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Parameter free treatment of a layered correlated van der Waals magnet: CrPS₄

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The electronic and magnetic structure of CrPS₄, a 2D magnetic semiconductor is examined by employing the SCAN meta-GGA density functional. We find the resulting magnetic moment and band gap are in excellent agreement with experiment. From the bulk magnetic configurations, we confirm the experimentally observed A-type antiferromagnetic (A-AFM) ordered ground state with a magnetic moment of 2.78 μ_B per chromium atom and band gap of 1.34 eV. To gain insight into the evolution of the ground state with layers, the total energy of each magnetic configuration is calculated for a variety of thicknesses. Monolayer CrPS₄ is predicted to be a ferromagnetic insulator with a band gap of 1.37 eV, and A-AFM for bilayer and trilayer, with band gaps of 1.35 eV and 1.30 eV, respectively. The electronic structure is reported for the single, two, three layer and bulk CrPS₄. Finally, we explore the optical properties of the 2D structure and report the dielectric tensor components and Kerr parameters for the monolayer.

I. INTRODUCTION

Recently, several reports of new 2D magnetic materials have appeared in the literature displaying a rich variety of magnetic structures [1], along with a myriad of competing topological and superconducting phases [2, 3]. The layer-dependent ferromagnetism exhibited by these compounds, such as CrI₃, offers a new pathway for the development of new spintronic devices because of their wide tunabilities using doping, electric field, light, and pressure [4]. However, the current workhorse CrI₃, and similar materials, are fundamentally limited due to their extreme sensitivity to air [5], requiring special glovebox environments and capping layers to preserve the material properties. Therefore, it is crucial to identify air-stable 2D ferromagnetic materials to advance the next generation spintronic, optoelectronic, and future quantum information technologies in general [1].

CrPS₄ has recently been singled out due to its intrinsic ferromagnetic ordering in the monolayer [6] and robust air-stability [7] similar to CrTe₂ [8–10]. These key properties have prompted a number of experimental [11–21] and theoretical [22–26] studies. Specifically, CrPS₄ is found to exhibit a canted ferromagnetic order within each van der waals layer. When stacked, no net magnetic moment is admitted for an even number of layers characteristic of an A-type AFM ground state [27]. The large magnetic polarization on each Cr site (2.81 μ_B /Cr) produces a 1.40 eV gap in the electronic states, suggesting CrPS₄ is well suited for switching [11] and neuromorphic computing [28] applications.

The limited theoretical works analyzing CrPS₄ have found mixed success. Density functional theory calculations at the generalized gradient approximation (GGA) level are able to find the correct A-AFM magnetic ground state, however, the Cr magnetic moments are underestimated (2.58 μ_B /Cr), along with the band gap (0.79 eV) by almost a factor of two [22, 27], as expected for Kohn-Sham theory. To remedy this, a Hubbard U parameter has been applied to the Cr-3d states to yield the cor-

TABLE I. Comparison between experimental and various DFT treatments of the magnetic [6] and electronic [27] properties of bulk CrPS₄. The SCAN results (this work) show improvement over previous PBE [22] and PBE+U (U=3 eV) [23] studies in capturing the experimental values.

Bulk CrPS ₄	SCAN	Experiment	PBE	PBE + U
Ground state	A-AFM	A-AFM	A-AFM	X-AFM
Band gap (eV)	1.34	1.40	0.79	1.66
Moment (μ_B /Cr)	3.00	2.81	2.58	3.00

rect magnetic moment [23]. Unfortunately, this correction predicts a X-type AFM ground state in contrast to neutron scattering measurements [27] and an exaggerated band gap of 1.66 eV. Due to the sensitivity of this system, there is currently no theoretical treatment that captures the delicate balance between the charge and magnetic degrees of freedom. Thus making predictions of magnetoelastic coupling, magneto resistive switching, and magnetic excitations quite challenging.

In this article, we present an accurate parameter-free description of the layer dependent magnetic and electronic properties of CrPS₄. Utilizing the newly constructed Strongly-Constrained-and-Appropriately-Normed (SCAN) meta-GGA density functional, the calculated magnetic moments (magnitude and direction) and electronic band gap are in excellent accord with reported experimental values. Our predicted magnetic ground state is in agreement with neutron diffraction studies, thereby overcoming the failure of the DFT+ U framework. Upon exfoliating the bulk crystal, we find the interlayer coupling to be extremely weak, between 36 to 49 meV, with the corresponding electronic bands exhibiting essentially no change in band dispersion with thickness. Finally, the dielectric tensor and Kerr parameters are obtained for the monolayer to stimulate further experimental works.

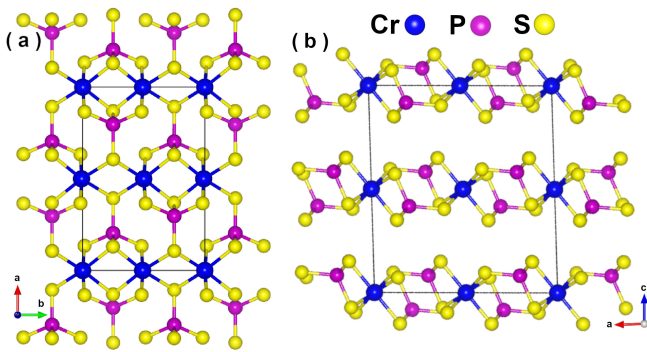


FIG. 1. Supercell of bulk CrPS₄ along (a) the c -axis and (b) the b -axis.

