Large magneto-optical effect and magnetic anisotropy energy in two-dimensional metallic ferromagnet Fe$_3$GeTe$_2$

Ming-Chun Jiang$^1$ and Guang-Yu Guo$^{1,2, *}$

$^1$Department of Physics and Center for Theoretical Physics, National Taiwan University, Taipei 10617, Taiwan
$^2$Physics Division, National Center for Theoretical Sciences, Taipei 10617, Taiwan

(Dated: September 17, 2021)

The recent discovery of long-range magnetic orders in atomically thin semiconductors Cr$_2$Ge$_2$Te$_6$ and CrI$_3$ as well as metal Fe$_3$GeTe$_2$ has opened up exciting opportunities for fundamental physics of two-dimensional (2D) magnetism and also for technological applications based on 2D magnetic materials. Due to their unique metallic nature, atomically thin Fe$_3$GeTe$_2$ films exhibit fascinating properties such as Fermi level-tunable Curie temperature, magnetic anisotropy energy and anomalous Hall effect, thus offering valuable applications for, e.g., voltage-controlled 2D spintronics at room temperature. Nevertheless, to exploit these 2D metallic magnets, the mechanisms that control their physical properties should be well understood. In this paper, based on systematic first principle density functional theory calculations, we study two relativity-induced properties, namely, magnetic anisotropy energy (MAE) and magneto-optical (MO) effects, of multilayers [monolayer, bilayer, trilayer, fourlayer and quintlayer] and bulk Fe$_3$GeTe$_2$ and also their connections with the underlying electronic structures of the materials. Firstly, all the considered Fe$_3$GeTe$_2$ structures are found to prefer the out-of-plane magnetization and have gigantic MAEs of $\sim$3.0 meV/f.u., being about 20 and 6 times larger than 2D ferromagnetic semiconductors Cr$_2$Ge$_2$Te$_6$ and CrI$_3$, respectively. This gigantic perpendicular anisotropy results from the large magnetocrystalline anisotropy energy (MCE) which is ten times larger than the competing magnetic dipolar anisotropy energy (MDE) which always favors an in-plane magnetization. The giant MCEs are attributed to the large Te px,y orbital density of states near the Fermi level and also to the topological nodal point just below the Fermi level at the K points in the Brillouin zone. Secondly, 2D and bulk Fe$_3$GeTe$_2$ also exhibit strong MO effects with their Kerr and Faraday rotation angles being comparable or even larger than that of best-known MO materials such as PtMnSb, Y$_3$Fe$_5$O$_{12}$ and Bi$_2$Fe$_5$O$_{12}$. The features in the Kerr and Faraday rotation spectra are almost thickness-independent although the Kerr rotation angles increase monotonically with film thickness. The strong MO Kerr and Faraday effects are found to result from the large MO conductivity (or strong magnetic circular dichroism) in these ferromagnetic materials. In particular, the calculated MO conductivity spectra are one order of magnitude larger than that of Y$_3$Fe$_5$O$_{12}$. The calculated MO conductivity spectra are analysed in terms of the symmetry of the band states and dipole-allowed optical transitions at high symmetry $\Gamma$, K and K' points, which further reveal that atomically thin Fe$_3$GeTe$_2$ films with odd layer-number would exhibit anomalous ferrovalley Hall effect. All these interesting findings thus suggest that 2D and bulk ferromagnetic Fe$_3$GeTe$_2$ are promising materials for high density MO and spintronic nanodevices.

I. INTRODUCTION

Recent material realization of intrinsic magnetism in atomically thin films of semiconducting Cr$_2$Ge$_2$Te$_6$ [1] and CrI$_3$ [2] as well as metallic Fe$_3$GeTe$_2$ [3, 4] has created numerous fascinating opportunities for two-dimensional (2D) magnetism. Fundamentally, the famous Mermin-Wagner theorem [5] dictates that thermal fluctuation prohibits any long-range magnetic order in isotropic 2D systems at any finite temperature. The discovery of the long-range ferromagnetic order in monolayers (MLs) CrI$_3$ [2] and Fe$_3$GeTe$_2$ [3, 4] thus demonstrates that theories of 2D magnetism need to go beyond the isotropic Heisenberg model. Magnetism at 2D limit is not only highly desirable for the fundamental physics but also for the technological applications ranging from magnetic memories to sensing, to spintronics to novel functionalities based on 2D materials. Among the magnetic 2D materials, few-layer Fe$_3$GeTe$_2$ structures are unique since they are apparently the only ferromagnetic metal that retains the long-range magnetic order down to the 2D limit [6, 7], and thus attract particularly strong attention. For example, owing to its metallic nature, Curie temperature ($T_C$) of trilayer (TL) Fe$_3$GeTe$_2$ was raised from 100 K to 300 K by ionic gating [8], thus offering application potential for voltage-controlled 2D spintronics at room temperature. Furthermore, it was demonstrated theoretically that the magnetocrystalline anisotropy energy (MCE) of ML Fe$_3$GeTe$_2$ is large and also tunable by either tensile strain [8] or electric gating [9]. Strong layer-dependent anomalous Hall effect in atomically thin Fe$_3$GeTe$_2$ was also predicted recently [10]. Interestingly, unlike 2D semiconductors CrGeTe$_3$ and CrI$_3$ which all have a centrosymmetric crystalline structure, few-layer Fe$_3$GeTe$_2$ with odd number of MLs have the broken inversion symmetry (see Table I below). Consequently, atomically thin Fe$_3$GeTe$_2$ with

* gyguo@phys.ntu.edu.tw
odd layer-number are expected to exhibit novel properties such as anomalous valley Hall effect [11] and magnetically tunable second-order nonlinear optical responses (e.g., second-harmonic generation and bulk photovoltaic effect) [12].

In this work, we concentrate on two relativity-induced properties of 2D Fe₃GeTe₂, namely, magnetic anisotropy energy (MAE) and magneto-optical (MO) effects. MAE is the energy needed to rotate the magnetization direction from the easy axis to the hard axis. MAE plays a crucial role in suppressing thermal fluctuation and thus stabilizes long-range magnetic orders in 2D systems. It is also an important factor that characterizes a magnetic material from the application viewpoint. In particular, a thin film with a large perpendicular magnetic anisotropy may find applications in high density magnetic data storage. It has two contributions, namely, the magnetocrystalline anisotropy energy (MCE) and the magnetic dipolar anisotropy energy (MDE). MCE is due to the difference between the relativistic band structures for two different magnetic orientations. On the other hand, MDE originates from the classical magnetic dipole-dipole interaction in the magnetic solid [13–14]. Interestingly, MDE is determined solely by the crystalline structure and geometric shape of the sample [13–14]. In a layered material, the MDE always prefers an in-plane magnetization while MCE could favor either an in-plane or the out-of-plane magnetization [15]. Although the MAE of bulk and ML Fe₃GeTe₂ has been studied both experimentally and theoretically [3, 9, 16], the MAE of atomically thin Fe₃GeTe₂ films of few-layer thickness has not been reported yet.

