 (2015).
[5] Tzu-Chiao Wei, Hsin-Ping Wang, Heng-Jui Liu, Dung-Sheng Tsai, Jr-Jian Ke, Chung-Lun Wu, Yu-Peng Yin, Qian Zhan, Gong-Ru Lin, Ying-Hao Chu, and Jr-Hau He, “Photostriiction of strontium ruthenate,” Nature Communications 8, 15018 (2017).
[6] B. Kundys, M. Viret, D. Colson, and D. O. Kundys, “Light-induced size changes in bifeo3 crystals,” Nature Materials 9, 803–805 (2010).
[7] Cheng Gong, Lin Li, Zhenglu Li, Huiwen Ji, Alex Stern, Yang Xia, Ting Cao, Wei Bao, Chenzhe Wang, Yuan Wang, Z. Q. Qu, R. J. Cava, Steven G. Louie, Jing Xia, and Xiang Zhang, “Discovery of intrinsic ferromagnetism in two-dimensional van der waals crystals,” Nature 546, 265–269 (2017).
[8] Bevin Huang, Genevieve Clark, Efrén Navarro-Moratalla, Dahlia R. Klein, Ran Cheng, Kyle L. Seyler, Ding Zhong, Emma Schmidtall, Michael A. McGuire, David H. Cobden, Wang Yao, Di Xiao, Pablo Jarillo-Herrero, and Xiaodong Xu, “Layer-dependent ferromagnetism in a van der waals crystal down to the monolayer limit,” Nature 546, 270–273 (2017).
[9] Xue Jiang, Qinxi Liu, Jianpei Xing, Nanshu Liu, Yu Guo, Zhiqiang Liu, and Jijun Zhao, “Recent progress on 2d magnets: Fundamental mechanism, structural design and modification,” Applied Physics Reviews 8, 031305 (2021).
[10] Yu Zhou, Di Wu, Yihan Zhu, Yujin Cho, Qing He, Xiao Yang, Kevin Herrera, Zhaodong Chu, Yu Han, Michael C. Downer, Hallin Peng, and Keki Lai, “Out-of-plane piezoelectricity and ferroelectricity in layered α-In2Se3 nanoflakes,” Nano Letters 17, 5508–5513 (2017).
[11] Kai Chang, Junwei Liu, Haicheng Lin, Na Wang, Kun Zhao, Anmin Zhang, Feng Jin, Yong Zhong, Xiaopeng Hu, Wenhu Duan, Qingming Zhang, Liang Fu, Qi-Kun Xue, Xi Chen, and Shuai-Hua Ji, “Discovery of robust in-plane ferroelectricity in atomic-thick snte,” Science 353, 274–278 (2016).
[12] Xiao Tang and Liangzhi Kou, “Two-dimensional ferroics and multiferroics: Platforms for new physics and applications,” The Journal of Physical Chemistry Letters 10, 6634–6649 (2019).
[13] Nicola A. Hill, “Why are there so few magnetic ferroelectrics?” The Journal of Physical Chemistry B 104, 6694–6709 (2000).
[14] Chao-Kai Li, Xu-Ping Yao, and Gang Chen, “Writing and deleting skyrmions with electric fields in a multiferroic heterostructure,” Phys. Rev. Research 3, L012026 (2021).
[15] Huai Yang, Longfei Pan, Mengqi Xiao, Jingzhi Fang, Chao-Kai Li, Xu-Ping Yao, and Gang Chen, “Writing and deleting skyrmions with electric fields in a multiferroic heterostructure,” Phys. Rev. Letters 113, 247601 (2020).
[16] Xiao Tang and Liangzhi Kou, “Two-dimensional ferroics and multiferroics: Platforms for new physics and applications,” The Journal of Physical Chemistry B 104, 6694–6709 (2000).
[17] Nicola A. Hill, “Why are there so few magnetic ferroelectrics?” The Journal of Physical Chemistry B 104, 6694–6709 (2000).
[18] Chao-Kai Li, Xu-Ping Yao, and Gang Chen, “Writing and deleting skyrmions with electric fields in a multiferroic heterostructure,” Phys. Rev. Research 3, L012026 (2021).
[19] Huai Yang, Longfei Pan, Mengqi Xiao, Jingzhi Fang, Yu Cui, and Zhongming Wei, “Iron-doping induced multiferroic in two-dimensional in2se3,” Science China Materials 63, 421–428 (2020).
[20] Xingwen Liu, Alexander P. Pyatakov, and Wei Ren, “Magnetoelastic coupling in multiferroic bilayer vs2,” Phys. Rev. Lett. 125, 247601 (2020).
[21] Jun-Jie Zhang, Lingfang Lin, Yang Zhang, Menghao Wu, Boris I. Yakobson, and Shuai Dong, “Type-ii multiferroic h2ve2f2 mxene monolayer with high transition temperature,” Journal of the American Chemical Society 140, 9768–9773 (2018).
[22] Jingshan Qi, Hua Wang, Xiaofang Chen, and Xiaofeng Qian, “Two-dimensional multiferroic semiconductors with coexisting ferroelectricity and ferromagnetism,” Applied Physics Letters 113, 043102 (2018).
[23] Changsong Xu, Peng Chen, Hengxin Tan, Yurong Yang, Hongjun Xiang, and L. Bellaiche, “Electric-field switching of magnetic topological charge in type-i multiferroics,” Phys. Rev. Lett. 125, 037203 (2020).
[20] Hengxin Tan, Menglei Li, Haitao Liu, Zhirong Liu, Yuanchang Li, and Weihui Duan, “Two-dimensional ferromagnetic-ferroelectric multiferroics in violation of the d^3 rule,” Phys. Rev. B **99**, 195434 (2019).