Computational Details.—Calculations were carried out by using the pseudopotential projector-augmented wave (PAW) method [29] implemented in the Vienna *ab initio* simulation package (VASP) [30, 31] with an energy cutoff of 260 eV for the plane-wave basis set. Exchange-correlation effects were treated by using the SCAN, meta-GGA scheme [32]. A $6 \times 7 \times 1$ Γ -centered k -point mesh was used to sample the single, two, and three layer structures. Whereas a $6 \times 7 \times 5$ mesh was used to sample the bulk material. After a systematic study of k -mesh densities, the $6 \times 7 \times 5$ mesh was found to converge the total energy to within 0.31 meV/Cr. The dielectric tensor components were calculated using 1296 virtual states. Spin-orbit coupling effects were included self-consistently. The CrPS₄ unit cell was built using experimentally obtained atomic positions and lattice parameters for the bulk, trilayer, bilayer and monolayer monoclinic symmetry with a space group $C2/m$ [33]. The magnetism is driven by the Cr³⁺ valence, with three $3d$ electrons spread in the t_{2g} sub-orbital occupations, yielding a spin moment of $S = 3/2$. A vacuum spacing of 19 Å was used to ensure no interactions occur between the periodic images. A total energy tolerance of 10^{-6} eV was used to determine the self-consistent charge density.

II. CRYSTAL STRUCTURE

Figure 1 shows the crystal structure of bulk CrPS₄ along the (a) c - and (b) b -axes. The chromium atoms (blue) sit on an orthorhombic lattice and are octahedrally coordinated by sulfur atoms (yellow) that are slightly distorted off center. Due to the orthorhombic Bravais lattice, the Cr atoms form linear chains of strong inter-site coupling along the b -axis, with weaker inter-chain interactions along the a -axis. The phosphorus atoms (purple) sit at the center of a sulfur tetrahedral cage, where its position alternates between above and below the Cr layer following the distorted sulfur octahedra. This puckering of the phosphorus sites constrains the primitive unit cell to accommodate four Cr atoms, rather than simply one. Moreover, the phosphorus atoms form a bridge between

Cr chains, thereby facilitating the weak inter-chain interactions. Along the c -axis, the atomically-thin layers are found to stack in an AA manner with a clear 3.75 Å vdW gap separating neighboring layers. This suggests the electronic states should be predominantly 2D in nature with very weak k_z dispersion.

III. MAGNETIC CONFIGURATIONS AND GROUND STATE

Figure 2 (a)-(b) shows the various collinear commensurate magnetic orders studied in bulk CrPS₄, along with the corresponding relative total energies of each magnetic configuration with values from previous PBE [22] and PBE+ U ($U=3$ eV) [23] studies overlayed. Since the bulk primitive cell of CrPS₄ has eight Cr atoms spanning two layers, nine distinct commensurate magnetic orders may be accommodated. To enumerate the phases, we initially assume FM coupling between all Cr sites to produce a FM phase with all magnetic moments pointing slightly canted off the c -axis. If inter-chain (intra-chain) interactions are switched to AFM, we perturb away from the FM phase yielding a stripe-like X-type (Y-, Y'-type) AFM order that varies along the a -axis (b -axis). Additionally, swapping the FM inter-layer coupling for AFM triggers an A-type AFM state where the direction of the magnetic moments alternate with CrPS₄ layers. Finally, by combining inter- and intra-chain, and inter-layer couplings the E-, F-, C-, X'-, and G-type AFM states are found.

Figure 2 (b) plots the energy of each magnetic configuration relative to the ground state using PBE [22] (green squares), PBE+ U ($U=3$ eV) [23] (blue circles), and SCAN (red $\times$) functionals. PBE correctly captures the correct ground state magnetic order and predicts the FM phase only 2 meV higher in energy. Moreover,

TABLE II. Energy differences (ΔE) relative to the predicted ground states of eight magnetic configurations for the bulk, bilayer, and trilayer, and two magnetic configurations for the monolayer.

Magnetic order	Bulk ΔE (meV/Cr)	Trilayer ΔE (meV/Cr)	Bilayer ΔE (meV/Cr)	Monolayer ΔE (meV/Cr)
FM	0.031	0.075	0.088	0
A-AFM	0	0	0	-
C-AFM	2.172	2.218	2.235	2.706
E-AFM	1.288	1.312	1.286	-
G-AFM	2.203	2.207	2.266	-
X-AFM	0.442	2.687	2.703	-
X'-AFM	0.445	2.687	2.735	-
Y-AFM	2.672	0.467	0.493	-

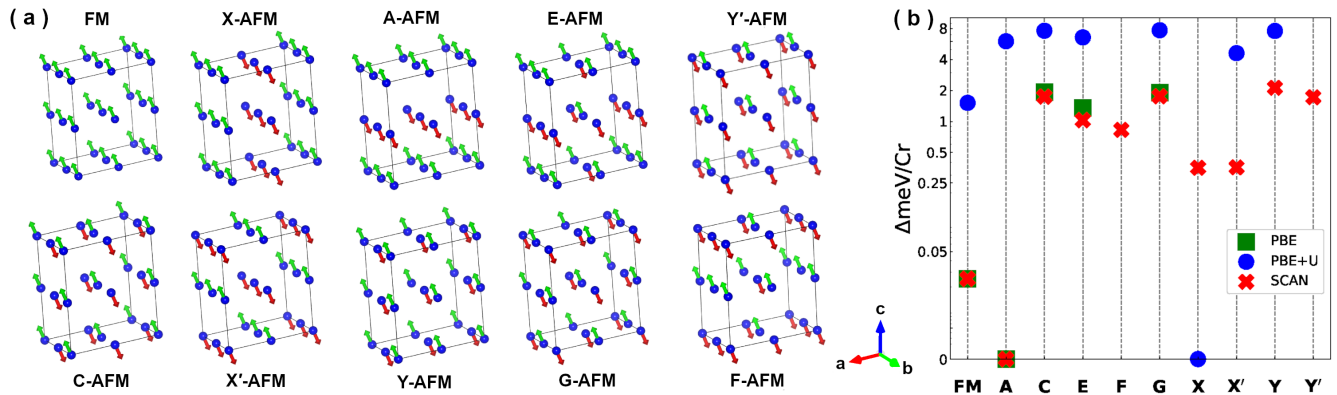


FIG. 2. (a) Ferromagnetic and the nine antiferromagnetic configurations considered for the ground-state ordering of CrPS₄. The green and red arrows represent the positive and negative magnetic moments of Cr in the unit cell, respectively. (b) Ground-state energies relative to most stable magnetic configuration by calculated by the PBE (green)[22], PBE+U (blue)[23], and SCAN (red) functionals.