MO effects are manifestations of the interplay between magnetism and light in magnetic solids [17, 18]. When a linearly polarized light beam hits a magnetic material, the principal axis of the reflected and transmitted light rotates with respect to the polarization direction of the incident light. The former is called the magneto-optical Kerr effect (MOKE) and the latter is known as the magneto-optical Faraday effect (MOFE). MO effects originate from the simultaneous presence of the relativistic spin-orbit coupling (SOC) and spontaneous magnetization in the magnetic solid. The spontaneous magnetization and the SOC result in energy band splitting and thus lead to different refractive indexes for the right- and left-circularly polarized light. As will be discussed in the next section, this magnetic circular dichroism (MCD) gives rise to the MOKE and MOFE. MOKE has been widely studied to apply the magnetic properties of thin films and surfaces [18]. Indeed, in Fe₃GeTe₂ and other 2D ferromagnets, long range magnetic orders were discovered by the MOKE and MCD experiments [13, 14]. Large MOKE and MOFE effects can also be exploited for fabricating high density MO data storage and MO sensors. [15, 20]

On the other hand, it is known that 3d transition metal alloys that contain heavy elements such as FePt would have large MO effects due to the large SOC strength on the heavy element atoms [21, 22]. Since Fe₃GeTe₂ contains heavy Te atoms, bulk and 2D Fe₃GeTe₂ are expected to have large MO effects. However, there has been no theoretical study on the optical and MO properties of bulk and few-layer Fe₃GeTe₂.

In this work, therefore, we carry out a systematic first principles density functional theory (DFT) study on the magnetic, electronic, optical and MO properties of monolayer (ML), bilayer (BL), trilayer (TL), fourlayer (FL) and quintlayer (QL) as well as bulk Fe₃GeTe₂. Indeed, we find that all the considered Fe₃GeTe₂ structures would exhibit strong MOKE and MOFE especially in the infrared and visible frequency range. Furthermore, we also find that all the structures have a large MAE, being comparable to that of FePt which has the largest MAE among the ferromagnetic transition metals and their alloys. These findings suggest that bulk and few-layer Fe₃GeTe₂ are promising ferromagnetic materials for nanoscale MO and spintronic devices.

The rest of this paper is organized as follows. In the next section, a brief description of the crystalline structure of the considered Fe₃GeTe₂ structure as well as the used theoretical methods and computational details is given. In Sec. III, the calculated magnetic properties and electronic band structures as well as the optical and MO properties are presented. The possible origins of the large MAEs are discussed in terms of orbital-decomposed density of states (DOSs) and also the topological features of the band structure near the Fermi level. Also, the peaks in the calculated MO conductivity spectra are analyzed in terms of the symmetry of the energy bands and main interband optical transitions at high symmetry Γ and K points in the Brillouin zone (BZ). Finally, the conclusions drawn from this work are summarized in section IV.

II. STRUCTURES AND METHODS

Bulk Fe₃GeTe₂ forms a layered hexagonal structure with space group P6₃/mmc (No. 194) and point group D₆₃h, and its experimental lattice constants are a = 3.991 Å and c = 16.33 Å [23]. Each unit cell contains two weak interacting Fe₃GeTe₂ MLs [see Fig. 1(a)]. Each Fe₃GeTe₂ ML consists of five 2D triangular atomic layers where two Te layers sandwich three ABA-stacked Fe layers [see Fig. 1(a)] with the Fe and Ge triangular lattices in the central layer forming a honeycomb lattice [see Fig. 1(c)]. The Fe atoms sit on two inequivalent sites, namely, the FeI site with C₃ᵥ site symmetry and the FeII site with D₃h site symmetry [see Fig. 1(a)].

The ab initio electronic structure and structural optimization calculations are based on the density functional theory with the generalized gradient approximation (GGA) [24] to exchange-correlation interaction. To accurately describe the structural properties of layered Fe₃GeTe₂ structures, we have included the DFT-D2 vdW correction of Grimme [25] in the present calculations. The present calculations are performed using the accurate projector-augmented wave (PAW) method [26] implemented in the Vienna ab initio simulation package.
The few-layer Fe₃GeTe₂ structures are modelled utilizing the slab-superlattice approach with the separations between the neighboring slabs being about 15 Å. A large plane wave cut-off energy of 400 eV is used. For the Brillouin zone integrations using the tetrahedron method [29], Γ-centered k-meshes of 16 × 16 × 4 and 16 × 16 × 1 are used for bulk and few-layer Fe₃GeTe₂, respectively. Since the experimental structural parameters for few-layer Fe₃GeTe₂ are unavailable, we have determined theoretically the lattice constants and atomic positions of both bulk and few-layer Fe₃GeTe₂. The calculated lattice constants are listed in Table I, together with the experimental lattice constants of bulk Fe₃GeTe₂. Note that the calculated lattice constants of bulk Fe₃GeTe₂ agree well with the corresponding experimental values (within 0.5 %) (see Table I), suggesting that the structural properties of few-layer Fe₃GeTe₂ should be well described by the GGA functional [24] plus the DFT-D2 vdW correction [25].

### Table I. Theoretical lattice constants and crystallographic point group of bulk and few-layer Fe₃GeTe₂.

| Point Group | Bulk | ML | BL | TL | FL | QL |
|-------------|------|----|----|----|----|----|
| D₃h         | a (Å) | 3.995 (3.991⁺) | 4.010 | 4.010⁺ | 4.010 | 4.010⁺ |
|             | c (Å) | 16.73 (16.33⁺) |        |        |        |    |
|             | d (Å) | 8.365 | 16.73 | 25.10 | 33.46 | 41.83 |

Reference [23] (X-ray diffraction experiment at 293K).

To determine the MCE, we first perform the total energy calculations for an in-plane magnetization (e.g., along the x-axis) and the out-of-plane magnetization (along the z-axis). Then, the MCE is given by the total energy difference \( \Delta E_c = E^{[100]} - E^{[001]} \). Denser k-point meshes of 24 × 24 × 6 and 32 × 32 × 1 are used for bulk and few-layer Fe₃GeTe₂, respectively. Thus-obtained MCEs are converged within 3 % with respect to the k-point meshes used.