[21] I. Dzyaloshinsky, “A thermodynamic theory of "weak" ferromagnetism of antiferromagnetics,” Journal of Physics and Chemistry of Solids 4, 241–255 (1958).

[22] Tōru Moriya, “Anisotropic superexchange interaction and weak ferromagnetism,” Phys. Rev. **120**, 91–98 (1960).

[23] Ning Ding, Jun Chen, Shuai Dong, and Alessandro Stroppa, “Ferroelectricity and ferromagnetism in a VO_2 monolayer: Role of the dzyaloshinskii-moriya interaction,” Phys. Rev. B **102**, 165129 (2020).

[24] V. de Alfaro, S. Fubini, and G. Furlan, “A new classical solution of the yang-mills field equations,” Phys. Lett, B **65**, 163–166 (Nov 1976).

[25] Michael A. Susner, Marius Chysanavichyus, Michael A. McGuire, Panchapakesan Ganesh, and Petko Maksymovych, “Metal thio- and selenophosphates as multifunctional van der waals layered materials,” Advanced Materials **29**, 1602852 (2017).

[26] Paolo Giannozzi et al., “Quantum espresso: a modular and open-source software project for quantum simulations of materials,” Journal of Physics: Condensed Matter **21**, 395502 (2009).

[27] P Giannozzi et al., “Advanced capabilities for materials modelling with quantum espresso,” Journal of Physics: Condensed Matter **29**, 465901 (2017).

[28] John P. Perdew, Kieron Burke, and Matthias Ernzerhof, “Generalized gradient approximation made simple,” Phys. Rev. Lett. **77**, 3865–3868 (1996).

[29] Stefan Grimme, Jens Antony, Stephan Ehrlich, and Helge Krieg, “A consistent and accurate ab initio parametrization of density functional dispersion correction (dft-d) for the 94 elements h-pu,” The Journal of Chemical Physics **132**, 154104 (2010).

[30] See Supplemental Material at [URL will be inserted by publisher] for more computational details, effects of electric fields or strain, phonon dispersions, magnetic parameters of the AFE-FM phase, and additional results of Monte-Carlo simulations. The supplemental material cites references [31–33].

[31] M.J. van Setten, M. Giantomassi, E. Bousquet, M.J. Verstraete, D.R. Hamann, X. Gonze, and G.-M. Rignanese, “The pseudodojo: Training and grading a 85 element optimization,” Journal of Applied Crystallography 44, 1272–1276 (2011).

[32] John P. Perdew, Adrienn Ruzsinszky, Gábor I. Csonka, P Giannozzi, Martin Siron, and Kristin A. Persson, “High-throughput determination of hubbard u and hund j values for transition metal oxides via linear response formalism,” (2022), arXiv:2201.04213.

[33] Chao Xu, Yancong Chen, Xiangbin Cai, Arno Meingast, Xuyun Guo, Fakun Wang, Ziyuan Liu, Tszi Wing Lo, Christian Maunders, Sorin Lazar, Ning Wang, Gangyan Lei, Yang Chai, Tianyou Zhai, Xin Luo, and Ye Zhu, “Two-dimensional antiferroelectricity in nanostripe-ordered in_2se_3,” Phys. Rev. Lett. **125**, 047601 (2020).