the magnetic moment direction and magnitude, though slightly underestimated [Table I], are also in good accord with powder and single crystal magnetic neutron diffraction results [6]. The remaining magnetic arrangements considered (C-, E-, and G-AFM) are separated from the A-AFM phase by ~ 2 eV/Cr, making them irrelevant to the low energy degrees of freedom. The close energetic proximity of FM and A-AFM states suggests a delicate balance between AFM and FM coupling between the CrPS₄ layers. Despite PBE's success in describing the magnetic state, it severely underestimates the electronic band gap [Table I] as is expected since the Kohn-Sham eigenvalues do not provide the value of the gap. To improve upon the PBE description of the ground state, Joe *et al.* [23] included a Hubbard U of 3 eV on the Cr- d states. By applying a U , charge localization is enhanced on the Cr atomic sites, thereby, increasing the magnetic moment and band gap [Table I]. Interestingly, the added Hubbard parameter disrupts the ratio of inter- and intra-layer exchange couplings, thus predicting a X-AFM ground state with all other phases at least 1.5 eV/Cr higher in energy.

We find the SCAN density functional to remedy the pitfalls of both previous approaches without the introduction of any empirical parameters. Specifically, SCAN recovers the experimental A-AFM ground state ordering and predicts magnetic moments of $3.00 \mu_B$ tilted off of the c -axis by 71.6° in excellent accord to the experimental powder and single crystal magnetic neutron diffraction values [6]. Regarding magnetic moments, the values obtained by neutron scattering involve uncertainties since the chromium form factor is not *a priori* known. Note that, when estimating the chromium magnetic moment, we have increased the Wigner-Seitz radius of the integration sphere beyond the default value from 1.323 Å (covalent radius) to 1.74 Å (3/4 of the Cr-S bond length) in order to fully capture the magnetic density centered on the chromium atomic site and the part originating from

hybridization between the chromium and sulfur atoms, see Appendix A for more details).

The A-AFM state stabilizes with a band gap of approximately 1.34 eV that opens up around the Fermi energy of the NM system. This gap is in good agreement with optical data [27]. The physical interpretation of the band gap obtained in the ground-state DFT calculations has been the subject of much debate in the literature over the years. We note that in assessing the physical content of the band gap, one must distinguish between the nature of the effective exchange-correlation potential obtained in the Kohn-Sham (KS) [34] and generalized Kohn-Sham (gKS) [35] formalisms underlying the construction of various functionals. Within the KS scheme one uses the electron density as a variational parameter, thereby yielding KS potentials that are inherently “multiplicative” and orbital independent. In sharp contrast, the Slater determinate is varied in the gKS formalism, this results in gKS potentials that are orbital dependent and are thus “nonmultiplicative.” In particular, LSDA/GGA band structures involve multiplicative effective potentials, while the current and common SCAN implementations involve nonmultiplicative potentials due to the inclusion of the kinetic energy density as an ingredient, and thus differ in their basic underlying designs. In this connection, Perdew *et al.* [36] have shown that for a given density functional, the gKS band gap is equal to the fundamental band gap in the solid, which is defined as the ground-state energy difference between systems with different numbers of electrons. There is thus a firm basis for comparing computed band gaps within the gKS-based SCAN formalism with the experimentally observed band gaps (excluding excitonic effects). The preceding considerations indicate that as a meta-GGA functional improves the description of the ground state, it will necessarily also lead to improvement in the band gap. To this end, the gKS-based SCAN formalism has demonstrated success in capturing not only the magnetic

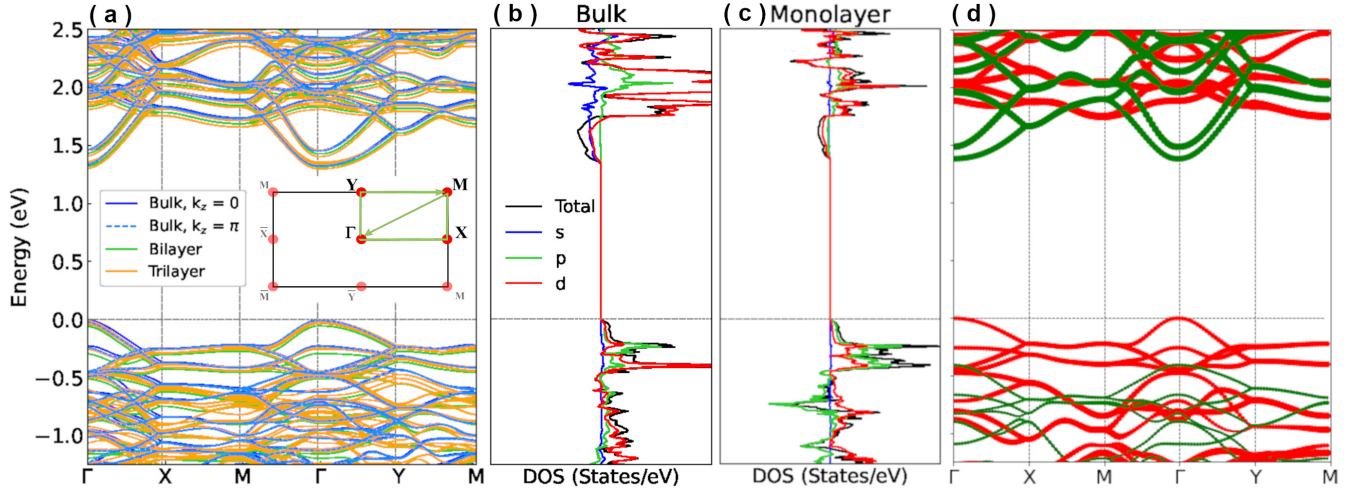


FIG. 3. (a) The electronic band structure and Brillouin zone route explored (inner panel) for the bulk, bilayer, and trilayer. (b), The total and atomically resolved density of states is related next to the band structure for the bulk. (c) monolayer atomically resolved density of states, with the corresponding (d) monolayer band structure with up (red) and down (green) bands.