Similarly, the MDE is given by the difference in the magnetic dipole interaction energy \( E_d \) between the magnetization along the x-axis and along the z-axis. For a ferromagnetic system, in atomic Rydberg units, [13, 14]

\[
E_d = \sum_{qq'} \frac{2m_qm_{q'}}{c^2} M_{qq'}
\]

where the speed of light \( c = 274.072 \) and the so-called magnetic dipolar Madelung constant

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

where \( R \) are the lattice vectors, \( q \) are the atomic position vectors in the unit cell, and \( m_q \) is the atomic magnetic moment (in units of \( \mu_B \)) on site \( q \). In a 2D system, all \( R \) and \( q \) are in-plane, and hence the second term in Eq. (2) would vanish for the out-of-plane magnetization. Thus, the \( E_d \) for an in-plane magnetization is always lower than that for the out-of-plane magnetization. Consequently, the MDE always prefers an in-plane magnetization rather than the out-of-plane magnetization in 2D magnetic systems [13, 13, 30]. This is a purely geometrical effect and thus MDE is also called the magnetic shape anisotropy energy.

For a solid with at least threefold rotational symmetry and a magnetization along rotational z-axis, the non-zero components for the optical conductivity are \( \sigma_{xx}, \sigma_{zz} \), and \( \sigma_{xy} \). We calculate these three independent elements using the linear-response Kubo formula [31, 32]. Thus, the
absorptive parts of these elements are given by
\[ \sigma_{\alpha\alpha}^1(\omega) = \frac{\pi e^2}{\hbar \omega m^2} \sum_{i,j} \int_{BZ} \frac{dk}{(2\pi)^3} \left| p_{ij}^\alpha \right|^2 \delta(k_j - \epsilon_{k_i} - \hbar \omega), \]
\[ \sigma_{xy}^2(\omega) = \frac{\pi e^2}{\hbar \omega m^2} \sum_{i,j} \int_{BZ} \frac{dk}{(2\pi)^3} \Im \left[p_{ij}^\alpha p_{ij}^\beta \right] \delta(k_j - \epsilon_{k_i} - \hbar \omega), \]
where \( \hbar \omega \) is the photon energy and \( \epsilon_{k_i} \) 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 \( p_{ij}^\alpha = (\mathbf{k}_j | \mathbf{p}_a | \mathbf{k}_i) \), where \( \mathbf{p}_a \) denotes the Cartesian component \( a \) of the dipole operator, are obtained from the relativistic band structure within PAW formalism [34]. The integration is over the whole Brillouin zone using the linear tetrahedron method [37]. The dispersive part of the optical conductivity elements can be obtained from its corresponding absorptive parts using the Kramers-Kronig relations,
\[ \sigma_{\alpha\alpha}^2(\omega) = \frac{2}{\pi} P \int_0^\infty \frac{\sigma_{\alpha\alpha}^1(\omega')}{\omega^2 - \omega'^2} d\omega', \]
\[ \sigma_{xy}^1(\omega) = \frac{2}{\pi} P \int_0^\infty \frac{\omega' \sigma_{xy}^2(\omega')}{\omega^2 - \omega'^2} d\omega', \]
where \( P \) denotes the principal value.

For a bulk magnetic material, the complex polar Kerr rotation angle is given by [21, 36]
\[ \theta_K + i\epsilon_K = \frac{-\sigma_{xy}}{\sigma_{xx} \sqrt{1 + i(4\pi/\omega)\sigma_{xx}}} \]
However, for a magnetic thin film on a nonmagnetic substrate, the complex polar Kerr rotation is given by [37, 38]
\[ \theta_K + i\epsilon_K = \frac{-2(Z_0 d \sigma_{xy})}{(n_s + Z_0 d \sigma_{xx})^2 - 1} \]
where \( n_s \) is the refractive index of the substrate, \( Z_0 \) is the impedance of free space, and \( d \) stands for the thickness of the magnetic layer. Since few-layer Fe\(_2\)GeTe\(_2\) were usually deposited on a SiO\(_2\)/Si substrate [4], the refractive index of bulk SiO\(_2\) (\( n_s = 1.5 \)) is used here. Similarly, the complex Faraday rotation angle for a thin film can be written as [38]
\[ \theta_F + i\epsilon_F = \frac{\omega d}{2c}(n_+ - n_-), \]
where \( n_+ \) and \( n_- \) represent the refractive indices for left- and right-polarized lights, respectively. The refractive indices are related to the optical conductivity and the dielectric function via expression \( n_\pm = \sqrt{\epsilon_\pm} = \sqrt{1 + \frac{4\pi i}{\omega} \sigma_\pm} = \sqrt{1 + \frac{4\pi i}{\omega} (\sigma_{xx} \pm i\sigma_{xy})} \approx 1 + \frac{4\pi i}{\omega} (\sigma_{xx} \pm \frac{1}{2} i\sigma_{xy}) \). As a result,
\[ \theta_F + i\epsilon_F \approx -\frac{2\pi d}{c} \sigma_{xy}. \]
Here the real parts of the optical conductivity \( \sigma_\pm \) can be written as
\[ \sigma_\pm^1(\omega) = \frac{\pi e^2}{\hbar \omega m^2} \sum_{i,j} \int_{BZ} \frac{dk}{(2\pi)^3} \left| \Pi_{ij}^\pm \right|^2 \delta(k_j - \epsilon_{k_i} - \hbar \omega), \]
where \( \Pi_{ij}^\pm = \langle k_j | \frac{\mathbf{p}_a}{\hbar} (\mathbf{p}_x \pm i\mathbf{p}_y) | k_i \rangle \). Clearly, \( \sigma_{xy} = \frac{1}{2i} (\sigma_+ - \sigma_-) \) and therefore \( \sigma_{xy} \) would be nonzero only if \( \sigma_+ \) and \( \sigma_- \) are different. In other words, magnetic circular dichroism is the fundamental cause of the nonzero \( \sigma_{xy} \) and hence the MO effect.

### III. RESULTS AND DISCUSSION

#### A. Magnetic moments and magnetic anisotropy energy

Since both bulk and few-layer Fe\(_3\)GeTe\(_2\) have been experimentally found to be ferromagnetic [3, 4, 23, 40], we consider only the ferromagnetic configuration in this paper. The calculated spin and orbital magnetic moments of the considered Fe\(_3\)GeTe\(_2\) structures are listed in Table II, together with related previous experimental and theoretical results. First of all, Table II shows that calculated magnetic moments in few-layer Fe\(_3\)GeTe\(_2\) hardly depend on their thickness (i.e., the number of MLs) and also they are very close to that in bulk Fe\(_3\)GeTe\(_2\). This can be expected from the fact that the interlayer interaction is weak in the considered Fe\(_3\)GeTe\(_2\) structures. As mentioned above, in all the considered systems there are two inequivalent Fe sites (FeI and FeII) with different site symmetries (see Fig. 6.35). We also notice that the calculated total spin moment is due to the small spin moments of Te and Ge which are antiparallel to that of Fe (see Table II). We also notice that the
The electronic structure calculations (see, e.g., [43, 44] including the so-called orbital polarization correction in moments by up to 40% (see, e.g., [43, 44] and refer-
XMCD measurement [42]. It is known that the GGA magnetic moments. The averaged calculated orbital moment in bulk Fe
3
Fe vacancies. Due to the well-known crystal-field quench-
eperimental and theoretical values are listed for compari-