[34] Andrius Dziaugys, Kyle Kelley, John A. Brehm, Lei Tao, Andrew Poretyz, Tianli Feng, Andrew O’Hara, Sabine Neumayer, Marius Chysanavichyus, Eugene A. Eliseev, Jurass Banys, Yuliyan Vysochanski, Feng Ye, Bryan C. Chakoumakos, Michael A. Susner, Michael A. McGuire, Sergei V. Kalinin, Panchapakesan Ganesh, Nina Balke, Sokrates T. Pantelides, Anna N. Morozovska, and Petko Maksymovych, “Piezoelectric domain walls in van der waals antiferroelectric cuinp2se6,” Nature Communications **11**, 3623 (2020).

[35] Hiroki Moriwake, Ayako Konishi, Takaumi Ogawa, Craig A. J. Fisher, Akihide Kuwabara, Kazuki Shibata, and Desheng Fu, “Polarization fluctuations in the perovskite-structured ferroelectric AgNbO_3,” Phys. Rev. B **97**, 224104 (2018).

[36] Rohit Batra, Tran Doan Huan, Jacob L. Jones, George Rossetti, and Rampi Ramprasad, “Factors favoring ferroelectricity in hafnia: A first-principles computational study,” The Journal of Physical Chemistry C **121**, 4139–4145 (2017).

[37] Yubo Qi, Sobhit Singh, Claudia Lau, Fei-Ting Huang, Xianxuan Xu, Frederick J. Walker, Charles H. Ahn, Sang-Wook Cheong, and Karin M. Rabe, “Stabilization of competing ferroelectric phases of hfo_2 under epitaxial strain,” Phys. Rev. Lett. **125**, 257603 (2020).

[38] Bheema Lingam Chittari, Youngju Park, Dongkyu Lee, Moonsup Han, Allan H. MacDonald, Euyheon Hwang, and Jeil Jung, “Electronic and magnetic properties of single-layer mPacman_3 metal phosphorous trichalcogenides,” Phys. Rev. B **94**, 184428 (2016).

[39] Stefan Grimme, “Semiempirical gga-type density functional constructed with a long-range dispersion correction,” Journal of Computational Chemistry **27**, 1787–1799 (2006).

[40] A Togo and I Tanaka, “First principles phonon calculations in materials science,” Scr. Mater. **108**, 1–5 (2015).

[41] R. D. King-Smith and David Vanderbilt, “Theory of polarization of crystalline solids,” Phys. Rev. B **47**, 1651–1654 (1993).

[42] Graeme Henkelman and Hannes Jónsson, “Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points,” The Journal of Chemical Physics **113**, 9978–9985 (2000).

[43] Wenjun Ding, Jianbao Zhu, Zhe Wang, Yanfei Gao, Di Xiao, Yi Gu, Zhenyu Zhang, and Wenguang Zhu, “Prediction of intrinsic two-dimensional ferroelectrics in In_2 Se 3 and other III _2-VI _3 van der Waals materials,” Nature Communications **8** (2017).

[44] John A. Brehm, Sabine M. Neumayer, Lei Tao, Andrew O’Hara, Marius Chysanavichyus, Michael A. Susner, Michael A. McGuire, Sergei V. Kalinin, Stephen Jesse, Panchapakesan Ganesh, Sokrates T. Pantelides, Petro
Maksymovych, and Nina Balke, “Tunable quadruple-well ferroelectric van der waals crystals,” Nature Materials 19, 43–48 (2020).

[49] Sifan Xu, Zhicheng Wu, Yuriy S Dedkov, and Elena Voloshina, “Adsorption of water on the pristine and defective semiconducting 2d CrPX3 monolayers (x: S, Se),” Journal of Physics: Condensed Matter (2021).

[50] Rui Gusmao, Zdenek Sofer, David Sedmidubsky, Stepan Huber, and Martin Pumera, “The role of the metal element in layered metal phosphorus triselenides upon their electrochemical sensing and energy applications,” ACS Catalysis 7, 8159–8170 (2017).

[51] Hongjun Xiang, Changhoon Lee, Hyun-Joo Koo, Xingao Gong, and Myung-Hwan Whangbo, “Magnetic properties and energy-mapping analysis,” Dalton Trans. 42, 823–853 (2013).