ground state, but the band gap in a wide array of materials including La₂CuO₄ [37–39], YBa₂Cu₃O₆ [40], Sr₂IrO₄ [41], and NiPS₃ [42]. In particular, the SCAN ground state has been shown to yield the key optical transitions in La₂CuO₄ [43] and NiPS₃ [44]. Therefore, the comprehensive agreement between magnetic and electronic properties in CrPS₄ stems from the reduction in self-interaction error in SCAN, as compared to PBE, and is not accidental.

Table II presents the relative total energy of each magnetic configuration with respect to the A-AFM state for various sample thicknesses. The A-AFM phase is found to be the ground state for all layered-films studied, with a robust FM order stabilizing in the monolayer. By comparing the energy of each magnetic state, the FM phase is the closest competing magnetic state, with only $\approx 2\text{--}7$ meV/Cr energy separation irrespective of thickness. Curiously, the energy difference between A-AFM and FM arrangements follow a non-monotonic evolution with number of CrPS₄ layers. Similarly, the remaining magnetic orders farther away from the ground state display a sensitive dependence on the number of layers. In particular, the X- and Y-AFM phases interchange energetic ordering from the bilayer to the bulk systems. This suggests the screening environment may play a key role in tuning the relative strength between the inter- and intra-chain interactions. Additionally, by comparing C-, G-, X-, and X'-AFM configurations, the interlayer exchange coupling is found to be on the order of a few meV/Cr.

IV. ELECTRONIC PROPERTIES

Figure 3 shows the (a) electronic band structure and (b) atomically resolved density of states of CrPS₄ in the A-AFM phase for the bulk, bilayer, and trilayer, with

separately the (c) monolayer atomically resolved density of states, and (d) corresponding band structure. For the multi-layer structures, the A-AFM magnetic order stabilizes a direct 1.34 eV band gap at Γ in the Brillouin zone of bulk CrPS₄. Interestingly, the band dispersions appear to be insensitive to k_z dispersion. Specifically, the bands for $k_z = 0$ (solid blue lines) and $k_z = \pi$ (dashed blue lines) are essentially identical, where small deviations are only exhibited along the M- Γ -Y path in momentum space. The band dispersion along Γ -Z is flat suggesting the interlayer coupling is weak and each atomically-thin layer is relatively electronically isolated, see Appendix B. As CrPS₄ is thinned, the band structure for the trilayer (orange solid lines) and bilayer (green solid lines) appears to be stationary and display nearly identical eigenvalues throughout the Brillouin zone, except for a slight rigid shift (~ 70 meV) due to the non-monotonic evolution of the gap. In contrast, the monolayer [Fig. 3(d)] displays an indirect band gap of 1.745 eV characterized by momentum-shift of (π, π) . The corresponding atomically resolved density of states [Figure 3(b) and (c)] reveals the valence bands to be predominantly composed of sulfur character 99%, whereas the conduction band is dominated by Cr states 27%. This stacking-of-states follows the Zaanen-Sawatzky-Allen classification of a charge-transfer insulator [45]. Therefore, in contrast to the Mott-Hubbard scenario, when a hole is doped into CrPS₄, the carrier would sit on the sulfur atomic sites rather than in the Cr sites. The percentage of metal cation (ligand anion) weight in the conduction (valence) band is relatively constant across the bulk, single-, and few-layer systems.

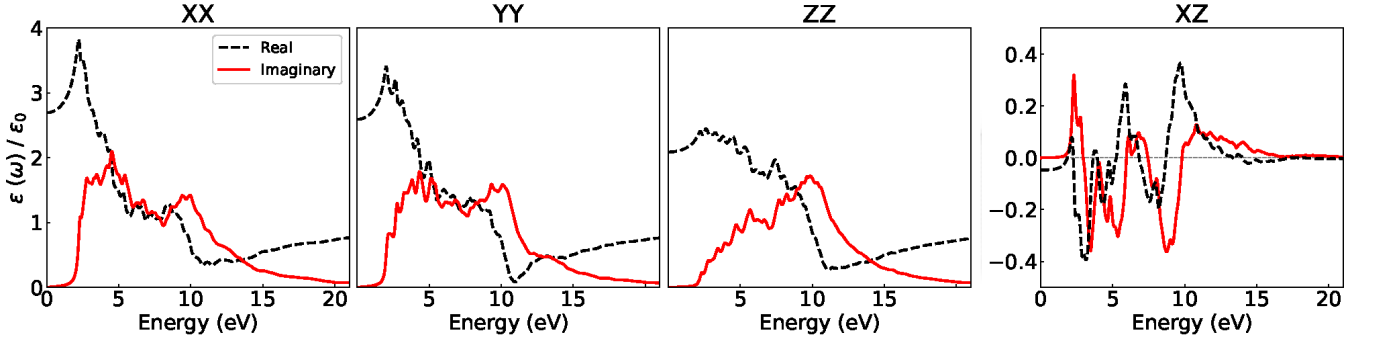


FIG. 4. Dielectric tensor components of CrPS₄ FM monolayer showing the real (dashed black line) and imaginary (red) components. The xy and yz components have little to no contribution to the system.