TABLE II. Calculated total spin magnetic moment ($m_s$), atomic (averaged) spin magnetic moment ($m_{Fe^{III}}$, $m_{Fe^{III}}$, $m_{Ge}$, $m_{Ge}$), and orbital magnetic moment ($m_{Fe^{III}}$, $m_{Fe^{III}}$, $m_{Ge}$, $m_{Ge}$), as well as density of states at the Fermi level [$D(E_F)$], magnetocrystalline anisotropy ($ΔE_m$), magnetic dipolar anisotropy energy ($ΔE_d$) and total magnetic anisotropy energy ($ΔE_{ma} = ΔE_m + ΔE_d$) of bulk and few-layer Fe$_3$GeTe$_2$. Positive $ΔE$ values mean that the out-of-plane magnetization is favored. The spin and orbital moments for two magnetization directions ($m||[001]$ and $m||[100]$) are listed. The related experimental and theoretical values are listed for comparison.

| System | $D(E_F)$ (1/eV/f.u.) | $m_s$ (μB/f.u.) | $m_{Fe^{III}}$ (μB/atom) | $m_{Fe^{III}}$ (μB/atom) | $m_{Ge}$ (μB/atom) | $m_{Ge}$ (μB/atom) | $ΔE_m$ (meV/f.u.) | $ΔE_d$ (meV/f.u.) |
|--------|----------------------|-----------------|--------------------------|--------------------------|-------------------|-------------------|-----------------|-----------------|
| bulk   |                      |                 |                          |                          |                   |                   |                 |                 |
| m||[001] | 3.25                | 6.29            | 2.41 (0.075)             | 1.53 (0.030)             | -0.10 (0.001)     | -0.04 (0.016)     | 3.37 (0.086)     | 3.28            |
| m||[100] | 4.95$^a$            | 2.18$^b$ (10$^3$) | 1.54$^b$ (10$^3$)       | -                        | -                 | -                 | ~3.4$^d$        | -               |
| ML m||[001] | 3.24                | 6.27            | 2.24 (0.076)             | 1.47 (0.033)             | -0.10 (0.001)     | -0.04 (0.018)     | 3.00 (0.32)      | 2.68            |
| BL m||[001] | 3.26                | 6.31            | 2.43 (0.076)             | 1.54 (0.033)             | -0.10 (0.001)     | -0.04 (0.017)     | 3.02 (0.33)      | 2.69            |
| TL m||[001] | 3.34                | 6.31            | 2.43 (0.076)             | 1.54 (0.032)             | -0.10 (0.001)     | -0.04 (0.017)     | 3.02 (0.33)      | 2.87            |
| FL m||[001] | 3.34                | 6.31            | 2.43 (0.076)             | 1.54 (0.032)             | -0.10 (0.001)     | -0.04 (0.017)     | 3.22 (0.33)      | 2.90            |
| QL m||[001] | 3.15                | 6.32            | 2.43 (0.076)             | 1.54 (0.032)             | -0.10 (0.001)     | -0.04 (0.017)     | 3.30 (0.32)      | 2.98            |
| m||[100] | 3.26                | 6.31            | 2.42 (0.085)             | 1.54 (0.052)             | -0.10 (0.003)     | -0.04 (0.006)     | -               | -               |

$^a$Reference [48] (SQUID experiment); $^b$Reference [11] (Neutron scattering experiment at 4K); $^c$Reference [42] (XMCD experiment: averaged orbital moment); $^d$Reference [8] (GGA); $^e$Reference [3] (LDA); $^f$Reference [2] (RMCD experiment); $^g$Reference [4] (LDA)

calculated total magnetic moment is significantly larger than that from the SQUID magnetization measurement (4.95 μB/f.u.) [48]. This may indicate that the samples used were nonstoichiometric or contained defects and Fe vacancies. Due to the well-known crystal-field quenching, the calculated orbital magnetic moments of the Fe atoms (e.g., 0.076 μB/Fe for FeI and 0.033 μB/Fe for II in bulk Fe$_3$GeTe$_2$) are much smaller than the spin magnetic moments. The averaged calculated orbital moment of the Fe atoms is ~0.06 μB/Fe, being smaller but in the same order of magnitude as that (0.10 μB/Fe) from the XMCD measurement [42]. It is known that the GGA and LDA functionals would give rise to too small orbital moments by up to 40% (see, e.g., [43, 44] and references therein). Nonetheless, these discrepancies between the experiment and theory can be largely removed by including the so-called orbital polarization correction in the electronic structure calculations (see, e.g., [43, 44] and references therein). Interestingly, Te orbital magnetic moments are comparable to Te spin magnetic moments and furthermore depend strongly on the magnetization direction (Table II). This is because the SOC in Te atoms is much stronger than in Fe and Ge atoms.

We present the calculated magnetocrystalline anisotropy energies ($ΔE$) in Table II. By definition ($ΔE = E^{[100]} - E^{[001]}$), a positive $ΔE$ value indicates an out-of-plane magnetization easy axis [i.e., the perpendicular magnetic anisotropy (PMA)]. Strikingly, Table II shows that all the considered Fe$_3$GeTe$_2$ structures have a very large PMA, being ~3.0 meV/f.u. or ~1.0 meV/Fe. These $ΔE_{ma}$ values not only are several times larger than that of 2D ferromagnetic semiconductors Cr$_2$Ge$_2$Te$_6$ (~0.1 meV/f.u.) [13] and CrI$_3$ (~0.5 meV/f.u.) [33] but also are comparable to that of heavy metal magnetic alloys such as FePt (2.75 meV/Fe) [15], which is known to have the largest MAE among the transition metal alloys. This large PMA would strongly suppress the magnetic fluctuations in these 2D materials and thus result in a higher ferromagnetic ordering temperature ($T_c$) than 2D ferromagnetic semiconductors CrI$_3$ [2] and Cr$_2$Ge$_2$Te$_6$ [1]. We note that the calculated MAE (2.9 meV/f.u.) of ML Fe$_3$GeTe$_2$ is in good agreement with the RMCD experimental data (2.0 meV/f.u.) [4]. The largeness of the PMA plus its electric tunability [3] suggests that 2D ferromagnetic metallic Fe$_3$GeTe$_2$ would have promising applications in high-density magnetic data storage and other spintronic devices.

