

Large magneto-optical effects and magnetic anisotropy energy in two-dimensional Cr₂Ge₂Te₆Yimei Fang,¹ Shunqing Wu,^{1,*} Zi-Zhong Zhu,^{1,2,†} and Guang-Yu Guo^{3,4,‡}¹*Department of Physics, Collaborative Innovation Center for Optoelectronic Semiconductors and Efficient Devices, Key Laboratory of Low Dimensional Condensed Matter Physics (Department of Education of Fujian Province), Jiujiang Research Institute,**Xiamen University, Xiamen 361005, China*²*Fujian Provincial Key Laboratory of Theoretical and Computational Chemistry, Xiamen 361005, China*³*Department of Physics and Center for Theoretical Physics, National Taiwan University, Taipei 10617, Taiwan*⁴*Physics Division, National Center for Theoretical Sciences, Hsinchu 30013, Taiwan*

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Atomically thin ferromagnetic (FM) films were recently prepared by mechanical exfoliation of bulk FM semiconductor Cr₂Ge₂Te₆. They provide a platform to explore novel two-dimensional (2D) magnetic phenomena, and they offer exciting prospects for new technologies. By performing systematic *ab initio* density functional calculations, here we study two relativity-induced properties of these 2D materials (monolayer, bilayer, and trilayer as well as bulk), namely magnetic anisotropy energy (MAE) and magneto-optical (MO) effects. Competing contributions of both magnetocrystalline anisotropy energy (C-MAE) and magnetic dipolar anisotropy energy (D-MAE) to the MAE are computed. The calculated MAEs of these materials are large, being on the order of ~ 0.1 meV/Cr. Interestingly, we find that out-of-plane magnetic anisotropy is preferred in all the systems except the monolayer, where in-plane magnetization is favored because here the D-MAE is larger than the C-MAE. Crucially, this explains why long-range FM order was observed in all the few-layer Cr₂Ge₂Te₆ except the monolayer because the out-of-plane magnetic anisotropy would open a spin-wave gap and thus suppress magnetic fluctuations so that long-range FM order could be stabilized at finite temperature. In the visible frequency range, large Kerr rotations up to $\sim 2.2^\circ$ in these materials are predicted, and they are comparable to that observed in famous MO materials such as PtMnSb and Y₃Fe₅O₁₂. Moreover, they are ~ 100 times larger than that of *3d* transition metal monolayers deposited on Au surfaces. Faraday rotation angles in these 2D materials are also large, being up to $\sim 120^\circ/\mu\text{m}$, and they are thus comparable to the best-known MO semiconductor Bi₃Fe₅O₁₂. These findings thus suggest that with large MAE and MO effects, atomically thin Cr₂Ge₂Te₆ films would have potential applications in novel magnetic, MO, and spintronic nanodevices.

DOI: [10.1103/PhysRevB.98.125416](https://doi.org/10.1103/PhysRevB.98.125416)**I. INTRODUCTION**

Two-dimensional (2D) materials are layer substances with a thickness of one monolayer or a few atomic or molecular monolayers (MLs). The vibrant field of 2D materials was triggered by the first isolation of graphene, a single atomic layer of graphite with carbon atoms arranged in a 2D honeycomb lattice, through mechanical exfoliation of graphite and also the discovery of its extraordinary transport properties in 2004 [1]. The recent intensive interest in graphene has also stimulated research efforts to fabricate and investigate other 2D materials [2,3]. Many of these 2D materials exhibit a variety of fascinating properties not seen in their bulk counterparts due to, e.g., symmetry breaking and quantum confinement. For example, a semiconductor MoS₂ crystal was found to exhibit an indirect to direct band-gap transition when thinned down to a ML [4]. Importantly, the broken inversion symmetry causes MLs of MoS₂ and other transition metal dichalcogenides to exhibit novel properties of fundamental

and technological interest, such as spin-valley coupling [5], piezoelectricity [6], and second-harmonic generation [7].

More recently, the family of 2D materials has also been extended to 2D magnets, crucial for the development of magnetic nanodevices and spintronic applications. For example, realization of 2D magnets by doping transition metals into nonmagnetic parent monolayers has been predicted by *ab initio* density functional calculations and also attempted experimentally by numerous research groups [3]. Hole-doping into a GaSe ML, which possesses a unique van Hove singularity near the top of its valance band, was recently predicted to induce tunable ferromagnetism and magneto-optical effects [8,9]. Experimental and theoretical evidence for the ferromagnetic (FM) MoS₂ ML at the MoS₂/CdS interface was also reported [10]. Several layered magnetic compounds have recently been investigated theoretically to determine whether their structure and magnetism can be retained down to ML thickness [11–14]. These intensive research efforts finally led two groups to successfully thin bulk ferromagnets CrI₃ and Cr₂Ge₂Te₆ down to few-layer ultrathin films and to observe the intrinsic ferromagnetism retained in one and two monolayers, respectively [15,16]. This successful fabrication of 2D magnets would allow us to study 2D magnetism and exotic magnetic phenomena, and

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it also offers exciting prospects for advanced technological applications.

In this paper, we focus on two relativity induced properties of atomically thin FM $\text{Cr}_2\text{Ge}_2\text{Te}_6$ films [16], namely magnetic anisotropy energy (MAE) and magneto-optical (MO) effects. For comparison, we also consider bulk $\text{Cr}_2\text{Ge}_2\text{Te}_6$, which is interesting in its own right. Bulk $\text{Cr}_2\text{Ge}_2\text{Te}_6$ belongs to the rare class of intrinsic FM semiconductors [17] and has recently been attracting renewed interest because of its layered, quasi-2D FM structure with weak van der Waals bonds. For example, its magnetic anisotropy energy was recently measured [18]. It was also used as a substrate for epitaxial growth of topological insulator Bi_2Te_3 to realize the quantum anomalous Hall effect [19].

Magnetic anisotropy energy refers to the total energy difference between the easy- and hard-axis magnetizations, i.e., the energy required to rotate the magnetization from the easy to the hard direction. Together with the magnetization and magnetic ordering temperature, MAE is one of the three important parameters that characterizes a FM material. Furthermore, MAE is especially important for 2D magnetic materials such as few-layer $\text{Cr}_2\text{Ge}_2\text{Te}_6$ structures because it helps to lift the Mermin-Wagner restriction [20], thus allowing the long-range ferromagnetic order to survive at finite temperature even in the ML limit [15]. Moreover, 2D magnets with a significant MAE would find spintronic applications such as high-density magnetic memory and data-storage devices. MAE consists of two contributions, namely the magnetocrystalline anisotropy energy (C-MAE) due to the effect of relativistic spin-orbit coupling (SOC) on the electronic band structure, and also the magnetic dipolar (shape) anisotropy energy (D-MAE) due to the magnetostatic interaction among the magnetic moments [21,22]. Note that the D-MAE always prefers an in-plane magnetization [21]. Although the D-MAE in isotropic bulk materials is generally negligibly small, the D-MAE could become significant in low-dimensional materials such as magnetic monolayers [21] and atomic chains [22]. Despite the recent intensive interest in few-layer $\text{Cr}_2\text{Ge}_2\text{Te}_6$ [11–14,16,23,24], no investigation into their MAE has been reported, although an experimental measurement on MAE [18] and a theoretical calculation of C-MAE [16] of bulk $\text{Cr}_2\text{Ge}_2\text{Te}_6$ were recently reported. Therefore, in this paper we carry out a systematic *ab initio* density functional investigation into the MAE as well as other magnetic properties of bulk and few-layer $\text{Cr}_2\text{Ge}_2\text{Te}_6$. Furthermore, both C-MAE and D-MAE are calculated here. Importantly, as will be reported in Sec. III, taking the D-MAE into account results in an in-plane magnetization for the $\text{Cr}_2\text{Ge}_2\text{Te}_6$ ML while all other considered $\text{Cr}_2\text{Ge}_2\text{Te}_6$ materials have out-of-plane magnetic anisotropy. Thus, this interesting finding could explain why the ferromagnetism was not observed in the $\text{Cr}_2\text{Ge}_2\text{Te}_6$ ML [16].

The magneto-optical Kerr effect (MOKE) and Faraday effect (MOFE) are two well-known MO effects [25,26]. When a linearly polarized light beam hits a magnetic material, the polarization vector of the reflected and transmitted light beams rotates. The former and latter are known as Kerr and Faraday effects, respectively. The Faraday effect has attracted much less attention than the Kerr effect simply because light can only transmit through ultrathin films. In contrast, MOKE has

been widely used to study the magnetic and electronic properties of solids, including surfaces and films [26]. Furthermore, magnetic materials with large MOKE would find valuable MO storage and sensor applications [27,28], and hence they have been continuously searched for in recent decades. The recent development of 2D magnetic materials [15,16] offers exciting possibilities of scaling the MO storage and sensing devices to the few-nanometer scale. However, detection and measurement of magnetism in these 2D materials will be difficult using traditional methods such as a superconducting quantum interference device (SQUID) magnetometer because ultrahigh sensitivity would be required for these ultrathin films. In this regard, MOKE and MOFE are powerful, noninvasive probes of spontaneous magnetization in these 2D materials. Indeed, long-range ferromagnetic orders in both $\text{Cr}_2\text{Ge}_2\text{Te}_6$ and CrI_3 atomically thin films were detected by using the MOKE technique [15,16,24]. In this paper, therefore, we perform a systematic *ab initio* density functional study of the magneto-optical and optical properties of bulk and atomically thin films of $\text{Cr}_2\text{Ge}_2\text{Te}_6$. Indeed, we find that both the bulk and the ultrathin films would exhibit large MOKE with Kerr rotation angles being as large as $\sim 2.2^\circ$. Furthermore, the calculated Faraday rotation angles of the thin films are also large, being $\sim 120^\circ/\mu\text{m}$. Therefore, bulk and ultrathin films $\text{Cr}_2\text{Ge}_2\text{Te}_6$ are promising magneto-optical materials for high-density MO recordings and magnetic nanosensors.