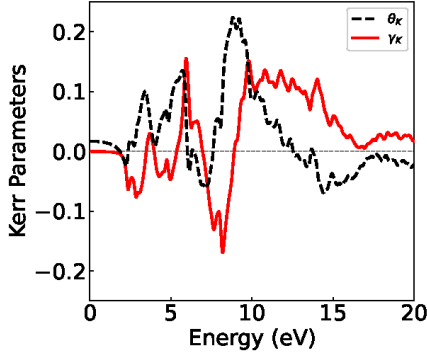


FIG. 5. The Kerr parameters of Monolayer CrPS₄ as a function of energy.

V. OPTICAL PROPERTIES

To accelerate the design of the next generation micro-electronic devices, it is necessary to be able to cross validate both theoretical calculations and experimental measurements. To this end, we first must judge the quality of our theoretically obtained description of CrPS₄. To address this issue we calculate the dielectric tensor – a key ingredient in the interaction between light and matter – and compare the results to experimental observations.

Figure 4 presents the non-zero matrix elements of the dielectric tensor (real and imaginary components) as a function of energy for a single-layer of CrPS₄. Two main blocks of transitions are seen spanning ≈ 2 eV - 6 eV and ≈ 9 eV - 11 eV in the imaginary part of the xx and yy tensor components. In contrast, $\epsilon_{zz}^{(2)}$ displays a very weak leading edge of transitions due to the 2D nature of the material and only retains the broad peak centered at 10 eV. Additionally, the sharp leading edge at ≈ 2 eV in $\epsilon_{zz}^{(2)}$ generates a strong polarization peak in $\epsilon_{xx}^{(1)}$ through the Kramer-Kronig relation. On average, the indicated peak structure is in good accord with optical spectroscopy reports [12].

Comparing to Fig. 3, the sharp transition edge at ≈ 2 eV is produced by promoting an electron from the valence- to conduction-band edges along X-M (Y-M).

The higher energetic transitions originate from bands 5.0 eV below the Fermi level connecting to the flat conduction bands along X-M and Y-M. Furthermore, our theoretically predicted electronic band gap is in very good agreement with the leading edge of the optical conductivity [27]. To allow for future experimental comparison, the refractive index and optical absorption spectrum are provided in Appendix C.

As a consequence of the canted ferromagnetism the off-diagonal xz component of the dielectric tensor exhibits a non-negligible response. Such a response may induce an appreciable Kerr angle in the polarization of the light reflected from a magnetic CrPS₄ layer. This makes the optical Kerr effect particularly useful in giving direct insight into the local, microscopic magnetism [46] and time-reversal symmetry breaking condensed-matter systems in general [47].

To estimate the Kerr response of CrPS₄, we compute the complex Kerr parameters according to the equation

$$\psi_K = \theta_K + i\gamma_K = \frac{-\epsilon_{xz}}{(\epsilon_{xx} - 1)\sqrt{\epsilon_{xx}}}, \quad (1)$$

which is the standard expression for the polar geometry in the small angles limit [48]. Here, the photon propagates along the y direction and describes a linearly polarized wave with the electric field along the x direction.

Figure 5 shows the real and imaginary Kerr parameters θ_K and γ_K , respectively, as a function of frequency. Both Kerr parameters oscillate about zero displaying a quite sensitive dependence on the frequency of light. Specifically, θ_K and γ_K change sign at ≈ 2 eV, followed by a number of additional fluctuations about zero until a maximum in both signals is achieved near 9 eV. Above 9 eV the Kerr parameters vary more smoothly with frequency. Additionally, θ_K and γ_K appear to be completely out of phase for all frequencies studied. Such a line shape in the Kerr signal is quite different from bulk 3d magnets, e.g. Fe, Co, and Ni, and more akin to other 2D magnets, e.g. NiPS₃ [42].

VI. CONCLUDING REMARKS

Our study has demonstrated that a first-principles parameter free treatment of the ground state magnetic and electronic properties of the air stable CrPS₄ 2D magnet is possible. Using the SCAN density functional we find a major improvement over standard PBE and PBE+U approaches, at nearly the same computational cost. Our study lays a firm foundation for the predictive exploration and design of new heterostructures and devices composed of CrPS₄ mitigating the need for purely experimental efforts. Furthermore, the highly anisotropic cross-coupling between spin, charge, and lattice also provide a path towards multifunctional devices ideal for monolithically integrating into semiconducting substrates for efficient interfaces between logic – interconnect – memory sectors in emerging 3D logic-memory architectures.

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Appendix A: Chromium Magnetic Moments as a Function of Wigner-Seitz Radius

Figure 6 shows the Cr atomic magnetic moment as a function of the Wigner-Seitz radius (r_{WS}), or integration sphere. The black dotted line denotes the default value of r_{WS} defined in VASP, which yields a magnetic moment of $2.78 \mu_B$. Upon expanding r_{WS} we find the magnetic moment to increase, since the integration sphere encapsulates more chromium magnetic density. At $r_{WS} = 1.74 \text{ \AA}$, a maximum in the magnetic moment is found with a value of $3.00 \mu_B$ (red dotted line). Moreover, as the integration sphere is expanded beyond the covalent radius of chromium, an admixture of sulfur density is included, thereby reducing the net effective moment. Note that the Cr moment for large r_{WS} values

will depend on the coordination number and thus on the crystal structure.

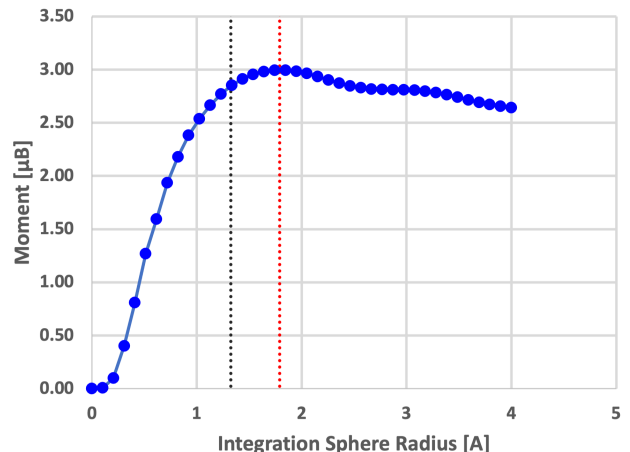


FIG. 6. (color online) The magnetic moment as a function of integration sphere radius of bulk CrPS₄ in the A-AFM phase.