Table II indicates that the MAE per f.u. increases slightly as one moves from ML to BL and then TL. However, the MAE per f.u. remains unchanged as the film thickness is further increased, e.g., to that of FL and QL (Table II). As mentioned before, the MAE consists of two competing contributions, namely, the MCE, which prefers PMA, and MDE, which always favors an in-plane magnetization. The MDE in 2D Fe$_3$GeTe$_2$ is in the same magnitude as that in 2D CrI$_3$ and Cr$_2$Ge$_2$Te$_6$. However, the magnitude of the MCE in 2D Fe$_3$GeTe$_2$ is nearly ten times larger than that of the MDE. This results in a gigantic MAE in 2D Fe$_3$GeTe$_2$. Note that these values are nearly three orders of magnitude larger than that of ferromagnetic Fe and Ni (4 μeV/f.u.) [45]. Bulk Fe$_3$GeTe$_2$ has an even larger MAE of 3.28 meV/f.u., simply because...
its MDE is much smaller than that in 2D Fe₃GeTe₂ (Table II). We notice that only one previous study, based on the local density approximation (LDA), on the MDE has been reported. Nevertheless, the calculated MDE for ML Fe₃GeTe₂ in Ref. is nearly three times smaller than the present calculations (Table II). This is mainly because the LDA spin magnetic moments reported in S9 are significantly smaller than the present GGA calculations (see Table II).

Table II also shows that while the spin magnetic moments are generally independent of the magnetization orientation, the orbital magnetic moments change significantly as the magnetization is rotated, e.g., from [001] to [100]. In particular, the Te orbital moment in ML Fe₃GeTe₂ gets reduced by nearly 60 % when the magnetization is rotated from [001] to [100], while that of Fe increases by about 12 % (Table II). This may suggest some correlation between the MCE and the anisotropy in the orbital magnetization. Indeed, a previous perturbative theory analysis showed that in elemental transition metal MLs, the easy axis is along the direction in which the orbital moment is largest. This supported by the *ab initio* calculations for Fe monolayers imbedded in noble metals. Interestingly, the orbital magnetic moments on heavy element Te atoms (which have the largest SOC) in all the considered Fe₃GeTe₂ structures with the perpendicular magnetization are much larger than that for an in-plane magnetization, thus indicating a possible connection with the strong PMA in these systems. Nevertheless, Table II shows that the Fe orbital moments in these Fe₃GeTe₂ structures are larger for an in-plane magnetization than for the perpendicular magnetization, indicating that the perturbative theory analysis for transition metal monolayers may not be wholly applicable to the present ternary compounds.

### B. Electronic structure

To understand the calculated magnetic and optical properties of the Fe₃GeTe₂ materials, we present the calculated electronic band structures. The band structures of ML, BL and bulk Fe₃GeTe₂ are displayed in Fig. and that of TL, FL and QL Fe₃GeTe₂ in Fig. S1 in the supplementary material (SM). Since the band structures of bulk and ML Fe₃GeTe₂ have already been reported in several previous papers and are also rather similar to that of TL, FL and QL Fe₃GeTe₂ due to the weak interlayer interaction, here we only summarize the salient features of the calculated band structures.

First of all, all the considered Fe₃GeTe₂ structures are metallic with multiple Fermi surface pockets (Fig. and Fig. S1 in the SM) and hence a large density of states (DOS) at the Fermi level (Eₚ) (Table II). In all the considered systems, there are many hole Fermi surface pockets centered at the Γ point and many electron Fermi surface pockets centered at the K point in the BZ (Figs. and Fig. S1 in the SM). Secondly, because bulk Fe₃GeTe₂ contains two MLs per unit cell and also the interlayer interaction is weak, the band structure of BL Fe₃GeTe₂ [Figs. 2(d), 2(e) and 2(f)] are almost identical to that of bulk Fe₃GeTe₂ [Figs. 2(g), 2(h) and 2(i)]. The band structure of ML Fe₃GeTe₂ is very similar to that of BL Fe₃GeTe₂ (Fig. 2) except that the number of the bands is only half of that for the BL. Similarly, the band structures of TL, FL and QL Fe₃GeTe₂ are overall nearly the same as that of the BL except with the increased number of bands (Fig. S1 in the SM).

Next, we present the total as well as site-, orbital-, and spin-projected DOS spectra of bulk and 2D Fe₃GeTe₂ in Figs. 3 and 4 as well as Figs. S2 and S3 in the SM. Figure 3 shows that for bulk Fe₃GeTe₂, the lower valence bands ranging from -5.0 to -2.2 eV result mainly from the hybridization among Fe d, Ge p, and Te p-orbitals. The upper valence bands and lower conduction bands (from -2.2 to 1.0 eV) are dominated by Fe d-orbitals together with minor contributions of Te p-orbitals around the Fermi level. Furthermore, Figs. (b) and (c) show that spin-splitting of Fe d bands is large, being more than 1 eV and thus indicating strong intra-atomic exchange interaction in bulk Fe₃GeTe₂. Interestingly, the local DOS spectra for the FeI and FeII sites are rather different, being consistent with the rather different magnetic moments on these sites (Table II). These differences are caused by their different local environments (coordination number and site symmetry). For example, the main spin-down FeI dₓz DOS peak is very sharp and is located at -0.8 eV [Fig. 3(b)] while the main spin-down FeII dₓz DOS peak is rather broad and is centered at 0.4 eV [Fig. 3(b)]. This is because there is no ligand atom lying above or below FeI [Figs. (a) and (c)] and thus FeI dₓz orbitals form a rather localized narrow band. In contrast, there is one Te atom sitting right above (or right below) the FeII atom [Figs. (a)]. Thus, FeII dₓz- and Te pₓz-orbitals hybridize and pushes FeII dₓz-orbital dominated antibonding band above the Fermi level [Fig. 3(c)].

Let us now discuss the possible origin of the large MCE in the Fe₃GeTe₂ systems in terms of the Fe d-orbital decomposed DOS spectra, e.g., Fig. 4. According to perturbation theory analysis, the occupied and empty d states near the Fermi level are coupled by the SOC and thus make most important contributions to the MCE. Moreover, for the same spin channel, the SOC matrix elements  and  are also rather similar to that of TL, FL and QL Fe₃GeTe₂, except for the weak interlayer interaction, here we only summarize the salient features of the calculated band structures.

First of all, all the considered Fe₃GeTe₂ structures are metallic with multiple Fermi surface pockets (Fig. and Fig. S1 in the SM) and hence a large density of states (DOS) at the Fermi level (Eₚ) (Table II). In all the considered systems, there are many hole Fermi surface pockets centered at the Γ point and many electron Fermi surface pockets centered at the K point in the BZ (Figs. and Fig. S1 in the SM). Secondly, because bulk Fe₃GeTe₂ contains two MLs per unit cell and also the interlayer interaction is weak, the band structure of BL Fe₃GeTe₂ [Figs. 2(d), 2(e) and 2(f)] are almost identical to that of bulk Fe₃GeTe₂ [Figs. 2(g), 2(h) and 2(i)]. The band structure of ML Fe₃GeTe₂ is very similar to that of BL Fe₃GeTe₂ (Fig. 2) except that the number of the bands is only half of that for the BL. Similarly, the band structures of TL, FL and QL Fe₃GeTe₂ are overall nearly the same as that of the BL except with the increased number of bands (Fig. S1 in the SM).