[52] N. D. Mermin and H. Wagner, “Absence of ferromagnetism or antiferromagnetism in one- or two-dimensional isotropic heisenberg models,” Phys. Rev. Lett. 17, 1133–1136 (1966).

[53] X. Z. Yu, W. Koshibae, Y. Tokunaga, K. Shibata, Y. Taguchi, N. Nagaosa, and Y. Tokura, “Transformation between meron and skyrmion topological spin textures in a chiral magnet,” Nature 564, 95–98 (2018).

[54] Gideon P. Müller, Markus Hoffmann, Constantin Dißelkamp, Daniel Schürhoff, Stefanos Mavros, Moritz Sallermann, Nikolai S. Kiselev, Hannes Jónsson, and Stefan Blügel, “Spirit: Multifunctional framework for atomistic spin simulations,” Phys. Rev. B 99, 224414 (2019).

[55] Xiaobo Lu, Ruixiang Fei, Linghan Zhu, and Li Yang, “Meron-like topological spin defects in monolayer crcl3,” Nature Communications 11, 4724 (2020).

[56] Mathias Augustin, Sarah Jenkins, Richard F. L. Evans, Kostya S. Novoselov, and Elton J. G. Santos, “Properties and dynamics of meron topological spin textures in the two-dimensional magnet crcl3,” Nature Communications 12, 185 (2021).

[57] N. Gao, S.-G. Je, M.-Y. Im, J. W. Choi, M. Yang, Q. Li, T. Y. Wang, S. Lee, H.-S. Han, K.-S. Lee, W. Chao, C. Hwang, J. Li, and Z. Q. Qiu, “Creation and annihilation of topological meron pairs in in-plane magnetized films,” Nature Communications 10, 5603 (2019).

[58] Manuel Pereiro, Dmitry Yudin, Jonathan Chico, Corina Etz, Olle Eriksson, and Anders Bergman, “Topological excitations in a kagome magnet,” Nature Communications 5, 4815 (2014).
S1. COMPUTATION DETAILS

In this study, unit cells and several distinct supercells are used. In detail, we employed 20-atom rectangle supercells for structural relaxation of monolayer structures. For bulk structures having interlayer-antiferroelectric or interlayer-antiferromagnetic orders, we utilized 40-atom monoclinic supercells, while for other bulk phases, we used 20-atom supercells. The hexagonal primitive cell with 10 atoms is used to calculate the band structure of the ferroelectric-ferromagnetic phase. We investigated the convergence of our results to supercell sizes for phonon calculations using the frozen phonon approach, estimation of Hubbard $U_{\text{eff}}$ using the linear response approach, and identification of magnetic exchange interactions. To separate periodic images of a monolayer, a vacuum region with a thickness of 15 Å is used. The Brillouin zone of the 20-atom monolayer unit cell is sampled using a $8 \times 5 \times 1$ k-point grid.

Throughout the research, optimized norm-conserving pseudopotentials [1] and a kinetic energy cutoff of 80 Ryd are employed. For structural relaxations, we optimized both lattice vectors and atomic coordinates such that forces are less than $1 \times 10^{-4}$ Ryd/Bohr and stresses are below 0.05 kbar. As illustrated in Table S1, we benchmarked different functionals for predicting the structure parameters for the centrosymmetric phase. Overall, PBEsol and LDA functional [2] outperforms PBE [3] and PBE+D3 [4]. When compared to LDA, PBEsol functional somewhat overestimates lattice constants, but gives better results of $\beta$ and the ratios between lattice constants. We also noticed that as $U_{\text{eff}}$ increases, the estimated lattice constants rise as well.

TABLE S1: Comparison between the structural parameters of the bulk centrosymmetric phase with the stripy arrangement calculated with different functionals. An effective Hubbard $U_{\text{eff}} = 3.6$ eV is used. Experimental data is from Ref [5].

| Method  | a (Å) | b (Å) | c (Å) | b/a | c/a | β     | cell volume (Å$^3$) |
|---------|-------|-------|-------|-----|-----|-------|---------------------|
| LDA     | 6.18  | 10.84 | 6.80  | 1.754 | 1.100 | 108.4 | 434.8               |
| PBE     | 6.37  | 11.15 | 7.15  | 1.750 | 1.122 | 108.0 | 485.6               |
| PBE+D3  | 6.34  | 11.09 | 7.01  | 1.749 | 1.106 | 108.3 | 470.9               |
| PBEsol  | 6.25  | 10.95 | 6.95  | 1.752 | 1.112 | 108.1 | 455.0               |
| Experiment | 6.13 | 10.66 | 6.86  | 1.739 | 1.119 | 107.1 | 428.4               |