II. STRUCTURES AND METHODS

In this paper, we study the electronic, magnetic, and magneto-optical properties of few-layer and bulk $\text{Cr}_2\text{Ge}_2\text{Te}_6$ structures. Bulk $\text{Cr}_2\text{Ge}_2\text{Te}_6$ forms a layered structure with MLs separated by the so-called van der Waals (vdW) gap [Fig. 1(a)] [17]. Each $\text{Cr}_2\text{Ge}_2\text{Te}_6$ ML consists of two AB-stacked compact hexagonal Te planes with one Ge dimer lying vertically at one of every three hexagon centers [Fig. 1(c)] and two Cr atoms occupying two of every three Te octahedron centers [Figs. 1(a), 1(c) and 1(d)]. These layers are ABC-stacked [Fig. 1(a)], thus resulting in a rhombohedral $R\bar{3}$ symmetry with one chemical formula unit (f.u.) per unit cell. The experimental lattice constants are $a = b = c = 7.916 \text{ \AA}$ [17]. This structure can also be regarded as an ABC-stacked hexagonal crystal cell with experimental lattice constants $a = b = 6.828 \text{ \AA}$ and $c = 20.5619 \text{ \AA}$ [17]. As explained in the next paragraph, we adopt the experimental rhombohedral unit cell in the bulk calculations, and for the few-layer $\text{Cr}_2\text{Ge}_2\text{Te}_6$ structures we adopt the hexagonal unit cell with the experimental bulk lattice constants and atomic positions [Fig. 1(c)]. For bilayer (BL) and trilayer (TL) $\text{Cr}_2\text{Ge}_2\text{Te}_6$ structures, we consider the AB and ABC stackings, respectively, as observed in bulk $\text{Cr}_2\text{Ge}_2\text{Te}_6$ [Fig. 1(d)]. The few-layer structures are modeled by using the slab-superlattice approach with the separations between MLs being at least 15 \AA .

Ab initio calculations are performed based on density functional theory. The exchange-correlation interaction is treated with the generalized gradient approximation (GGA) parametrized by the Perdew-Burke-Ernzerhof formula [29]. To improve the description of on-site Coulomb interaction between Cr $3d$ electrons, we adopt the GGA+U scheme [30]. It was reported in Ref. [16] that a physically appropriate value

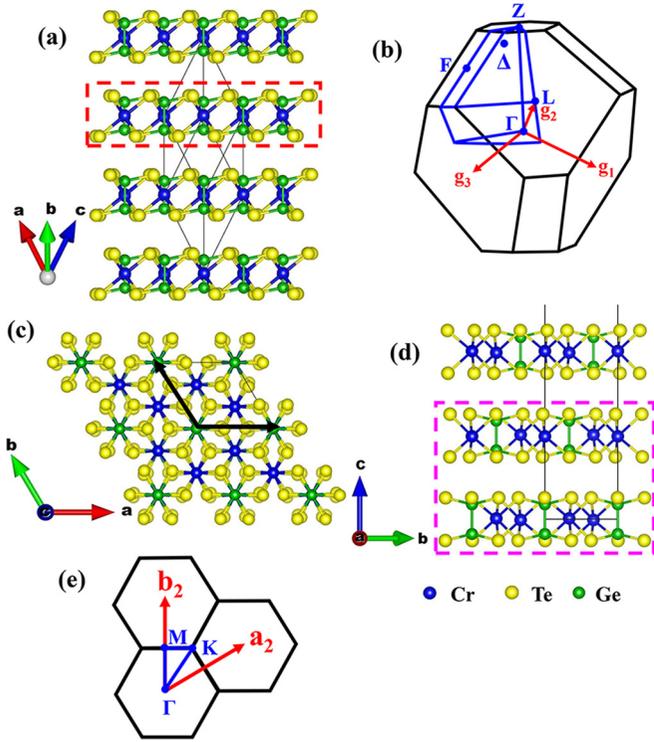


FIG. 1. (a) Crystalline structure of bulk rhombohedral $\text{Cr}_2\text{Ge}_2\text{Te}_6$ with the red dashed rectangle indicating one monolayer (ML) $\text{Cr}_2\text{Ge}_2\text{Te}_6$, and (b) the corresponding Brillouin zone with its irreducible wedge indicated by blue lines. (c) Top and (d) side views of trilayer (TL) $\text{Cr}_2\text{Ge}_2\text{Te}_6$ structure in ABC stacking. In (d), the magenta dashed rectangle indicates a bilayer (BL) unit cell. (e) Two-dimensional hexagonal Brillouin zone for ML, BL, and TL $\text{Cr}_2\text{Ge}_2\text{Te}_6$ with its irreducible wedge indicated by blue lines.

of the effective on-site Coulomb energy U should be within the range of $0.2 < U < 1.7$ eV. Therefore, here we use $U = 1.0$ eV [see also the supplementary note in the supplementary material (SM) [31] for explanations]. The accurate projector-augmented wave [36] method, as implemented in the Vienna ab initio Simulation Package (VASP) [37,38], is used. A large plane-wave cutoff energy of 450 eV is used throughout. For the Brillouin zone integrations, k -point meshes of $16 \times 16 \times 16$ and $20 \times 20 \times 1$ are used for bulk and few-layer $\text{Cr}_2\text{Ge}_2\text{Te}_6$, respectively. The structural optimization within the GGA+U scheme for bulk $\text{Cr}_2\text{Ge}_2\text{Te}_6$ results in lattice constants $a = 6.931$ Å and $c = 22.695$ Å. This theoretical c is more than 10% larger than the experimental c , although the calculated a is only 1.5% too large. This is because the GGA+U tends to largely overestimate the vdW gaps in layered materials. To account for the vdW dispersion interactions, we further perform the structural optimization with the GGA+U plus vdW-density functional of Langreth and co-workers [39] as implemented in the VASP, and we obtain $a = 6.905$ Å and $c = 20.074$ Å. The discrepancy in c between the calculation and experiment [17] is much reduced to -2.3% , but the calculated a is still more than 1.0% too large. The GGA+U structural optimization for ML $\text{Cr}_2\text{Ge}_2\text{Te}_6$ results in $a = 6.925$ Å, which deviates only slightly from the theoretical bulk a (by less than 0.1%). This shows that

structural relaxation in ML $\text{Cr}_2\text{Ge}_2\text{Te}_6$ is much smaller than the errors in the GGA+U and GGA+U+vdW correction schemes. Therefore, we use the experimentally determined bulk atomic structure in all the subsequent calculations.

To understand the magnetism and also estimate the magnetic ordering temperature (T_c) for bulk and few-layer $\text{Cr}_2\text{Ge}_2\text{Te}_6$, we determine the exchange coupling parameters by mapping the calculated total energies of different magnetic configurations onto the classical Heisenberg Hamiltonian, $E = E_0 - \sum_{i,j} J_{ij} \hat{\mathbf{e}}_i \cdot \hat{\mathbf{e}}_j$, where E_0 denotes the nonmagnetic ground-state energy, J_{ij} is the exchange coupling parameter between sites i and j , and $\hat{\mathbf{e}}_i$ is the unit vector representing the direction of the magnetic moment on site i . Specifically, the total energies of the four intralayer magnetic configurations for one $\text{Cr}_2\text{Ge}_2\text{Te}_6$ layer can be expressed as a set of four linear equations of J_1 , J_2 , and J_3 : $E_{\text{FM}} = E_0 - 3J_1 - 6J_2 - 3J_3$, $E_{\text{AF-Neel}} = E_0 + 3J_1 - 6J_2 + 3J_3$, $E_{\text{AF-zigzag}} = E_0 - J_1 + 2J_2 + 3J_3$, and $E_{\text{AF-stripe}} = E_0 + J_1 + 2J_2 - 3J_3$. Given the calculated total energies, one can solve this set of linear equations to obtain the J_1 , J_2 , and J_3 values. Similarly, given the calculated E_{FM} and $E_{\text{AF-interlayer}}$, one can obtain the J_{z1} value.

As described in Sec. I, magnetic anisotropy energy (MAE) consists of two parts, namely magnetocrystalline anisotropy energy (C-MAE) and magnetic dipolar anisotropy energy (D-MAE). To determine C-MAE, we first perform two self-consistent relativistic electronic structure calculations for the in-plane and out-of-plane magnetizations, and then we obtain the C-MAE as the total energy difference between the two calculations. Highly dense k -point meshes of $25 \times 25 \times 25$ and $30 \times 30 \times 1$ are used for bulk and few-layer $\text{Cr}_2\text{Ge}_2\text{Te}_6$, respectively. Test calculations using different k -point meshes show that thus-obtained C-MAE converges within 1%. For a FM system, the magnetic dipolar energy E_d in atomic Rydberg units is given by [21,22]

$$E_d = \sum_{qq'} \frac{2m_q m_{q'}}{c^2} M_{qq'}, \quad (1)$$

where the so-called magnetic dipolar Madelung constant

$$M_{qq'} = \sum_{\mathbf{R}}' \frac{1}{|\mathbf{R} + \mathbf{q} + \mathbf{q}'|^3} \left\{ 1 - 3 \frac{[(\mathbf{R} + \mathbf{q} + \mathbf{q}') \cdot \hat{\mathbf{m}}_q]^2}{|\mathbf{R} + \mathbf{q} + \mathbf{q}'|^2} \right\}, \quad (2)$$

which is evaluated by Ewald's lattice summation technique [40]. \mathbf{R} are the lattice vectors and \mathbf{q} are the atomic position vectors in the unit cell. The speed of light $c = 274.072$, and m_q is the atomic magnetic moment (in units of μ_B) on site q . Thus, given the calculated magnetic moments, the D-MAE is obtained as the difference in E_d between the in-plane and out-of-plane magnetizations. In a 2D material, all the \mathbf{R} and \mathbf{q} are in-plane. Thus, the second term in Eq. (2) would be zero for the out-of-plane magnetization, thereby resulting in the positive $M_{qq'}$, while for an in-plane magnetization the $M_{qq'}$ are negative. For example, in ML $\text{Cr}_2\text{Ge}_2\text{Te}_6$, the calculated M_{11} (M_{12}) is 11.0246 (23.0628) a^{-3} for the out-of-plane magnetization, and it is -5.5123 (-11.5314) a^{-3} for an in-plane magnetization. Therefore, the D-MAE always prefers an in-plane magnetization in a 2D material. This is purely a

geometric effect, and consequently the D-MAE is also known as the magnetic shape anisotropy energy.