Next, we present the total as well as site-, orbital-, and spin-projected DOS spectra of bulk and 2D Fe₃GeTe₂ in Figs. 3 and 4 as well as Figs. S2 and S3 in the SM. Figure 3 shows that for bulk Fe₃GeTe₂, the lower valence bands ranging from -5.0 to -2.2 eV result mainly from the hybridization among Fe d, Ge p, and Te p-orbitals. The upper valence bands and lower conduction bands (from -2.2 to 1.0 eV) are dominated by Fe d-orbitals together with minor contributions of Te p-orbitals around the Fermi level. Furthermore, Figs. (b) and (c) show that spin-splitting of Fe d bands is large, being more than 1 eV and thus indicating strong intra-atomic exchange interaction in bulk Fe₃GeTe₂. Interestingly, the local DOS spectra for the FeI and FeII sites are rather different, being consistent with the rather different magnetic moments on these sites (Table II). These differences are caused by their different local environments (coordination number and site symmetry). For example, the main spin-down FeI dₓz DOS peak is very sharp and is located at -0.8 eV [Fig. 3(b)] while the main spin-down FeII dₓz DOS peak is rather broad and is centered at 0.4 eV [Fig. 3(b)]. This is because there is no ligand atom lying above or below FeI [Figs. (a) and (c)] and thus FeI dₓz orbitals form a rather localized narrow band. In contrast, there is one Te atom sitting right above (or right below) the FeII atom [Figs. (a)]. Thus, FeII dₓz- and Te pₓz-orbitals hybridize and pushes FeII dₓz-orbital dominated antibonding band above the Fermi level [Fig. 3(c)].

Let us now discuss the possible origin of the large MCE in the Fe₃GeTe₂ systems in terms of the Fe d-orbital decomposed DOS spectra, e.g., Fig. 4. According to perturbation theory analysis, the occupied and empty d states near the Fermi level are coupled by the SOC and thus make most important contributions to the MCE. Moreover, for the same spin channel, the SOC matrix elements  and  for the out-of-plane anisotropy, while  and  and  and  favour an in-plane anisotropy. The ratios of these matrix elements are  and  :  and  :  and  :  and  = 4 : 1 : 3 : 1. Figure(3b) shows that FeI dₓz, and dₓz-y² orbitals dominate Fe d-orbital decomposed DOS spectra in spin-up and spin-down channels, respectively. Consequently, the SOC matrix elements  and  would make dominating contributions to the MCE, thereby giving rise to
the large PMA in bulk Fe$_3$GeTe$_2$. For the FeII sites, the situation is more complicated [Fig. 3(c)]. In addition to the prominent $d_{yz, xz}$ orbitals, there are the pronounced $d_z$ orbital in both spin channels and also the prominent spin-down $d_{xy, x^2-y^2}$ orbitals. Consequently, there are competing contributions to the MCE from the SOC matrix elements of $\langle d_{yz} | H_{SO} | d_{x^2-y^2} \rangle$ and $\langle d_{yz} | H_{SO} | d_{zz} \rangle$, which prefers the PMA, and $\langle d_{yz} | H_{SO} | d_{z} \rangle$, which favors an in-plane magnetization. However, since the ratios of these matrix elements are $\langle d_{yz} | H_{SO} | d_{x^2-y^2} \rangle^2 : \langle d_{yz} | H_{SO} | d_{z} \rangle^2 : \langle d_{yz} | H_{SO} | d_{z} \rangle^2 = 4 : 1 : 3$, we believe that FeII atoms would make positive contributions to the PMA although they may be much smaller than FeI atoms.

Figures 3 and 4 show that there are pronounced occupied and unoccupied $p$-orbital DOSs from heavy Te atoms in the vicinity of $E_F$. To examine the possible contribution of these $p$-orbital states to the MCE, following [56] we derive the SOC matrix elements in the basis of $p$ orbitals, which are listed in Table III. Among the nonzero SOC elements, we find that $\langle p_x; \uparrow | H_{SO} | p_y; \uparrow \rangle$ prefers the out-of-plane magnetization but
FIG. 3. Scalar-relativistic site-, orbital-, and spin-projected DOS of bulk Fe$_3$GeTe$_2$. The Fermi level is at 0 eV.

Unlike that for $d$ orbitals [56], the expectation values of all nonzero elements $\langle p_y(p_x); \uparrow | H_{SO} | p_y(p_x); \uparrow \rangle$ are identical. Interestingly, Fig. 3 and 4 show that the Te $p_x$ and $p_y$ make a prominent contribution to the spin-up DOSs near the Fermi level. Since $\langle p_x; \uparrow | H_{SO} | p_y; \uparrow \rangle$ prefers the perpendicular anisotropy and also Te atoms have a much stronger SOC than Fe atoms, the large MCE found in bulk and 2D Fe$_3$GeTe$_2$ may result mainly from the presence of pronounced Te $p_{x,y}$-orbital DOSs near the Fermi level.

The site-, orbital- and spin-projected DOS spectra of ML Fe$_3$GeTe$_2$ are shown in Fig. 4. All the features of the DOS spectra are similar to that of bulk Fe$_3$GeTe$_2$ (Fig. 3). One pronounced difference is the appearance of FeII $d_{z^2}$ orbital dominated peaks near -3.0 eV in the lower valence bands. This can be attributed to the lack of the interlayer coupling because there is no Fe$_3$GeTe$_2$ ML above and below it. The absence of the hybridization among FeII $d_{z^2}$ orbitals from neighboring MLs (via Te $p_z$ orbitals) makes FeII $d_{z^2}$ orbitals localized and the corresponding band narrow. On the contrary, the peaks of FeI $d_{z^2}$ orbitals in bulk and ML Fe$_3$GeTe$_2$ are nearly the same because no ligand atom sits along the c direction. The site-, orbital- and spin-projected DOSs of BL and TL Fe$_3$GeTe$_2$ are displayed in Figs. S2 and S3 in the SM [48], where the spectral features fall in between that of ML and bulk Fe$_3$GeTe$_2$.