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To get a reasonable estimate of $U_{\text{eff}}$, we used the linear response approach proposed by Cococcioni and Gironcoli [6] to estimate effective Hubbard $U_{\text{eff}}$ parameters. The Hubbard $U_{\text{out}}^{\text{eff}}$ are determined using the ground state of PBEsol+$U_{\text{in}}^{\text{eff}}$ calculations. We calculated Hubbard $U_{\text{out}}^{\text{eff}}$ for a series of $U_{\text{in}}$, then perform linear extrapolation to get self-consistent $U_{\text{eff}}$ parameters [7]. We have done convergence tests with respect to supercell size. Fig. S1 (a) suggests that a 40-atoms supercell is sufficient to converge the calculated $U_{\text{eff}}$ within 50 meV. Comparing Fig. S1 (a) and (b), we found $U_{\text{eff}}$ of FE and AFE phases are close (about 2.8 eV). Fig. S1 (c) demonstrates that PE-ST and PE-FM phase has the same self-consistent $U_{\text{eff}}$. In other words, $U_{\text{eff}}$ is not sensitive to the magnetic order. We emphasize that $U_{\text{eff}}$ is a model parameter which depends on the pseudopotentials. A recent high-throughput computational study by Guy et al. [8] show that 2.0 eV to 3.0 eV is a reasonable range of $U_{\text{eff}}$ for Cr. This agrees well with what we find here, considering different methods we adopted.

FIG. S1: Hubbard $U_{\text{out}}^{\text{eff}}$ versus input parameter $U_{\text{in}}^{\text{eff}}$ for PBEsol+$U_{\text{eff}}$ calculations. The self-consistent $U_{\text{eff}}$ are highlighted as with horizontal lines.

S2. TOTAL ENERGIES OF MULTIFERROIC CONFIGURATIONS

We show the schematic plots of of ferroelectric (FE), antiferroelectric (AFE), centrosymmetric (PE), and interlayer-antiferroelectric (iAFE) structures in Fig. S2. The total energies of different multiferroic configurations calculated with a range of $U_{\text{eff}}$ parameters are presented in Table S2 and Table S3. We note that the exact energy differences between various phases can be dependent on the pseudopotential and exchange-correlation function used. For example, using LDA functional, we find the PE-ST, FE-FM, and AFE-FM phases have nearly the same energies when $U_{\text{eff}} = 3.0$, as shown in Table S4. Nevertheless, the overall trend discussed in the main text holds the same.

FIG. S2: Schematic plot of FE, PE, AFE, and iAFE structures.
TABLE S2: Total energies of monolayer configurations calculated with PBEsol+U using a range of Hubbard $U_{eff}$ parameters. The energy of the FE-FM phase is set to zero. “–” means the calculations for corresponding structures do not converge (not local minima).

| $U_{eff}$ (eV) | FE (meV/f.u.) | AFE (meV/f.u.) | PE (meV/f.u.) |
|---------------|---------------|----------------|---------------|
|               | FM | ZZ | ST | NL | FM | ZZ | ST | NL | FM | ZZ | ST | NL |
| 0.0           | 0  | 30 | 58 | 74 | -14| 4  | 6  | 26 | 125| 152| 230| -   |
| 2.0           | 0  | 44 | 64 | 83 | -9 | 20 | 39 | 47 | 107| 152| 71 | 126 |
| 3.0           | 0  | 46 | 59 | 83 | -3 | 25 | 48 | 50 | -50| -8 | -69 | -31 |
| 3.6           | 0  | 50 | -  | 82 |  7 | 31 | 58 | 56 | -138| -99| -147| -116 |

TABLE S3: Total energies of different bulk configurations calculated with PBEsol+U using a range of Hubbard $U_{eff}$ parameters. The energy of the FE-FM phase is set to zero. “–” means the calculations for corresponding structures do not converge.