Appendix B: Γ -Z Band Dispersion

Figure 7 shows the electronic band structure along Γ -Z in the Brillouin zone for bulk CrPS₄ in the A-AFM phase. The majority of bands are essentially flat, with only a few valence states below -0.75 eV displaying a dispersive nature. This suggests the inter-layer coupling in CrPS₄ is quite weak, rendering the atomically-thin layers even in the bulk compound electronically isolated.

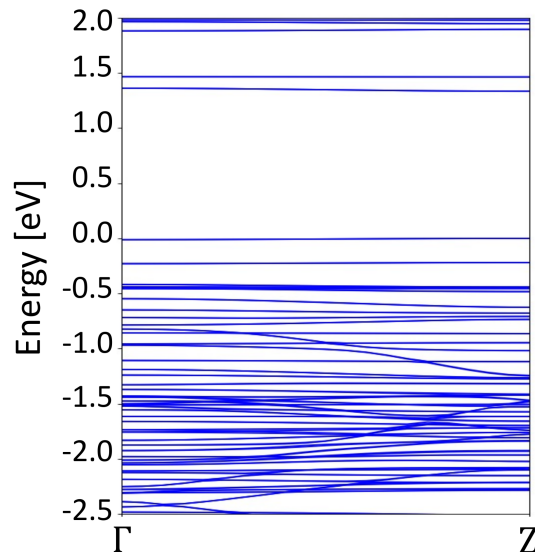


FIG. 7. (color online) Electronic band structure along Γ -Z in the Brillouin zone for bulk CrPS₄ in the A-AFM phase.

Appendix C: Refractive Index and Optical Absorption Spectrum

Figure 8 presents the refractive index and optical absorption for monolayer CrPS₄ in the FM phase. The refractive index n_{ii} is related to the diagonal parts of the dielectric tensor by

$$n_{ii} = \sqrt{\frac{|\varepsilon_{ii}| + \Re \varepsilon_{ii}}{2}}, \quad (\text{C1})$$

whereas the absorption coefficient

$$\alpha_{ii} = \frac{2\omega k_{ii}}{c}, \quad (\text{C2})$$

is proportional to the dielectric tensor through extinction coefficient,

$$k_{ii} = \sqrt{\frac{|\varepsilon_{ii}| - \Re \varepsilon_{ii}}{2}}. \quad (\text{C3})$$

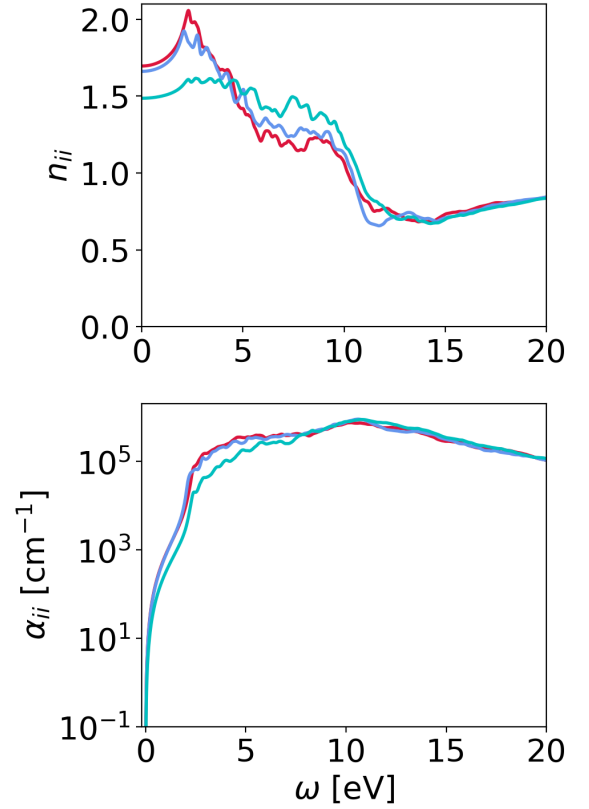


FIG. 8. (color online) Refractive index and optical absorption for monolayer CrPS₄ in the FM phase. The red, blue, and teal lines are for the xx , yy , and zz components, respectively.