For a FM solid possessing at least a trigonal symmetry with the magnetization along the rotational z -axis, the optical conductivity tensor can be reduced in the form

$$\sigma = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & 0 \\ -\sigma_{xy} & \sigma_{xx} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}. \quad (3)$$

We calculate the three independent elements of the conductivity tensor using the Kubo formula within the linear-response theory [41–43]. Here the absorptive parts of these elements, i.e., the real diagonal and imaginary off-diagonal elements, are given by

$$\sigma_{aa}^1(\omega) = \frac{\pi e^2}{\hbar\omega m^2} \sum_{i,j} \int_{\text{BZ}} \frac{d\mathbf{k}}{(2\pi)^3} |p_{ij}^a|^2 \delta(\epsilon_{\mathbf{k}j} - \epsilon_{\mathbf{k}i} - \hbar\omega), \quad (4)$$

$$\sigma_{xy}^2(\omega) = \frac{\pi e^2}{\hbar\omega m^2} \sum_{i,j} \int_{\text{BZ}} \frac{d\mathbf{k}}{(2\pi)^3} \text{Im}[p_{ij}^x p_{ji}^y] \delta(\epsilon_{\mathbf{k}j} - \epsilon_{\mathbf{k}i} - \hbar\omega), \quad (5)$$

where $\hbar\omega$ is the photon energy and $\epsilon_{\mathbf{k}i}$ is the i th band energy at point \mathbf{k} . Summations i and j are over the occupied and unoccupied bands, respectively. Dipole matrix elements $p_{ij}^a = \langle \mathbf{k}j | \hat{p}_a | \mathbf{k}i \rangle$, where \hat{p}_a denotes Cartesian component a of the dipole operator, are obtained from the band structures within the PAW formalism [44] as implemented in the VASP package. The integration over the Brillouin zone is carried out by using the linear tetrahedron method (see [45] and references therein). The dispersive parts of the optical conductivity elements can be obtained from the corresponding absorptive parts using the Kramers-Kronig relations

$$\sigma_{aa}^2(\omega) = -\frac{2\omega}{\pi} \text{P} \int_0^\infty \frac{\sigma_{aa}^1(\omega')}{\omega'^2 - \omega^2} d\omega', \quad (6)$$

$$\sigma_{xy}^1(\omega) = \frac{2}{\pi} \text{P} \int_0^\infty \frac{\omega' \sigma_{xy}^2(\omega')}{\omega'^2 - \omega^2} d\omega', \quad (7)$$

where P donates the principal value. To take the finite quasi-particle lifetime effects into account, we convolute all the optical conductivity spectra with a Lorentzian of linewidth Γ . For layered vdW materials such as graphite, Γ is about 0.2 eV [see, e.g., Figs. 1(a) and 1(b) in Ref. [46]], which is thus used in this paper.

We should note that the optical conductivity calculated using Eqs. (4) and (5) is based on the independent-particle approximation, i.e., the many-body effects, namely the quasi-particle self-energy corrections and excitonic effects, are neglected. These many-body effects on the optical properties of 2D systems such as MoS₂ and SiC monolayers [47,48] are especially pronounced due to the reduced dimensionality. Nevertheless, here the self-energy corrections are taken into account by the scissors correction using the band gaps from the hybrid functional HSE06 [49,50] calculations, as reported in the next section (Sec. III B), and the quasi-particle lifetime effects are accounted for by convoluting all the optical conductivity spectra with a Lorentzian, as mentioned

above. Weak or moderate electron-hole interaction would merely enhance the peaks near the absorption edge [51]. However, strong electron-hole interaction in, e.g., the MoS₂ monolayer could give rise to additional prominent excitonic peaks below the absorption edge [47]. Nonetheless, in contrast to the direct-band-gap MoS₂ monolayer, all the Cr₂Ge₂Te₆ systems considered here have an indirect band gap and hence one could expect no strong excitonic effect on their optical and MO properties. Indeed, no excitonic transition peak was observed in ultrathin indirect-band-gap GaSe films in a very recent experiment [52].

Here we consider the polar MOKE and MOFE. For a bulk magnetic material, the complex polar Kerr rotation angle is given by [53,54]

$$\theta_K + i\epsilon_K = \frac{-\sigma_{xy}}{\sigma_{xx} \sqrt{1 + i(4\pi/\omega)\sigma_{xx}}}. \quad (8)$$

For a magnetic thin film on a nonmagnetic substrate, however, the complex polar Kerr rotation angle is given by [9,55,56]

$$\theta_K + i\epsilon_K = i \frac{2\omega d}{c} \frac{\sigma_{xy}}{\sigma_{xx}^s} = \frac{8\pi d}{c} \frac{\sigma_{xy}}{(1 - \epsilon_{xx}^s)}, \quad (9)$$

where c stands for the speed of light in vacuum, d is the thickness of the magnetic layer, and ϵ_{xx}^s (σ_{xx}^s) is the diagonal part of the dielectric constant (optical conductivity) of the substrate. Experimentally, atomically thin Cr₂Ge₂Te₆ films were prepared on SiO₂/Si [16]. Thus, the optical dielectric constant of bulk SiO₂ (2.25) is used as ϵ_{xx}^s . Similarly, the complex Faraday rotation angle for a thin film can be written as [57]

$$\theta_F + i\epsilon_F = \frac{\omega d}{2c} (n_+ - n_-), \quad (10)$$

where n_+ and n_- represent the refractive indices for left- and right-handed polarized lights, respectively, and they are related to the corresponding dielectric function (or optical conductivity) via expressions $n_\pm^2 = \epsilon_\pm = 1 + \frac{4\pi i}{\omega} \sigma_\pm = 1 + \frac{4\pi i}{\omega} (\sigma_{xx} \pm i\sigma_{xy})$. Here the real parts of the optical conductivity σ_\pm can be written as

$$\sigma_\pm^1(\omega) = \frac{\pi e^2}{\hbar\omega m^2} \sum_{i,j} \int_{\text{BZ}} \frac{d\mathbf{k}}{(2\pi)^3} |\Pi_{ij}^\pm|^2 \delta(\epsilon_{\mathbf{k}j} - \epsilon_{\mathbf{k}i} - \hbar\omega), \quad (11)$$

where $\Pi_{ij}^\pm = \langle \mathbf{k}j | \frac{1}{\sqrt{2}} (\hat{p}_x \pm i\hat{p}_y) | \mathbf{k}i \rangle$. Clearly, $\sigma_{xy} = \frac{1}{2i} (\sigma_+ - \sigma_-)$, and this shows that σ_{xy} would be nonzero only if σ_+ and σ_- are different. In other words, magnetic circular dichroism is the fundamental cause of the nonzero σ_{xy} and hence the magneto-optical effects.

III. RESULTS AND DISCUSSION

A. Magnetic moments and exchange coupling

We consider four intralayer magnetic configurations for each Cr₂Ge₂Te₆ ML comprising the FM as well as three antiferromagnetic (AF) structures, labeled AF-Néel, AF-zigzag, and AF-stripe in Fig. 2. The FM state is found to be the ground state in all the considered materials. The

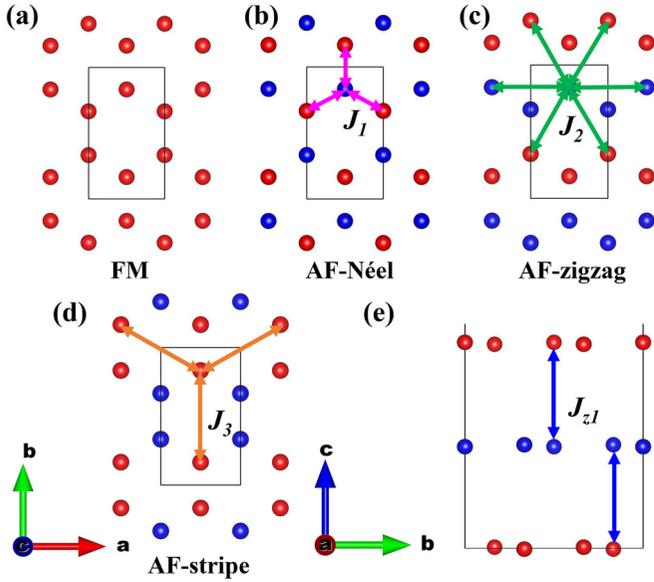


FIG. 2. Four considered intralayer magnetic configurations: (a) FM, (b) AF-Néel, (c) AF-zigzag, and (d) AF-stripe types. Only magnetic Cr atoms are shown with red (blue) balls indicating up (down) spins. Intralayer exchange coupling parameters J_1 , J_2 , and J_3 are indicated by magenta, green, and orange arrows, respectively. (e) Interlayer AF configuration with the interlayer exchange coupling parameter J_{z1} indicated by blue lines.

lowest-energy AF state is the AF-zigzag, which is, however, more than 0.05 eV/f.u. higher in energy than the FM state in all the systems considered. For the bilayer, trilayer, and bulk systems, we also consider the interlayer AF state [see Fig. 2(e)]. We find that the interlayer AF state is only slightly (i.e., a couple of meV/f.u.) above the interlayer FM state. Calculated spin and orbital magnetic moments of $\text{Cr}_2\text{Ge}_2\text{Te}_6$ in the FM state are listed in Table I. The Cr spin magnetic moment in all the structures is $\sim 3.2\mu_B$, being in good agreement with the experimental value of $\sim 3.0\mu_B$ [19]. This is consistent with three unpaired electrons in the $\text{Cr}^{3+}(d^3; t_{2g}^{3\uparrow})$ ionic configuration in these materials. The calculated Cr orbital magnetic moment is negligibly small (Table I), further

TABLE I. Total spin magnetic moment (m_s^t), atomic (averaged) spin (m_s^{Cr} , m_s^{Ge} , m_s^{Te}), and orbital (m_o^{Cr} , m_o^{Ge} , m_o^{Te}) magnetic moments as well as band gap (E_g) of bulk and few-layer FM $\text{Cr}_2\text{Ge}_2\text{Te}_6$ (magnetization being perpendicular to the layers) calculated using the GGA+U scheme with the spin-orbit coupling included. Also listed are the total magnetic anisotropy energy (ΔE_{ma}), the magnetocrystalline anisotropy energy (ΔE_b), and the magnetic dipolar anisotropy energy (ΔE_d). Positive ΔE_{ma} means that the out-of-plane magnetization is the easy axis. For comparison, the available experimental E_g and ΔE_{ma} values are also listed. The band gaps (E_g^{HSE06}) calculated using the hybrid HSE06 functional are also included here.