| $U_{eff}$ (eV) | FE (meV/f.u.) | AFE (meV/f.u.) | PE (meV/f.u.) | ilAFE (meV/f.u.) |
|---------------|---------------|----------------|---------------|-----------------|
|               | FM | ilAFM | ZZ | ST | NL | FM | ilAFM | ZZ | ST | NL | FM | ilAFM | ZZ | ST | NL |
| 2.0           | 0  | 3    | 42 | 59 | 79 | -16| -5  | 16 | 33 | 46 | 115| 126 | 196| 81 | 144 | -8 | -8 | 35 | 51 | 70 |
| 3.0           | 0  | 5    | 43 | 51 | 43 | -11| -6  | 21 | 42 | 48 | -41| -29 | 37 | -59| -13 | -7 | -2 | 44 | 50 | 68 |
| 3.6           | 0  | 3    | 46 | -  | 75 | -4 | -3  | 26 | 47 | 52 | -129| -117| -139| -100| -5 | -2 | 48 | 71 |

TABLE S4: Comparison between the total energies of monolayer CrPSe$_3$ calculated with different functionals.

| Method            | PE-ST (meV/f.u.) | FE-FM (meV/f.u.) | AFE-FM (meV/f.u.) |
|-------------------|------------------|------------------|-------------------|
| PBEsol+U (U=3.0 eV) | 0                | 69               | 66                |
| LDA+U (U=3.0 eV)   | 0                | 6                | 3                 |
| LDA+U (U=2.9 eV)   | 0                | -9               | -11               |
S3. EFFECTS OF ELECTRIC FIELD AND STRAIN

We studied the effects of uniaxial strain and out-of-plane electric field $E_z$ on the relative energy between AFE-FM and FE-FM phase. We found both strain and electric field can effectively tune the energy ordering between these two phases. As shown in Fig. S3 (a), an electric field of 1.7 V/nm perpendicular to the plane is sufficient to reverse the energy ordering between the AFE-FM and FE-FM phase. In Fig. S3 (b) and (c), we plot the strain dependent energies by changing lattice constant $a$ and $b$. One can see small uniaxial strain (about 1.5 %) can make the energy of the AFE-FM phase higher than the FE-FM phase. These calculations are performed with PBEsol+U ($U_{\text{eff}} = 2.8$ eV).

FIG. S3: (a) The energy difference between the AFE-FM phase and the FE-FM phase under electric field along out-of-plane direction. (b) and (c) Energies of the AFE-FM phase and FE-FM phase by changing lattice constant $a$ and $b$.

S4. ELECTRON AND PHONON BAND STRUCTURES

The band structure of FE-FM and AFE-FM phases are shown in Fig. S4 (a) and (b). Interestingly, the band gaps of the FE-FM and AFE-FM phases both decrease as the effective Hubbard parameter $U_{\text{eff}}$ parameter increases. The phonon band structure of the AFE-FM phase is plotted in Fig. S4 (c), which does not show any imaginary phonon modes. It demonstrate the dynamical stability of the AFE-FM phase.

The phonon spectra of monolayer PE-ST, monolayer PE-FE, and bulk PE-ST phase are shown in Fig. S5. Interestingly, all of them are stable without imaginary phonon modes. Usually, the corresponding PE structure of common FE materials should have imaginary phonon modes. The stability of PE phases is counterintuitive since our calculations show adding small distortions to PE phase can drive CrPSe$_3$ to the FE phase. To better understand such an unexpected result, we conducted further analysis. In detail, we calculate the projections (i.e., inner products) of zone-center phonon modes to the atomic displacements from the PE-FM to the FE-FM structure. We find four optical-phonon modes (two modes with $A_{2u}$ symmetry and two modes with $A_{1g}$ symmetry, shown in Fig. S5 (b)) that contribute significantly to the atomic displacements from the PE-FM structure to the FE-FM structure. These four phonon modes exhibit strong anharmonicity. The atomic displacements of these four zone-center modes are shown in Fig. S6.