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- [1] M. Gibertini, M. Koperski, A. Morpurgo, and K. Novoselov, Magnetic 2D materials and heterostructures, *Nat. Nanotechnol.* **14**, 408 (2019).
 - [2] Y. Li, N. Zaki, V. O. Garlea, A. T. Savici, D. Fobes, Z. Xu, F. Camino, C. Petrovic, G. Gu, P. D. Johnson, *et al.*, Electronic properties of the bulk and surface states of $\text{Fe}_{1+y}\text{Te}_{1-x}\text{Se}_x$, *Nature Materials* **20**, 1221 (2021).
 - [3] K. Kim, J. Seo, E. Lee, K.-T. Ko, B. Kim, B. G. Jang, J. M. Ok, J. Lee, Y. J. Jo, W. Kang, *et al.*, Large anomalous hall current induced by topological nodal lines in a ferromagnetic van der waals semimetal, *Nature Materials* **17**, 794 (2018).
 - [4] K. S. Burch, D. Mandrus, and J.-G. Park, Magnetism in two-dimensional van der waals materials, *Nature* **563**, 47 (2018).
 - [5] D. Shcherbakov, P. Stepanov, D. Weber, Y. Wang, J. Hu, Y. Zhu, K. Watanabe, T. Taniguchi, Z. Mao, W. Windl, *et al.*, Raman spectroscopy, photocatalytic degradation, and stabilization of atomically thin chromium tri-iodide, *Nano Letters* **18**, 4214 (2018).
 - [6] S. Calder, A. Haglund, Y. Liu, D. Pajerowski, H. Cau, T. Williams, V. Garlea, and D. Mandrus, Magnetic structure and exchange interactions in the layered semiconductor CrPS₄, *Physical Review B* **102**, 024408 (2020).
 - [7] J. Son, S. Son, P. Park, M. Kim, Z. Tao, J. Oh, T. Lee, S. Lee, J. Kim, K. Zhang, K. Cho, T. Kamiyama, J. Lee, K. Mak, J. Shan, M. Kim, J. Park, and J. Lee, Air-Stable and Layer-Dependent Ferromagnetism in Atomically Thin van der Waals CrPS₄, *ACS Nano* **15**, 16904 (2021).
 - [8] L. Meng, Z. Zhou, M. Xu, S. Yang, K. Si, L. Liu, X. Wang, H. Jiang, B. Li, P. Qin, *et al.*, Anomalous thickness dependence of curie temperature in air-stable two-dimensional ferromagnetic 1t-crte2 grown by chemical vapor deposition, *Nature Communications* **12**, 809 (2021).
 - [9] A. Purbawati, S. Sarkar, S. Pairis, M. Kostka, A. Hadj-Azzem, D. Dufeu, P. Singh, D. Bourgault, M. Nuñez-Regueiro, J. Vogel, *et al.*, Stability of the in-plane room temperature van der waals ferromagnet chromium ditelluride and its conversion to chromium-interleaved crte2 compounds, *ACS Applied Electronic Materials* (2023).
 - [10] W. L. Huey, A. M. Ochs, A. J. Williams, Y. Zhang, S. Kraguljac, Z. Deng, C. E. Moore, W. Windl, C. N. Lau, and J. E. Goldberger, Cr x pt1-x te2 ($x \leq 0.45$): A family of air-stable and exfoliatable van der waals ferromagnets, *ACS nano* **16**, 3852 (2022).
 - [11] Q. Pei, X. Luo, G. Lin, J. Song, L. Hu, Y. Zou, L. Yu, W. Yong, W. Song, W. Lu, and Y. Sun, Spin dynam-