Structure	m_s^t (μ_B /f.u.)	m_s^{Cr} (m_o^{Cr}) (μ_B /at)	m_s^{Ge} (m_o^{Ge}) (μ_B /at)	m_s^{Te} (m_o^{Te}) (μ_B /at)	ΔE_b (ΔE_d) (meV/f.u.)	ΔE_{ma} (meV/f.u.)	E_g (E_g^{exp}) (eV)	E_g^{HSE06} (eV)
monolayer	6.00	3.23 (0.003)	0.024 (0.001)	-0.144 (-0.003)	0.107 (-0.153)	-0.05	0.23	0.56
bilayer	6.00	3.23 (0.003)	0.024 (0.001)	-0.145 (-0.003)	0.274 (-0.153)	0.12	0.13	0.44
trilayer	6.00	3.23 (0.003)	0.025 (0.001)	-0.145 (-0.001)	0.297 (-0.153)	0.14	0.09	0.41
bulk	6.00	3.23 (0.003)	0.025 (0.001)	-0.146 (-0.003)	0.471 (-0.067)	0.40 (0.05 ^a)	0.04 (0.74 ^b)	0.33

^aReference [18].

^bReference [19].

TABLE II. Intralayer first-, second-, and third-neighbor exchange coupling parameters (J_1 , J_2 , J_3) as well as interlayer first-neighbor exchange coupling constant (J_{z1}) in monolayer (ML), bilayer (BL), trilayer (TL), and bulk $\text{Cr}_2\text{Ge}_2\text{Te}_6$, derived from the calculated total energies for various magnetic configurations (see the text). Ferromagnetic transition temperatures estimated using the derived J_1 values within the mean-field approximation (T_c^m) and within the mean-field approximation plus spin wave gap correction (T_c) (see the text) are also included. For comparison, the available experimental T_c values [16] are also listed in parentheses.

System	J_1 (meV)	J_2 (meV)	J_3 (meV)	J_{z1} (meV)	T_c^m (K)	T_c (T_c^{exp}) (K)
ML	12.74	-0.09	0.29		149	0
BL	14.26	-0.47	1.07	0.40	169	71 (28 ^a)
TL	14.75	-0.57	1.29	0.74	176	76 (35 ^a)
bulk	15.74	-0.78	1.74	1.08	189	99 (66 ^a)

^aReference [16].

suggesting that the Cr ions are in the ($d^3; t_{2g}^{3\uparrow}$) configuration. Interestingly, the induced spin magnetic moment on the Te site is significant ($\sim 0.15\mu_B$) and also antiparallel to that of the Cr atoms, although the spin moment on the Ge atom is five times smaller (Table I). This results in exactly $6.0\mu_B$ /f.u., and is in good agreement with the measured bulk magnetization [19]. The mechanism of ferromagnetism in all the $\text{Cr}_2\text{Ge}_2\text{Te}_6$ structures could be attributed to the dominant FM superexchange coupling between half-filled Cr t_{2g} and empty e_g states via Te p orbitals, against the AF direct exchange interactions of Cr t_{2g} states [11]. This is further supported by our finding of significant spin moments of Te atoms which are antiparallel to the Cr spin moments (Table I).

Using the calculated total energies of the magnetic configurations considered here, we estimate the intralayer first-, second-, and third-neighbor exchange coupling parameters (J_1 , J_2 , J_3) as well as the first-neighbor interlayer coupling constant (J_{z1}) by mapping the total energies to the effective Heisenberg Hamiltonian model as described above in Sec. II. The estimated exchange coupling parameters are listed in Table II. The large, positive J_1 values in all the structures show that the nearest-neighbor Cr-Cr coupling is strongly

ferromagnetic. In contrast, the second-nearest-neighbor coupling (J_2) is about 20 times weaker and antiferromagnetic. Interestingly, calculated J_3 values are three times larger than J_2 , although they are about ten times smaller than J_1 . The calculated interlayer exchange coupling parameter (J_{z1}) is about as large as J_2 but ferromagnetic. Table I shows that all the exchange interaction parameters increase monotonically with the increasing number of layers. This suggests that the magnetism is strengthened as one moves from the ML to the BL and eventually to the bulk. Our J_1 values agree quite well with that of the previous *ab initio* calculation (~ 12 meV) reported in Ref. [11]. Nonetheless, all the present J values appear to be about twice as large as that of the *ab initio* calculation of Ref. [16], although the trends are very similar. This discrepancy in the calculated J values between Ref. [16] and the present calculation could be attributed to the fact that the LSDA+U is used in Ref. [16] while the GGA+U is exploited in this paper. This is because the LSDA tends to underestimate the tendency of magnetism. Note that for comparison of the previous *ab initio* calculations [11,16] with the present results, the J values reported in Refs. [11] and [16] should be multiplied by a factor of $S^2 = 9/4$.

B. Magnetic anisotropy energy and ferromagnetic transition temperature

As described in Sec. I, magnetic anisotropy energy consists of magnetocrystalline anisotropy energy (ΔE_b) due to the SOC effect on the band structure, and magnetic dipolar anisotropy energy (ΔE_d) due to the magnetostatic interaction among the magnetic dipoles [21,22]. Although the D-MAE in bulk materials is generally negligibly small, the D-MAE could become significant in low-dimensional materials such as magnetic monolayers [21] and atomic chains [22]. Therefore, we calculate both C-MAE and D-MAE, and Table I lists all calculated C-MAE (ΔE_b), D-MAE (ΔE_d), and MAE (ΔE_{ma}). Indeed, ΔE_d is comparable to ΔE_b in the ML and BL (Table I). Note that the D-MAE always prefers an in-plane magnetization [21], and it thus competes with the C-MAE, which prefers the out-of-plane magnetic anisotropy in all the systems considered here. In fact, the magnitude of the D-MAE in the ML is larger than that of the C-MAE, and this results in an in-plane magnetization.

Table I shows clearly that calculated MAEs for all the investigated materials except the ML are large, and more importantly they prefer the out-of-plane magnetization (i.e., having a positive MAE value). In particular, they are two orders of magnitude larger than that (~ 5 $\mu\text{eV}/\text{at}$) of elemental ferromagnets Fe and Ni [58]. They are also comparable to that of layered heavy element magnetic alloys such as FePt and CoPt [59], which have the largest MAEs among magnetic transition metal alloys. Because of the appreciable out-of-plane anisotropy, all the $\text{Cr}_2\text{Ge}_2\text{Te}_6$ materials except the ML could have possible applications in high-density magnetic data storage.

Since J_1 is dominant (Table II), we estimate FM ordering temperatures within the mean-field approximation, i.e., $k_B T_c^m = \frac{1}{3} z J_1$, where z is the number of first-nearest-neighbor Cr atoms [60] and $z = 3$ in the present cases (Fig. 2). Table II shows that T_c^m increases from 149 to 189 K as one goes

from the ML to the bulk, a trend that is consistent with the monotonic increase in the J values mentioned above. This trend also agrees with the experimental result [16], although the T_c^m values are several times too large (see Table II). The much larger obtained T_c^m values could be caused by the mean-field approximation and perhaps also by our neglect of oscillatory (see Table II) longer distance exchange couplings [61]. The mean-field approximation works well for bulk magnets with a high number of neighboring magnetic atoms such as Fe and Ni metals [60]. Nevertheless, it would substantially overestimate the T_c for 2D materials with a much reduced coordination number such as Fe and Co MLs because it neglects transverse spin fluctuations [62,63]. More importantly, the mean-field approximation violates the Mermin-Wagner theorem [20], which says that long-range magnetic order at finite temperature cannot exist in an isotropic 2D Heisenberg magnet. However, the out-of-plane anisotropy can stabilize long-range magnetic orders at finite temperature by opening a gap in the spin-wave spectrum that suppresses transverse spin fluctuations [62,63]. Note that in-plane magnetic anisotropy would not produce a gap in the spin-wave spectrum. Thus, a better approach is the spin-wave theory with random-phase approximation [62], which takes the out-of-plane anisotropy into account and hence agrees with the Mermin-Wagner theorem [20]. The T_c values estimated within the spin-wave theory with random-phase approximation for Fe and Co MLs are about a factor of 3 smaller than that from the mean-field approximation [62]. It was reported that taking the out-of-plane anisotropy into account within self-consistent spin-wave theory would lead to a renormalization of T_c^m by a factor of $\log(k_B T_c^m / \Delta E_{ma})$ [63]. Based on the calculated MAE values, we come up with a set of renormalized T_c values as listed in Table II. The renormalized T_c values agree reasonably well with the corresponding experimental values (Table II). The T_c for the ML is zero because it has an in-plane easy axis of magnetization. This also explains why the long-range FM ordering was not observed in the ML [16].