Next, we calculated the energy landscape in the vicinity of the FE-FM and the PE-FM phase. In detail, we shifted the atoms by

$$\vec{d} = Q_1 \cdot (c_{A_{2u}[1]} \cdot \vec{u}_{A_{2u}[1]} + c_{A_{2u}[2]} \cdot \vec{u}_{A_{2u}[2]}) + Q_2 \cdot (c_{A_{1g}[1]} \cdot \vec{u}_{A_{1g}[1]} + c_{A_{1g}[2]} \cdot \vec{u}_{A_{1g}[2]})$$

and calculate the energy of the distorted system $E(Q_1, Q_2)$. Here the $\vec{u}_i$ is the eigenvector of phonon mode $i$ and the coefficient $c_i$ is calculated by projecting a phonon mode $\vec{u}_i$ to the relative atomic displacements between the PE-FM and the FE-FM phase. For example, $\vec{u}_{A_{2u}[1]}$ is the eigenvector of phonon mode $A_{2u}[1]$. We plot the contour of $E(Q_1, Q_2)$ in Fig. S7, which clearly show three local minima. The PE-FM phase is located at a shallow local minimum in the center of Figure A5, while the FE phases correspond to the two other local minima. Fig. S7 suggests the PE-FM phase is metastable, however, adding small displacements to the PE-FM structure may cause a transition to the FE-FM phase. It also demonstrates the complexity of the energy landscape of CrPSe$_3$. 
FIG. S4: Electron band structure of (a) the FE-FM and (b) AFE-FM phase calculated with different $U_{\text{eff}}$. (c) Phonon band structure of AFE-FM phase calculated with PBEsol+U ($U_{\text{eff}} = 2.8$ eV).

FIG. S5: Phonon band structure of (a) monolayer PE-ST (b) monolayer PE-FE (c) Bulk PE-ST phases, calculated with PBEsol+U.
FIG. S6: Four phonon modes that contribute to the transition from the PE structure to the FE structure. Only a few atoms in the unit cell are shown for clarity.

FIG. S7: The energy landscape near the PE-FM and FE-FM phase, showing three local minima. The top two minima correspond to the FE-FM phase. The shallow minima in the center corresponds to the PE-FM phase. The result is calculated with PBEsol+U (U_{eff} = 2.0 eV).
S5. MAGNETIC PARAMETERS OF THE AFE-FM PHASE

For the AFE phase, we considered exchange couplings between Cr atoms up to next-nearest neighbors and DMI between nearest neighbors. The calculated exchange parameters for AFE phase are shown in Table S5. The definitions of $J_{kl}$ ($k = 1, 2$ and $l = a, b, c$) are schematically shown in Fig. S8. We can see although the nearest-neighbor couplings $J_{1l}$ are all ferromagnetic, the coupling strength varies with respect to bonding directions. The AFE phase also demonstrates an easy-plane anisotropy. However, different from the FE phase, the AFE phase loses the C$_3$ symmetry and the magnetic moments prefer $y$-direction. In particular, the magnetic moments prefer to align along the $y$-direction. By estimating the DMI strength, we found the DMI coupling is significant only when the nearest-neighboring Cr pairs lie along the $y$-direction. This can be understood by examining the local inversion center or dihedral angles spanned by Cr pairs and the Se atoms connecting them, as we discussed in the main text. As shown in Fig. S8, we found $\angle$SeCr$_1$Cr$_2$Se $= 172^\circ$, while $\angle$SeCr$_2$Cr$_3$Se $= 180^\circ$. This suggests SeCr$_2$Cr$_0$Se (SeCr$_3$Cr$_0$Se) form a parallelogram, which have an inversion center and can not create DMI between Cr$_2$ and Cr$_0$ (Cr$_3$ and Cr$_0$).

![Diagram of exchange couplings and dihedral angles](image)

FIG. S8: (a) A schematic plot showing the definitions of exchange couplings between Cr in the AFE phase (b) A side view of the AFE structure

| $J_{1a}$ | $J_{1b}$ | $J_{1c}$ | $J_{2a}$ | $J_{2b}$ | $J_{2c}$ | $D_{1a}$ | $A_x$ | $A_y$ |
|---------|---------|---------|---------|---------|---------|--------|------|------|
| -8.7    | -29.2   | -8.8    | -3.2    | -2.6    | -6.2    | [-0.65,0,-0.5] | -0.07 | -0.15 |

S6. MONTE CARLO SIMULATIONS

For Monte-Carlo (MC) simulations of the FE-FM phase, we used a 200 $\times$ 200 spin lattice, which includes $8 \times 10^4$ spin sites. In order to observe the evolution of meron and antimerons, we performed MC simulation up to $10^6$ MC steps for each temperature. We used a modified version of Spirit [9]. For a continuous unit vector field $n(r)$ on a plane, the topological charge is defined as

$$Q[n(r)] = \frac{1}{4\pi} \int_{\mathbb{R}^2} n \cdot (\partial_x n \times \partial_y n) d^2r$$