- ics, electronic, and thermal transport properties of two-dimensional CrPS₄ single crystal, *Journal of Applied Physics* **119**, 043902 (2016).
- [12] J. Lee, T. Ko, J. Kim, H. Bark, B. Kang, S. Jung, T. Park, Z. Lee, S. Ryu, and C. Lee, Structural and Optical Properties of Single- and Few-layer Magnetic Semiconductor CrPS₄, *ACS Nano* **11**, 10935 (2017).
 - [13] A. Budniak, N. Killileaw, S. Zelewski, M. Syntnyk, Y. Kauffmann, Y. Amouyal, R. Kudrawiec, W. Heiss, and E. Lifshitz, Exfoliated CrPS₄ with Promising Photoconductivity, *Nano Micro Small* **16**, 1905924 (2020).
 - [14] P. Gu, Q. Tan, Y. Wan, Z. Li, Y. Peng, J. Lai, J. Ma, X. Yao, S. Yang, K. Yuan, *et al.*, Photoluminescent quantum interference in a van der waals magnet preserved by symmetry breaking, *ACS Nano* **14**, 1003 (2019).
 - [15] S. Kim, J. Lee, G. Jin, M. Jo, C. Lee, and S. Ryu, Crossover between Photochemical and Photothermal Oxidations of Atomically Thin Magnetic Semiconductor CrPS₄, *Nano Letters* **19**, 4043 (2019).
 - [16] S. Kim, J. Lee, C. Lee, and S. Ryu, Polarized raman spectra and complex raman tensors of antiferromagnetic semiconductor crps₄, *The Journal of Physical Chemistry C* **125**, 2691 (2021).
 - [17] H. Zhang, Y. Li, X. Hu, J. Xu, L. Chen, G. Li, S. Yin, J. Chen, C. Tan, X. Kan, *et al.*, In-plane anisotropic 2d crps₄ for promising polarization-sensitive photodetection, *Applied Physics Letters* **119**, 171102 (2021).
 - [18] M. Shin, M. J. Lee, C. Yoon, S. Kim, B. H. Park, S. Lee, and J.-G. Park, Charge-trapping memory device based on a heterostructure of mos₂ and crps₄, *Journal of the Korean Physical Society* **78**, 816 (2021).
 - [19] M. Riesner, R. Fainblat, A. K. Budniak, Y. Amouyal, E. Lifshitz, and G. Bacher, Temperature dependence of fano resonances in crps₄, *The Journal of Chemical Physics* **156**, 054707 (2022).
 - [20] S. Kim, S. Yoon, H. Ahn, G. Jin, H. Kim, M.-H. Jo, C. Lee, J. Kim, and S. Ryu, Photoluminescence path bifurcations by spin flip in two-dimensional crps₄, *ACS Nano* (2022).
 - [21] G. Xu, D. Liu, S. Li, Y. Wu, Z. Zhang, S. Wang, Z. Huang, and Y. Zhang, Binary-ternary transition metal chalcogenides interlayer coupling in van der waals type-ii heterostructure for visible-infrared photodetector with efficient suppression dark currents, *Nano Research* **15**, 2689 (2022).
 - [22] H. Zhuang and J. Zhou, Density functional theory study of bulk and single-layer magnetic semiconductor CrPS₄, *Physical Review B* **94**, 195307 (2016).
 - [23] M. Joe, H. Lee, M. Alyoruk, J. Lee, S. Kim, C. Lee, and J. Lee, A comprehensive study of piezomagnetic response in CrPS₄ monolayer: mechanical, electronic properties and magnetic ordering under strains, *JoP: Condensed Matter* **29**, 405801 (2017).
 - [24] Q. Chen, Q. Ding, Y. Wang, Y. Xu, and J. Wang, Electronic and Magnetic Properties of a Two-Dimensional Transition Metal Phosphorous Chalcogenide TMPS₄, *J. Phys. Chem. C* **124**, 12075 (2020).
 - [25] J. Deng, J. Guo, H. Hosono, T. Ying, and X. Chen, Two-dimensional bipolar ferromagnetic semiconductors from layered antiferromagnets, *Physical Review Materials* **5**, 034005 (2021).
 - [26] J. Yang, S. Fang, Y. Peng, S. Liu, B. Wu, R. Quhe, S. Ding, C. Yang, J. Ma, B. Shi, *et al.*, Layer-dependent giant magnetoresistance in two-dimensional crps₄ magnetic tunnel junctions, *Physical Review Applied* **16**, 024011 (2021).
 - [27] A. Louisy, G. Ouvrard, D. Schleich, and R. Brec, Physical properties and lithium intercalates of CrPS₄, *Solid State Communications* **28**, 61 (1978).
 - [28] M. Lee, S. Lee, S. Lee, K. Balamurugan, C. Yoon, J. Jang, S. Kim, D. Kwon, M. Kim, J. Ahn, D. Kim, J. Park, and B. Park, Synaptic devices based on two-dimensional layered single-crystal chromium thiophosphate (CrPS₄), *NPG Asia Materials* **10**, 23 (2018).
 - [29] G. Kresse and D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Physical Review B* **59**, 1758 (1999).
 - [30] G. Kresse and J. Hafner, *Ab initio* molecular dynamics for open-shell transition metals, *Physical Review B* **48**, 13115 (1993).
 - [31] G. Kresse and J. Furthmuller, Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set, *Physical Review B* **54**, 11169 (1996).
 - [32] J. Sun, A. Ruzsinszky, and J. Perdew, Strongly Constrained and Appropriately Normed Semilocal Density Functional, *Physical Review Letters* **115**, 036402 (2015).
 - [33] R. Diehl and C. Carpentier, The Crystal Structure of Chromium Thiophosphate, CrPS₄, *Acta Crystallographica Section B* **B33**, 1399 (1976).
 - [34] W. Kohn and L. J. Sham, Self-consistent equations including exchange and correlation effects, *Physical review* **140**, A1133 (1965).
 - [35] A. Seidl, A. Görling, P. Vogl, J. A. Majewski, and M. Levy, Generalized kohn-sham schemes and the band-gap problem, *Physical Review B* **53**, 3764 (1996).
 - [36] J. P. Perdew, W. Yang, K. Burke, Z. Yang, E. K. Gross, M. Scheffler, G. E. Scuseria, T. M. Henderson, I. Y. Zhang, A. Ruzsinszky, *et al.*, Understanding band gaps of solids in generalized kohn-sham theory, *Proceedings of the National Academy of Sciences* **114**, 2801 (2017).
 - [37] J. W. Furness, Y. Zhang, C. Lane, I. G. Buda, B. Barbiellini, R. S. Markiewicz, A. Bansil, and J. Sun, An accurate first-principles treatment of doping-dependent electronic structure of high-temperature cuprate superconductors, *Communications Physics* **1**, 11 (2018).
 - [38] C. Lane, J. W. Furness, I. G. Buda, Y. Zhang, R. S. Markiewicz, B. Barbiellini, J. Sun, and A. Bansil, Antiferromagnetic ground state of la 2 cuo 4: A parameter-free ab initio description, *Physical Review B* **98**, 125140 (2018).
 - [39] K. Pokharel, C. Lane, J. W. Furness, R. Zhang, J. Ning, B. Barbiellini, R. S. Markiewicz, Y. Zhang, A. Bansil, and J. Sun, Sensitivity of the electronic and magnetic structures of cuprate superconductors to density functional approximations, *npj Computational Materials* **8**, 31 (2022).
 - [40] Y. Zhang, C. Lane, J. W. Furness, B. Barbiellini, J. P. Perdew, R. S. Markiewicz, A. Bansil, and J. Sun, Competing stripe and magnetic phases in the cuprates from first principles, *Proceedings of the National Academy of Sciences* **117**, 68 (2020).
 - [41] C. Lane, Y. Zhang, J. W. Furness, R. S. Markiewicz, B. Barbiellini, J. Sun, and A. Bansil, First-principles calculation of spin and orbital contributions to magnetically ordered moments in sr 2 iro 4, *Physical Review B* **101**, 155110 (2020).
 - [42] C. Lane and J.-X. Zhu, Thickness dependence of electronic structure and optical properties of a correlated van

- der waals antiferromagnetic NiPS_3 thin film, Physical Review B **102**, 075124 (2020).
- [43] C. Lane and J.-X. Zhu, Landscape of coexisting excitonic states in the insulating single-layer cuprates and nickelates, Physical Review B **101**, 155135 (2020).
 - [44] C. Lane and J.-X. Zhu, An ab initio study of electron-hole pairs in a correlated van der waals antiferromagnet: NiPS_3 , arXiv preprint arXiv:2209.13051 (2022).
 - [45] J. Zaanen, G. Sawatzky, and J. Allen, Band gaps and electronic structure of transition-metal compounds, Physical Review Letters **55**, 418 (1985).
 - [46] J. L. Erskine and E. Stern, Calculation of the magneto-optical absorption spectrum of ferromagnetic nickel, Physical Review B **12**, 5016 (1975).
 - [47] J. Xia, Y. Maeno, P. T. Beyersdorf, M. Fejer, and A. Kapitulnik, High resolution polar kerr effect measurements of Sr_2RuO_4 : Evidence for broken time-reversal symmetry in the superconducting state, Physical Review Letters **97**, 167002 (2006).
 - [48] D. Sangalli, A. Marini, and A. Debernardi, Pseudopotential-based first-principles approach to the magneto-optical kerr effect: From metals to the inclusion of local fields and excitonic effects, Physical Review B **86**, 125139 (2012).