C. Electronic structure

To understand the electronic, magnetic, and optical properties of the $\text{Cr}_2\text{Ge}_2\text{Te}_6$ materials, we calculate their electronic band structures. Relativistic band structures of bulk and monolayer $\text{Cr}_2\text{Ge}_2\text{Te}_6$ are displayed in Fig. 3, while that of bilayer and trilayer $\text{Cr}_2\text{Ge}_2\text{Te}_6$ are shown in Fig. S1 in the SM [31]. It is clear from Figs. 3 and S1 that all four structures are indirect band-gap semiconductors with the valence-band maximum (VBM) being at the Γ -point. The conduction-band minimum (CBM) in the $\text{Cr}_2\text{Ge}_2\text{Te}_6$ multilayers is located somewhere along the Γ - K symmetry line (see Figs. 3 and S1) while that of bulk $\text{Cr}_2\text{Ge}_2\text{Te}_6$ is located at a general k -point of $(0.4444, -0.3704, 0.2222)2\pi/a$. Interestingly, calculated spin-polarized scalar-relativistic band structures (see Fig. S2 in [31]) indicate that both the CBM and VBM are of purely spin-up character. The calculated band gaps (E_g) are listed in Table I. It is seen that the theoretical band gap of bulk $\text{Cr}_2\text{Ge}_2\text{Te}_6$ is much smaller than the experimental value. This significant discrepancy between experiment and theory is due to the well-known underestimation of the band gaps by the GGA. To obtain accurate optical properties that are calculated

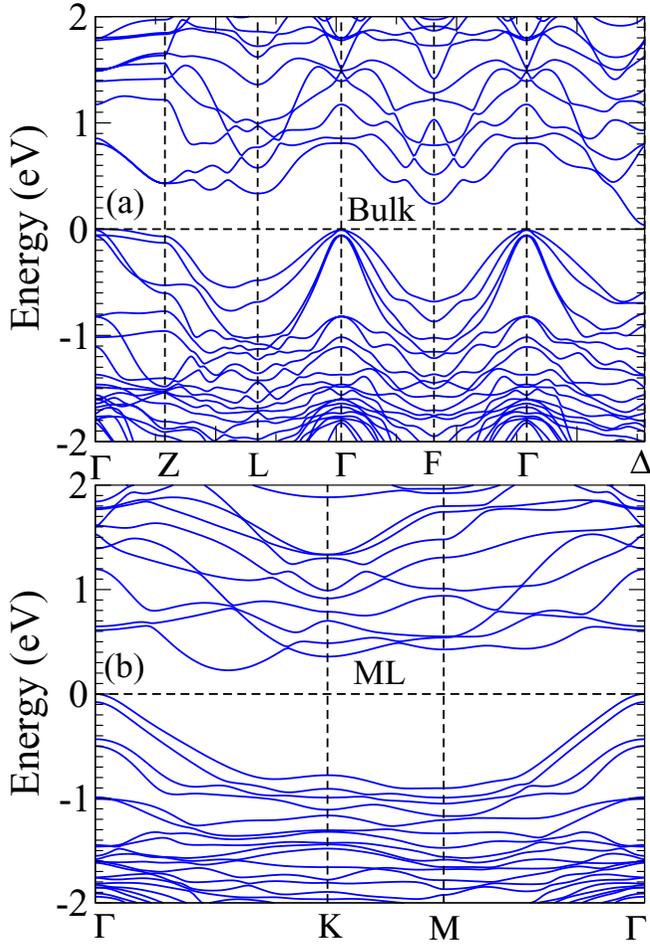


FIG. 3. Relativistic band structures of (a) bulk and (b) ML $\text{Cr}_2\text{Ge}_2\text{Te}_6$ in the FM state with out-of-plane magnetization. Horizontal dashed lines denote the top of the valence band.

from the band structure, we also perform the band-structure calculations using the hybrid Heyd-Scuseria-Ernzerhof (HSE) functional [49,50]. The HSE band structures are displayed in Fig. S3 in the SM [31] and the HSE band gaps are listed in Table I. The HSE band gap of bulk $\text{Cr}_2\text{Ge}_2\text{Te}_6$ is now comparable to the experimental value (Table I). Therefore, the optical properties of all the $\text{Cr}_2\text{Ge}_2\text{Te}_6$ materials are calculated from the GGA band structures within the scissors correction scheme [64] using the differences between the HSE and GGA band gaps (Table I).

We also calculate total as well as site-, orbital-, and spin-projected densities of states (DOSs) for all the $\text{Cr}_2\text{Ge}_2\text{Te}_6$ materials. In Fig. 4, we display site-, orbital-, and spin-projected DOSs of bulk $\text{Cr}_2\text{Ge}_2\text{Te}_6$. It can be seen that the upper valence band ranging from -4.0 to -0.3 eV and also the lower conduction band ranging from 0.4 to 4.0 eV originate mainly from Cr d orbitals with minor contributions from Te p orbitals due to the hybridization between Cr d and Te p orbitals. The valence bands below these spin-up Cr d -dominant bands are primarily derived from Te p orbitals. Furthermore, the upper valence band ranging from -3.3 to -0.3 eV consists of a broad peak of mainly spin-up Cr d_{xy, x^2-y^2} orbitals. The lower conduction bands ranging from 0.4 to 1.5 eV are mainly

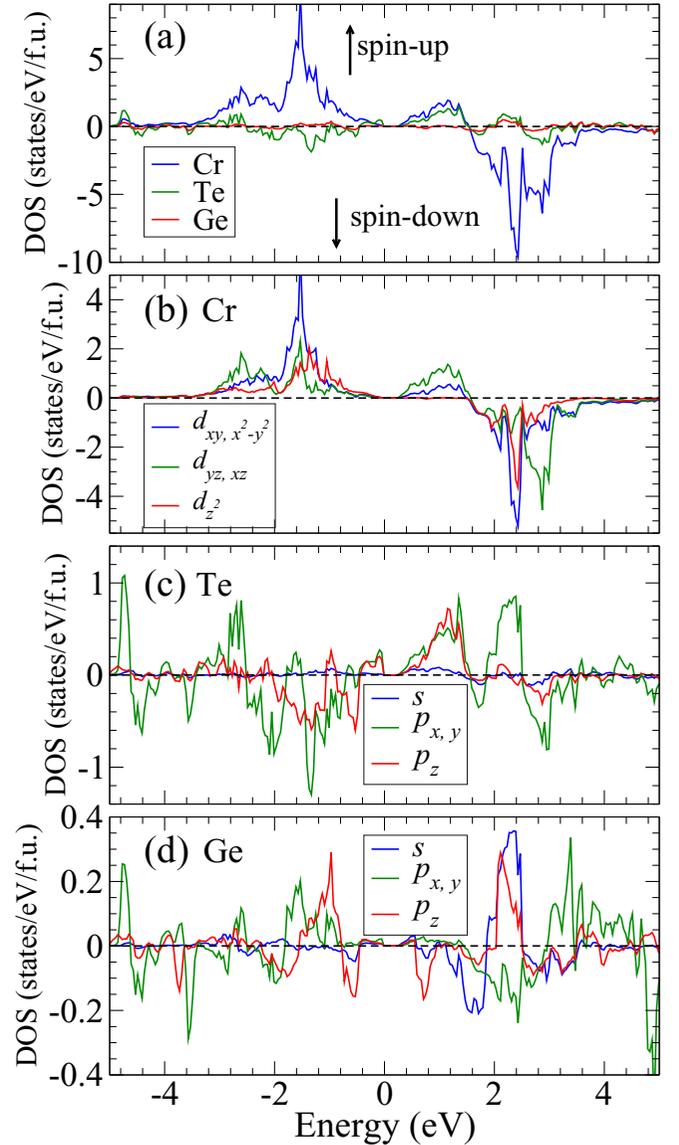


FIG. 4. Scalar-relativistic site-, orbital-, and spin-projected DOS of ferromagnetic bulk $\text{Cr}_2\text{Ge}_2\text{Te}_6$. The top of the valence band is at 0 eV.

made up of spin-up Cr $d_{xz, yz}$ orbitals. This suggests that the band gap is created by the crystal-field splitting of spin-up Cr d_{xy, x^2-y^2} and $d_{xz, yz}$ bands. Above this up to 3.6 eV, the conduction band consists of a pronounced peak of spin-down Cr d_{xy, x^2-y^2} and d_{z^2} orbitals.

Site-, orbital-, and spin-projected DOSs of ML $\text{Cr}_2\text{Ge}_2\text{Te}_6$ are shown in Fig. 5. Clearly, the features in the DOS spectra of the ML are rather similar to that in the DOS spectra of bulk $\text{Cr}_2\text{Ge}_2\text{Te}_6$ (Fig. 4). The main difference appears to be that the contributions from the p orbitals of Te and Ge atoms are enhanced in the higher-energy region. Another difference is the enhanced band gap in the ML mainly due to the lack of interlayer interaction. Site-, orbital-, and spin-projected DOSs of BL and TL $\text{Cr}_2\text{Ge}_2\text{Te}_6$ fall between that of ML and bulk $\text{Cr}_2\text{Ge}_2\text{Te}_6$ and thus are not shown here.