Finally, we notice a topological nodal point just below $E_F$ at the K point in the scalar-relativistic band structure of bulk Fe$_3$GeTe$_2$ [Fig. 2(g)]. This nodal point extends along the K-H line, and thus forms a topological nodal line. [49] Interestingly, for the perpendicular magnetization, this nodal line becomes split by a large band gap of $\sim$60 meV when the SOC is switched-on [Fig. 2(h)]. This results in the upper band being pushed upwards nearly above $E_F$ at the K point and the lower band moving downwards [Fig. 2(h)]. Furthermore, as reported before [49], these SOC-split bands have very large Berry curvatures with opposite signs near the nodal points, thus leading to the large observed anomalous Hall effect in bulk Fe$_3$GeTe$_2$. [49] Here we want to emphasize that this gap-opening at the nodal point also lowers the total band energy. On the other hand, these nodal points remain gapless when the magnetization is in-plane and hence the total band energy would remain much unchanged. Clearly, this would give rise to a significant contribution to the large MCE in bulk Fe$_3$GeTe$_2$ (see Table II). We notice that all 2D Fe$_3$GeTe$_2$ structures except ML Fe$_3$GeTe$_2$ have such a nodal point at the K point [see
Fig. 2 and Fig. S1 in the SM]. Therefore, we may conclude that to some extent, the large MCE found in bulk and 2D Fe₃GeTe₂ also originate from the gap-opening of the topological nodal point at the K point in these structures. We also notice that in ML Fe₃GeTe₂, although there is no such a nodal point, the top valence band at the K point is lowered by \( \sim 19 \) meV when the magnetization becomes in-plane. Clearly, such band movements due to the presence of the SOC and the change of magnetization direction would also contribute significantly to the large MCE in ML Fe₃GeTe₂.

C. Optical and magneto-optical conductivity

![Graphs showing optical and magneto-optical conductivity](image)

**FIG. 5.** 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] Fe₃GeTe₂ in the ferromagnetic state with the out-of-plane magnetization. All the spectra have been convoluted with a Lorentzian of 0.1 eV to simulate the finite electron lifetime effects.

We present the calculated optical and MO conductivity tensors for bulk and ML Fe₃GeTe₂ in Fig. 5 and also for BL and TL as well as for FL and QL Fe₃GeTe₂ in Figs. S4 and S4 in the SM [48], respectively. First of all, we can see that all spectra are rather similar. This similarity is due to the weak interlayer interaction in these materials. Such behaviour has also been reported in other 2D magnetic materials such as few-layer CrI₃ [30] and Cr₂Ge₂Te₆ [15]. Therefore, below we will analyze only the main features in the optical and MO conductivity spectra of ML and bulk Fe₃GeTe₂ in detail as representatives of these materials.

Figures 5(a) and 5(c) show that the diagonal elements of the optical conductivity \( \sigma_{xx} \) and \( \sigma_{zz} \) differ significantly. Since the \( \sigma_{xx} \) (\( \sigma_{zz} \)) is the linear optical response of the materials to an in-plane electric field polarization \( E \perp c \) (out-of-plane electric field polarization \( E||c \)), such difference indicates a large optical anisotropy. This can be expected for 2D or quasi-2D materials [15,30]. Specifically, the absorptive part of the diagonal element \( (\sigma_{xx}^{\prime}) \) for bulk Fe₃GeTe₂ (Fig. 5(a)) is larger than \( \sigma_{zz}^{\prime} \) in the low-energy region of 0.0-3.0 eV, but becomes smaller than \( \sigma_{zz}^{\prime} \) in the high-energy region of 3.0-6.0 eV. Compared to that of bulk, ML Fe₃GeTe₂ has a similar difference between \( \sigma_{xx}^{\prime} \) and \( \sigma_{zz}^{\prime} \). Nevertheless, as expected, such difference gets slightly enhanced, because ML Fe₃GeTe₂ is a truly 2D material. We notice that this optical anisotropy can be further understood in terms of the calculated orbital-projected DOS spectra. Note that the \( p_{x,y} \) and \( d_{xy,x^2-y^2} \) (\( p_{z} \) and \( d_{xz,yz} \)) states can only be excited by \( E \perp c \) (\( E||c \)) polarized light while the \( d_{xz,yz} \) states can be excited by both. Figures 5(b) and 5(d) indicate that the upper valence bands stem mainly from Fe \( d \) as well as Ge and Te \( p \) orbitals. In the energy region between -3.0 and 0.0 eV, the overall weight of \( d_{xy,x^2-y^2} \) states is slightly larger than that of \( d_{xz,yz} \) orbital (excited by \( E||c \)), thus leading to the slightly higher peaks of \( \sigma_{xx}^{\prime} \) in the photon energy region below 3.0 eV [Figs. 5(a) and 5(c)]. Further, broad peaks of Te \( p_{x,y} \) DOS in the energy range from -1.0 to 1.0 eV [Figs. 5(b) and 5(d)] also contribute to the higher peaks of \( \sigma_{zz}^{\prime} \) below 3.0 eV. On the other hand, significant FeII \( d_{xz,yz} \) and Te \( p_{z} \) states appear at lower valance bands from -5.0 to -3.0 eV. This would explain the increase of \( \sigma_{zz}^{\prime} \) (\( E||c \)) above 4.4 eV. Interestingly, among all considered structures, ML Fe₃GeTe₂ has a particularly sharp Te \( p_{z} \) peak [see Figs. 5(c) and 5(d)] due to the lack of interlayer coupling, as described above. This results in the largest optical anisotropy in ML Fe₃GeTe₂.

The calculated real \( (\sigma_{xy}^{1}) \) and imaginary \( (\sigma_{xy}^{2}) \) parts of the off-diagonal optical conductivity elements are displayed in Figs. 5(b) and 5(h) (d) for bulk Fe₃GeTe₂ and in Figs. 5(f) and 5(h) for ML Fe₃GeTe₂. First of all, we note that in the DC-limit \( (\omega \rightarrow 0) \), \( \sigma_{xy}^{1}(\omega) \) is actually the anomalous Hall conductivity (AHC). The AHCs calculated this way are 233 S/cm, 312 S/cm, 241 S/cm and 287 S/cm for bulk, ML, BL and TL Fe₃GeTe₂, respectively. The AHC value for bulk Fe₃GeTe₂ agrees quite well with the experimental AHC value of \(~360\) S/cm [57] and also previous theoretical one of \(~287\) S/cm [58]. Second, as expected, the overall features in the \( \sigma_{xy}(\omega) \) spectra for bulk and ML Fe₃GeTe₂ are similar. For example, for both structures, the \( \sigma_{xy}(\omega) \) spectra oscillates significantly with several high peaks. Prominent peaks occur...
FIG. 6. Relativistic site- and orbital-projected band structures of bulk ferromagnetic Fe₃GeTe₂. The Fermi level is at 0 eV. The main interband transitions at the Γ and K point, as well as the corresponding peaks in the $\sigma_{xy}^2$ spectrum in Fig. 5(d) are indicated by red and blue arrows, respectively. Also, the optical transitions in the vicinity of the Γ point are indicated by the magenta arrows, namely, A1 is at (0.04,0.04,0) $2\pi/a$ and A2 is at (0.03,0.03,0) $2\pi/a$.