In comparison, for unit vector fields on a discrete 2D lattice, the topological charge is given by

$$Q = \frac{1}{4\pi} \sum_i A_i$$
where \( l \) runs over all the triangles of a triangulation of the spin lattice sites and \( A_l \) can be recognized as the local topological charge, which is

\[
\cos \left( \frac{A_l}{2} \right) = \frac{1 + n_i \cdot n_j + n_i \cdot n_k + n_j \cdot n_k}{\sqrt{2(1 + n_i \cdot n_j)(1 + n_j \cdot n_k)(1 + n_k \cdot n_i)}}.
\]

(3)

The spin sites \( i, j, \) and \( k \) of a triangle \( l \) are numbered in a counter-clockwise order. The sign of \( A_l \) is \( \text{sign}[n_i \cdot (n_j \times n_k)] \).

In Fig. S9, we show some screenshots of the spin lattice under \( T = 5 \text{ K} \). At MC step 50000, there are 7 pairs of merons (or antimerons). As the simulation goes, vortex and antivortex attract and annihilate each other. At MC step 500000, only one pair of merons left. We observed meron-meron, meron-antimeron, and antimeron-antimeron annihilation in our simulations. This indicates the pair annihilation processes do not depend on the polarity (the \( z \) component of the core) of merons (or antimerons).

FIG. S9: Selected steps in the MC simulation of FE-FM phase at \( T = 5K \). The spins are colored in red or blue according to their \( z \)-components of magnetic moments.
We also performed MC calculations for the AFE-FM phase using a spin lattice with 80000 spin sites. The initial spin configurations were set to either randomized spin directions or out-of-plane ferromagnetic (zFM) configurations. Our calculations show only randomized initial spin configurations can yield merons in MC simulations. The zFM initial spin configuration only yields in-plane ferromagnetic domains with topological trivial domain boundaries. This is in contrast with the FE-FM phase, where MC simulations with zFM initial configuration also produce merons. In Fig. S10, we show typical screenshots of a MC simulation for the AFE-FM phase starting with a randomized initial spin configuration. Vortex and anti-vortex merons are observed. Compared to the FE-FM phase, the size of merons are larger. Furthermore, we observed some stable meron pairs showing long lifetimes in MC simulations. For example, Fig. S11 shows some pairs of vortex and antivortex merons stabilized at the upper domain boundary between two FM domains. Interestingly, four meron pairs on the upper boundary (marked with green rectangle boxes) do not show the tendency of annihilating each other after $2 \times 10^6$ MC steps.

FIG. S10: Selected snapshots of the MC simulation of AFE-FM phase at $T = 5K$. The spins are colored in red or blue according to their z-components of magnetic moments. After 300000 MC steps, the spin lattice becomes a single ferromagnetic domain with magnetic moments pointing along negative y-direction.
FIG. S11: A snapshot of the MC simulation of AFE-FM phase at $T = 5$ K. The spins are colored according to their (a) $z$-components and (b) $y$-components of magnetic moments.

[1] M. van Setten, M. Giantomassi, E. Bousquet, M. Verstraete, D. Hamann, X. Gonze, and G.-M. Rignanese, Computer Physics Communications 226, 39 (2018).
[2] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, Phys. Rev. Lett. 100, 136406 (2008).
[3] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[4] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, The Journal of Chemical Physics 132, 154104 (2010).
[5] M. A. Susner, M. Chyasnavichyus, M. A. McGuire, P. Ganesh, and P. Maksymovych, Advanced Materials 29, 1602852 (2017).
[6] M. Cococcioni and S. de Gironcoli, Phys. Rev. B 71, 035105 (2005).
[7] H. J. Kulik, M. Cococcioni, D. A. Scherlis, and N. Marzari, Phys. Rev. Lett. 97, 103001 (2006).
[8] G. C. Moore, M. K. Horton, A. M. Ganose, M. Siron, and K. A. Persson, “High-throughput determination of hubbard $u$ and hund $j$ values for transition metal oxides via linear response formalism,” (2022), arXiv:2201.04213.
[9] G. P. Müller, M. Hoffmann, C. Diffélcamp, D. Schürhoff, S. Mavros, M. Sallermann, N. S. Kiselev, H. Jönsson, and S. Blügel, Phys. Rev. B 99, 224414 (2019).