According to perturbation theory analysis, only the occupied and unoccupied Cr d states near the Fermi

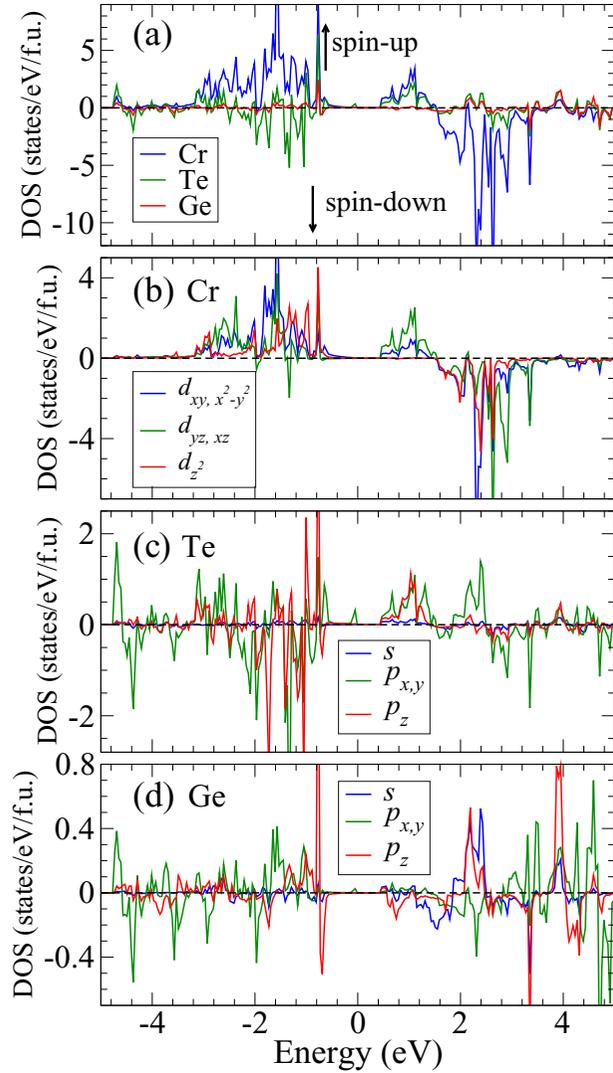


FIG. 5. Scalar-relativistic site-, orbital-, and spin-projected DOS of FM ML $\text{Cr}_2\text{Ge}_2\text{Te}_6$.

level, which are coupled by the SOC, would significantly contribute to the magnetocrystalline anisotropy [65]. Moreover, the SOC matrix elements $\langle d_{xz} | H_{\text{SO}} | d_{yz} \rangle$ and $\langle d_{x^2-y^2} | H_{\text{SO}} | d_{xy} \rangle$ are found to prefer the out-of-plane anisotropy, while $\langle d_{x^2-y^2} | H_{\text{SO}} | d_{yz} \rangle$, $\langle d_{xy} | H_{\text{SO}} | d_{xz} \rangle$, and $\langle d_{z^2} | H_{\text{SO}} | d_{yz} \rangle$ favor an in-plane anisotropy [66]. The ratios of these matrix elements are $\langle d_{xz} | H_{\text{SO}} | d_{yz} \rangle^2 : \langle d_{x^2-y^2} | H_{\text{SO}} | d_{xy} \rangle^2 : \langle d_{x^2-y^2} | H_{\text{SO}} | d_{yz} \rangle^2 : \langle d_{xy} | H_{\text{SO}} | d_{xz} \rangle^2 : \langle d_{z^2} | H_{\text{SO}} | d_{yz} \rangle^2 = 1 : 4 : 1 : 1 : 3$. Figures 4(b) and 5(b) show that in both bulk and ML $\text{Cr}_2\text{Ge}_2\text{Te}_6$, the Cr d_{z^2} DOS is almost zero in the CBM region of 0.4–1.5 eV, and consequently, matrix element $\langle d_{z^2} | H_{\text{SO}} | d_{yz} \rangle$ would be negligibly small and thus hardly contribute to the C-MAE. In contrast, the Cr d_{xy, x^2-y^2} DOS has prominent peaks in both the VBM and CBM regions, and hence matrix element $\langle d_{x^2-y^2} | H_{\text{SO}} | d_{xy} \rangle$ would be large. This would give rise to a dominating contribution to the C-MAE. All these together would then lead to a C-MAE that prefers the out-of-plane anisotropy in the $\text{Cr}_2\text{Ge}_2\text{Te}_6$ materials.

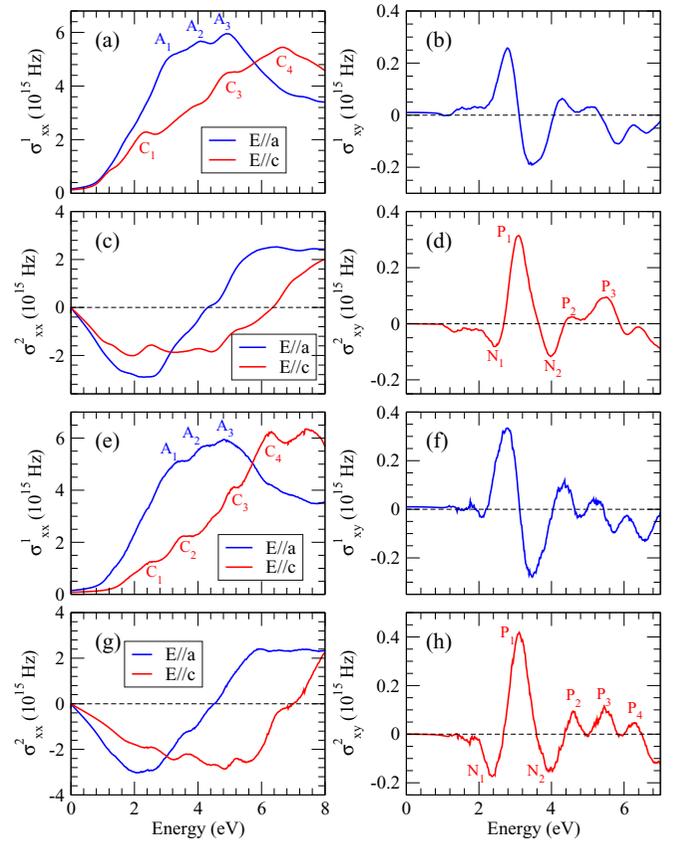


FIG. 6. Real (a) [(e)] diagonal and (b) [(f)] off-diagonal, imaginary (c) [(g)] diagonal components and (d) [(h)] off-diagonal components of the optical conductivity tensor of bulk (ML) $\text{Cr}_2\text{Ge}_2\text{Te}_6$ in the FM state with out-of-plane magnetization. All the spectra have been convoluted with a Lorentzian of 0.2 eV to simulate the finite electron lifetime effects.

D. Optical conductivity

We calculate the optical conductivity tensors for all the considered $\text{Cr}_2\text{Ge}_2\text{Te}_6$ materials with the scissor corrections. Calculated optical conductivity elements are displayed in Fig. 6 for bulk and ML $\text{Cr}_2\text{Ge}_2\text{Te}_6$ as well as in Fig. S4 for the BL and in Fig. S5 for the TL in the SM [31]. Overall, the calculated optical spectra for all the systems are rather similar (Figs. 6, S4, and S5). This could be expected from the weak interlayer interaction in layered vdW materials such as $\text{Cr}_2\text{Ge}_2\text{Te}_6$. Therefore, in what follows, we will take that of bulk and ML $\text{Cr}_2\text{Ge}_2\text{Te}_6$ as examples to perform a detailed analysis (Fig. 6). First of all, the diagonal elements σ_{xx} (for in-plane electric field polarization $E \perp c$) and σ_{zz} (for out-of-plane polarization $E \parallel c$) of the optical conductivity for both systems are significantly different (Fig. 6), i.e., these materials exhibit rather strong optical anisotropy. For example, the absorptive part of σ_{xx}^1 is much larger than σ_{zz}^1 in the low-energy range of 1.0–5.5 eV, while it is smaller than σ_{zz}^1 in the energy range above 6.0 eV. This pronounced optical anisotropy could be expected from a 2D or quasi-2D material, and it can also be qualitatively explained by the Cr d -orbital-projected DOSs. As mentioned above, the upper valence band ranging from -4.0 to -0.3 eV is dominated by Cr d orbitals. In particular,

Figs. 5(b) and 6(b) show that in this region, the overall weight of Cr d_{xy,x^2-y^2} is much larger than that of Cr d_{z^2} . Given that d_{xy,x^2-y^2} (d_{z^2}) states can be excited by only $E \perp c$ ($E \parallel c$) polarized light while Cr $d_{xz,yz}$ states can be excited by light of both polarizations, σ_{xx}^1 would obviously be larger than σ_{zz}^1 in the low-energy region, as shown in Figs. 6(a) and 6(e).

For both bulk and ML Cr₂Ge₂Te₆, σ_{xx}^1 increases steeply from the absorption edge (~ 1.0 eV) to ~ 3.0 eV, and then further increases up to ~ 4.9 eV with a much smaller slope. Beyond ~ 4.9 eV, σ_{xx}^1 decreases monotonically with the energy (see Fig. 6). σ_{zz}^1 also increases steadily from the absorption edge to ~ 6.5 eV with a smaller slope, however, and then decreases as the energy increases further (Fig. 6). The σ_{xx}^2 and σ_{zz}^2 spectra from bulk and ML Cr₂Ge₂Te₆ share several common characteristics: (a) a broad valley centered at ~ 2.5 eV (~ 4.0 eV) in σ_{xx}^2 (σ_{zz}^2), (b) a sign change in σ_{xx}^2 (σ_{zz}^2) occurring at ~ 4.5 eV (~ 6.5 eV), and (c) a plateau in σ_{xx}^2 above 6.0 eV [see Figs. 6(c) and 6(g)].

Figure 6 shows that both real (σ_{xy}^1) and imaginary (σ_{xy}^2) parts of the off-diagonal element of the optical conductivity of bulk and ML Cr₂Ge₂Te₆ are also rather similar. For example, all these spectra exhibit pronounced oscillatory peaks, although the peak amplitude decreases with the energy. Notably, both σ_{xy}^1 and σ_{xy}^2 show a large positive peak at ~ 2.8 and ~ 3.0 eV, respectively (Fig. 6). They also have a pronounced negative peak at ~ 3.5 and ~ 4.0 eV, respectively.

As Eqs. (4), (5), and (11) suggested, the absorptive parts of the optical conductivity elements (σ_{xx}^1 , σ_{zz}^1 , σ_{xy}^2 , σ_{\pm}^1) are directly related to the dipole-allowed interband transitions. This would allow us to understand the origins of the main peaks in the σ_{xx}^1 , σ_{zz}^1 , and σ_{xy}^2 spectra by determining the symmetries of the calculated band states and also the dipole selection rules. As discussed above, the features in the σ_{xx}^1 , σ_{zz}^1 , and σ_{xy}^2 spectra for all the considered systems are rather similar. Therefore, as an example, here we perform a symmetry analysis for ML Cr₂Ge₂Te₆ only (see the SM [31]). The found symmetries of the band states at the Γ -point of the scalar-relativistic and relativistic band structures of ML Cr₂Ge₂Te₆ are displayed in Figs. S6 and 7, respectively. Using the dipole selection rules (Table S3), we could assign the main peaks in the σ_{xx}^1 and σ_{zz}^1 spectra [Fig. 6(e)] to the interband transitions at the Γ -point displayed in Fig. S6. For example, we could relate the A_1 peak at 3.4 eV in σ_{xx}^1 [Fig. 6(e)] to the interband transition from the Γ_3^- state at the top of the spin-down valence band to the conduction-band state Γ_3^+ at ~ 3.1 eV [Fig. S6(b)]. Of course, in addition to this, there may be contributions from different interband transitions at other k -points. Note that without the SOC, the Γ_3^+ and Γ_3^- band states are doubly degenerate (Fig. S6), and the absorption rates for left- and right-handed polarized lights are the same. When the SOC is included, these band states split (Fig. 7), and this results in magnetic circular dichroism. Therefore, we could assign the main peaks in σ_{xy}^2 to the principal interband transitions at the Γ -point only in the relativistic band structure, e.g., displayed in Fig. 7. In particular, we could attribute the pronounced peak P_1 at ~ 3.0 eV in σ_{xy}^2 [Fig. 6(b)] to the interband transition from the Γ_4^- and Γ_6^- states at the top of the valence band to the conduction-band state Γ_6^+ at ~ 2.8 eV (Fig. 7).

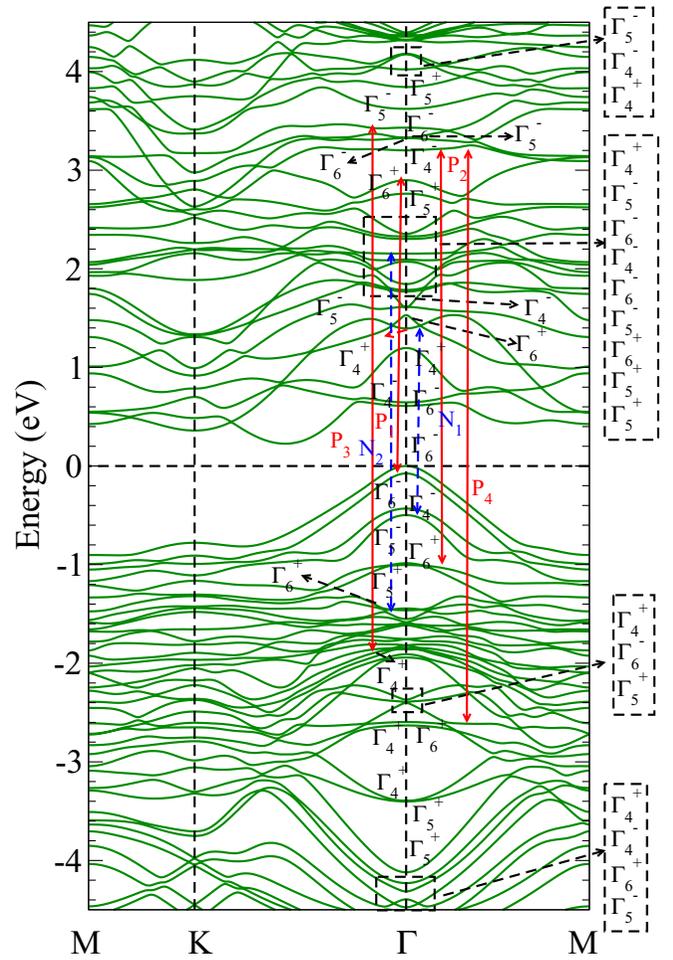


FIG. 7. Relativistic band structure of ferromagnetic monolayer Cr₂Ge₂Te₆ with out-of-plane magnetization. Horizontal dashed lines denote the top of the valence band. The symmetry of the band states at the Γ -point is labeled according to the irreducible representation of the C_{3i} double point group. The principal interband transitions and the corresponding peaks in σ_{xy} in Fig. 6(b) are indicated by green arrows.

E. Magneto-optical Kerr and Faraday effects

Here we consider the polar Kerr and Faraday effects for all the systems considered, and we calculate their complex Kerr and Faraday rotation angles as a function of photon energy, as plotted in Figs. 8 and 9, respectively. Figure 8 shows that for the three multilayers, the spectra are negligibly small below ~ 1.2 eV but become large and oscillatory in the incident photon energy range from 1.2 to 7.0 eV. In particular, the Kerr rotation angle in all the multilayers is remarkably large in the vicinity of 2.8 eV, reaching up to 0.9° for the ML, 1.5° for the BL, and 2.2° for the TL. The shapes of the Kerr rotation spectra for all the multilayers are similar, indicating the weakness of the vdW interlayer interaction. The Kerr rotation spectrum for the bulk is similar to that of the multilayers, except it is not negligible below 1.2 eV where bulk Cr₂Ge₂Te₆ also shows significant Kerr rotations [see Fig. 8(a)], which will be explained below.

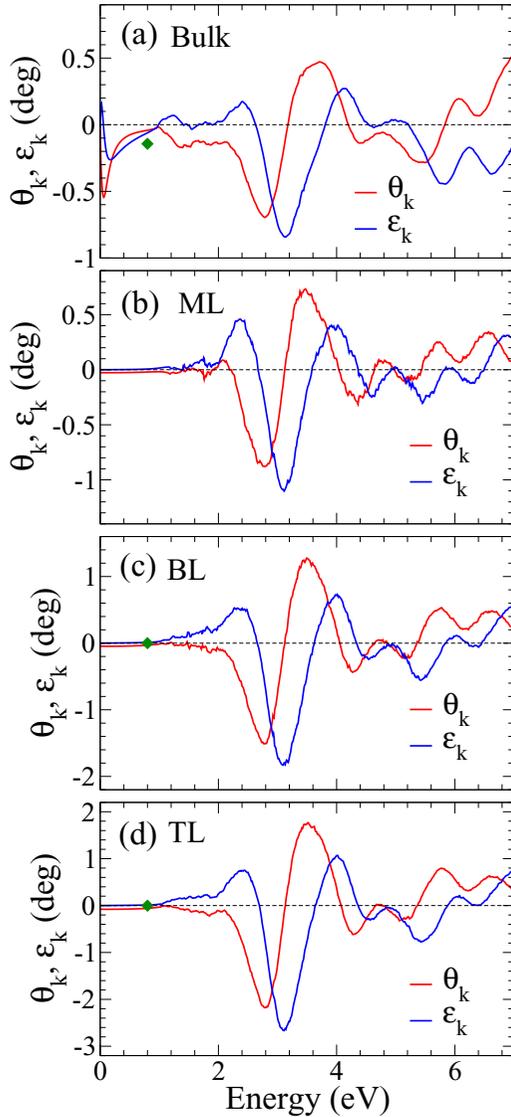


FIG. 8. Kerr rotation (θ_K) and ellipticity (ε_K) spectra for (a) bulk, (b) ML, (c) BL, and (d) TL $\text{Cr}_2\text{Ge}_2\text{Te}_6$ in the FM state with out-of-plane magnetization. Green diamonds denote the θ_K value from the recent experiments [16].

A comparison of Fig. 8 with Fig. 6 would reveal that the Kerr rotation (θ_K) and Kerr ellipticity (ε_K) spectra in all the systems resemble, respectively, the corresponding real part (σ_{xy}^1) and imaginary part (σ_{xy}^2) of the off-diagonal conductivity element. This is not surprising because the Kerr effect and the off-diagonal conductivity element are connected via Eqs. (8) and (9). Indeed, Eqs. (8) and (9) indicate that the complex Kerr rotation angle would be linearly related to σ_{xy} if the longitudinal conductivity (σ_{xx}) of the bulk and substrate is more or less constant. For the $\text{Cr}_2\text{Ge}_2\text{Te}_6$ multilayers, the latter is true because here we assume that the substrate is SiO_2 with dielectric constant $\varepsilon_s = 2.25$. For bulk $\text{Cr}_2\text{Ge}_2\text{Te}_6$, the Kerr rotation could become large if σ_{xx} , which is in the denominator of Eq. (8), becomes very small. This explains that the Kerr rotation of the bulk is still visible below 1.2 eV (Fig. 8).

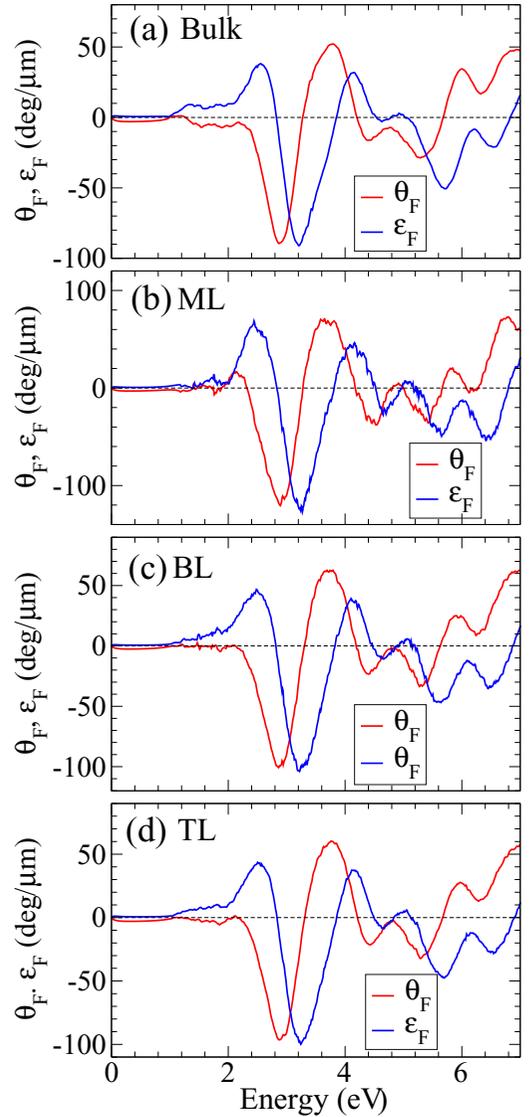


FIG. 9. Faraday rotation (θ_F) and ellipticity (ε_F) spectra for (a) ML, (b) BL, and (c) TL $\text{Cr}_2\text{Ge}_2\text{Te}_6$ in the FM state with out-of-plane magnetization.

Let us now compare the calculated Kerr rotation angles in the $\text{Cr}_2\text{Ge}_2\text{Te}_6$ materials with that found in several well-known MO materials. Ferromagnetic 3d transition metals and their alloys form an important class of metallic MO materials [26]. Kerr rotation angles of these metals seldom exceed 0.5° except a few of them such as heavy element Pt intermetallics FePt, Co_2Pt [67], and PtMnSb [68], where the strong SOC in the Pt atoms plays an important role [67]. Manganese pnictides also have excellent MO properties. In particular, MnBi films possess a large Kerr rotation angle of 2.3° at 1.84 eV at low temperatures [57,69]. Remarkably, calculated Kerr rotation angles of bulk and few-layer $\text{Cr}_2\text{Ge}_2\text{Te}_6$ (Fig. 8) are comparable to that of these traditional excellent MO materials. Furthermore, they are generally more than 10 times larger than that of FM 3d transition-metal MLs deposited on metallic substrates. For example, BL Fe epitaxially grown on an Au (001) surface exhibits the largest Kerr rotation angle of only $\sim 0.025^\circ$ at ~ 2.75 eV [70]. In this

context, the Kerr rotation angles of atomically thin $\text{Cr}_2\text{Ge}_2\text{Te}_6$ films could be regarded as gigantic.

Among famous MO semiconductors, $\text{Y}_3\text{Fe}_5\text{O}_{12}$ exhibits a significant Kerr rotation of 0.23° at 2.95 eV [71]. Recently, dilute magnetic semiconductors were reported to show significant Kerr rotation angles of $\sim 0.4^\circ$ in the vicinity of 1.80 eV [72]. Remarkably, Feng *et al.* recently studied theoretically the MO properties of hole-doped group-IIIa metal-monochalcogenide MLs and predicted that many of these FM MLs would exhibit significant Kerr rotations of $\sim 0.3^\circ$ at optimal hole concentrations [9]. On the whole, the Kerr rotation angles predicted for bulk and few-layer $\text{Cr}_2\text{Ge}_2\text{Te}_6$ here are comparable to these important MO semiconductors. Therefore, because of their excellent MO properties, $\text{Cr}_2\text{Ge}_2\text{Te}_6$ materials could find promising applications for, e.g., MO sensors and high-density MO data-storage devices. Moreover, MOKE in atomically thin films as well as bulk $\text{Cr}_2\text{Ge}_2\text{Te}_6$ at low temperatures has been measured using the highly sensitive Sagnac interferometer with a light wavelength of 1550 nm (a photon energy of 0.8 eV). [16] The measured θ_K value of $\sim 0.14^\circ$ of the bulk is of the same order of magnitude as our theoretical prediction [see Fig. 8(a)]. The θ_K values for the thin films are, however, much smaller, ranging from 0.0007° in bilayer to 0.002° in trilayer [16]. Such small measured θ_K values could be attributed to the fact that the energy of the light beam used falls almost within the band gap where MOKE is negligibly small (Fig. 8). Indeed, the θ_K value of $\sim 0.28^\circ$ of the CrI_3 ML measured using a 633-nm HeNe laser (a photon energy of 1.96 eV) [15] is orders of magnitude larger than the $\text{Cr}_2\text{Ge}_2\text{Te}_6$ thin films reported in [16].

Complex Faraday rotation angles for all the considered structures are displayed in Fig. 9. The Faraday rotation spectra are similar to the corresponding Kerr rotation spectra (Fig. 8) as well as σ_{xy} (see Fig. 6). Figure 6 shows that σ_{xx} is generally much larger than σ_{xy} . Thus, $n_{\pm} = [1 + \frac{4\pi i}{\omega}(\sigma_{xx} \pm i\sigma_{xy})]^{1/2} \approx [1 + \frac{4\pi i}{\omega}\sigma_{xx}]^{1/2} \mp \frac{2\pi}{\omega}(\sigma_{xy}/\sqrt{1 + \frac{4\pi i}{\omega}\sigma_{xx}})$. Consequently, Eq. (10) can be approximately written as $\theta_F + i\epsilon_F \approx -\frac{2\pi d}{c}(\sigma_{xy}/\sqrt{1 + \frac{4\pi i}{\omega}\sigma_{xx}})$ or $\theta_F + i\epsilon_F \approx -\frac{2\pi d}{c}\frac{\sigma_{xy}}{\sqrt{\epsilon_{xx}}}$, where ϵ_{xx} is the dielectric function. This explains why the complex Faraday rotation follows closely σ_{xy} (Figs. 6 and 9).

Remarkably, calculated maximum Faraday rotation angles are as large as $\sim 120^\circ/\mu\text{m}$ in 2D $\text{Cr}_2\text{Ge}_2\text{Te}_6$ (see Fig. 9). In the visible frequency range (below 4.0 eV), they are more than ten times larger than the predicted Faraday rotations in group-IIIa metal-monochalcogenide monolayers at optimal hole dopings [9]. They are even comparable to that of prominent bulk MO metals such as manganese pnictides. In particular, among manganese pnictides, MnBi films possess the largest Faraday rotations of $\sim 80^\circ/\mu\text{m}$ at 1.77 eV at low temperatures [57,69]. Even the famous MO semiconductor $\text{Y}_3\text{Fe}_5\text{O}_{12}$ exhibits a Faraday rotation only as large as $0.19^\circ/\mu\text{m}$ at 2.07 eV [73]. However, substituting Y with Bi could substantially enhance Faraday rotations up to $\sim 35.0^\circ/\mu\text{m}$ at 2.76 eV in $\text{Bi}_3\text{Fe}_5\text{O}_{12}$ [74]. Clearly, the Faraday rotation angles reported here for few-layer multilayer $\text{Cr}_2\text{Ge}_2\text{Te}_6$ are comparable or even superior to many well-known MO materials. This suggests that one could also exploit the large Faraday effect to probe the long-range magnetic orders in these quasi-2D magnetic

materials. Furthermore, due to their excellent MO properties, $\text{Cr}_2\text{Ge}_2\text{Te}_6$ materials could find valuable applications for magnetic-optical devices.

IV. CONCLUSION

We have investigated magnetism as well as the electronic, optical, and magneto-optical properties of atomically thin FM films recently exfoliated from bulk FM semiconductor $\text{Cr}_2\text{Ge}_2\text{Te}_6$ by performing systematic GGA+U calculations. In particular, we focus on two relativity-induced properties of these 2D materials, namely magnetic anisotropy energy and MO effects. First, we find that calculated MAEs of these materials are large, being on the order of ~ 0.1 meV/Cr. Interestingly, the out-of-plane anisotropy is found in all the considered systems except the ML. In contrast, in the ML an in-plane magnetization is preferred simply because the D-MAE is larger than the C-MAE. Crucially, this would explain why long-range FM order was recently observed in all the few-layer $\text{Cr}_2\text{Ge}_2\text{Te}_6$ except the ML. This is because the out-of-plane anisotropy would open a spin-wave gap and thus suppress magnetic fluctuations so that long-range FM order could be stabilized at finite temperature. Secondly, large Kerr rotations up to $\sim 2.2^\circ$ in these FM materials are found in the visible frequency range, and they are comparable to that observed in famous MO materials such as FM metal PtMnSb and semiconductor $\text{Y}_3\text{Fe}_5\text{O}_{12}$. Moreover, they are two orders of magnitude larger than that of 3d transition metal MLs deposited on Au surfaces, and thus they can be called gigantic. Thirdly, calculated maximum Faraday rotation angles in these 2D materials are also large, being up to $\sim 120^\circ/\mu\text{m}$, and they are comparable to the best-known MO semiconductor $\text{Bi}_3\text{Fe}_5\text{O}_{12}$. These findings thus suggest that with large MO effects plus significant MAE, atomically thin films of $\text{Cr}_2\text{Ge}_2\text{Te}_6$ might find valuable applications in 2D magnetic, magneto-electric, and MO devices such as high-density data-storage and nanomagnetic sensors. Fourthly, calculated Kerr rotation angles at 1550 nm wavelength are in reasonable agreement with recent MO Kerr effect experiments. The FM transition temperatures estimated using the calculated exchange coupling parameters within the mean-field approximation plus the spin-wave gap correction agree quite well with the measured transition temperatures. Finally, the calculated C-MAE and MO properties of these 2D materials are analyzed in terms of their electronic band structures.

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