Figures 6 and 7 depict the orbital-projected relativistic band structures of bulk and ML Fe₃GeTe₂, respectively. We label the main dipole-allowed optical transitions on high symmetry points Γ and K of bulk Fe₃GeTe₂ in Fig. 6 and also on high symmetry points Γ, K and K′ for ML Fe₃GeTe₂ in Fig. 7. Based on the calculated transition matrix elements (Tables S4 and S5) and the derived selection rules (Tables S2 and S3), we assign the peaks in the absorptive part of the magnetic-optical conductivity $\sigma_{xy}^2$ [see Figs. 5(d) and 5(h)] to the main optical transitions near the high symmetry points in Figs. 6 and 7 as indicated by red, blue and magenta symbols and arrows.

Equations (3), (4) and (11) indicate that the absorbptive parts of the optical conductivity elements ($\sigma_{xx}^1$, $\sigma_{zz}^1$, $\sigma_{xy}^2$, $\sigma_{zz}^1$) are directly related to the dipole-allowed interband transitions. This allows us to further understand the origin of the prominent peaks in the optical spectra in terms of the band state symmetries and dipole selection rules of the considered materials here. To this end, we perform a symmetry analysis on the band states and dipole selection rules at high symmetry Γ and K points, as described in the supplementary note 1 in the SM [48].
range from -4.0 eV to 2.0 eV. Interestingly, we find that in this energy range, significant optical transitions would occur only from Fe $d$ orbital dominated states which hybridize with Te $p$ and Ge $p$ orbitals. This results from a direct impact of the strong SOC of heavy elements on the MO effects. Thus, we could also link the main transitions to the calculated DOS spectra presented in the previous section. For example, peak $P9$ of $\sigma_{xy}$ of bulk Fe$_3$GeTe$_2$ [Fig. 6(d)] originates mainly from an optical transition from the valence states at -3.0 eV to the conduction states at $\sim$ 2.0 eV [Fig. 6], which coincides with the Te peak A to the Ge peak B in Figs. 6(d) and 6(e), respectively. Similarly, peak $P10$ of bulk Fe$_3$GeTe$_2$ [Fig. 6(d)] originates mainly from an optical transition from -4.0 eV to $\sim$ 0.8 eV [Fig. 6], which coincides with the Ge peak C to the FeI and FeII peak D from Figs. 6(b) and 6(c). Such connection can also be seen in ML Fe$_3$GeTe$_2$ since the DOS spectra from the two structures are similar. Furthermore, we show that the considerable hybridization of Fe $d$ orbitals with $p$ orbitals of heavy elements in the vicinity of the $\Gamma$ point in the energy range from around -0.2 eV to $\sim$0.2 eV also contribute to the first prominent peak in all the considered Fe$_3$GeTe$_2$ structures. We indicate two of such transitions as a representative by magenta arrows in Figs. 6 and 7.

Importantly, the main optical transitions would reveal not only the effect of orbital hybridizations but also the impact of crystalline symmetry and the SOC. First let us look into the effect of SOC-lifted degeneracies. Figures 6 and 7 show that pairs of right- and left-circular dipole-allowed transitions appear, such as peaks $P7$ and $N7$ in Fig. 6 for bulk Fe$_3$GeTe$_2$ and also peaks $P6$ and $N6$ in Fig. 7 or ML Fe$_3$GeTe$_2$. As explained in the supplementary note 1 [48], lifted degeneracies would lead to different irreducible representations (irreps) and thus difference in the optical transitions due to left- and right-circularly polarized light. From Table S4 and S5 we could directly observe the magnetic circular dichroism by sign and value differences of the transition matrix elements. Second, we examine the effect of the crystalline symmetry. Figure 7 indicates that optical transitions of ML Fe$_3$GeTe$_2$ sometimes come in pairs at the K and K’ point, e.g., peaks $N1$ and $P1$ as well as peaks $N5$ and $P5$. This results from the inversion symmetry breaking which leads to an interchange of irreps between the K and K’ point. With the inclusion of the SOC and the spontaneous exchange field due to the intrinsic magnetization, ML Fe$_3$GeTe$_2$ could be a possible ferrovalley material [11]. From Table S5 in the SM [48], we can see the transition energy ($\Delta E_{ij}$) to be different for transitions $P1$ and $N1$. However, in the absence of ferromagnetism, the dipole-allowed transitions would still be of opposite chirality but with the same $\Delta E_{ij}$ due to the broken inversion symmetry. The large difference of $\sim$0.13 eV in $\Delta E_{ij}$ is thus an indication of possible strong ferrovalley effect in few-layer Fe$_3$GeTe$_2$ containing odd number of MLs. Nevertheless, the $\sigma_{xy}$ spectra from different few-layer structures (Fig. 5 as well as Figs. S4 and S5) are similar. This suggests that although the broken inversion symmetry in the odd-layer structures affects the transition matrix elements at the K and K’ point, it does not change the magneto-optical spectrum significantly. Finally, it should be emphasized that the crucial factor for the large MO conductivity in these structures is the orbital hybridization between the magnetic (Fe) atoms which introduce magnetization and heavy elements (Te) which bring about strong SOC.

D. Magneto-optical Kerr and Faraday effects

Finally, we plot the calculated MOKE and MOFE spectra as a function of photon energy in Fig. 8 and 9 respectively. Figures 8 and 9 show that for all the few-layer structures of Fe$_3$GeTe$_2$, the patterns of the MOKE and MOFE spectra look similar to that of bulk Fe$_3$GeTe$_2$ [Fig. 8(a) and Fig. 9(a)], especially the Kerr and Faraday rotation spectra of BL, TL, FL and QL Fe$_3$GeTe$_2$. As for the optical conductivity spectra, this similarity of the MO spectra among all the considered structures is due to the weak interlayer coupling in these Fe$_3$GeTe$_2$ systems.
Fe₃GeTe₂ systems in, e.g., MO devices, we now compare the magnitudes of Kerr rotation angles to several popular MO materials. Let us start with 3d transition metals and their alloys. We notice that bcc Fe metal has a Kerr rotation of -0.5° at 1.0 eV, hcp Co metal has a Kerr rotation of -0.42° at 5.0 eV, and fcc Ni metal has a Kerr rotation of -0.25° at 4.0 eV [18, 21, 32]. Clearly, the calculated Kerr rotation angles of few-layer and also bulk Fe₃GeTe₂ are generally larger than that of elemental 3d transition metals. In particular, the magnitudes of both the Kerr rotation angle and ellipticity of all the considered Fe₃GeTe₂ structures are larger than 1.0° at around 2.5 eV. They are also comparable or even larger than the MOKE in 3d transition metal alloys with heavy elements such as Pt and Bi which have the strong SOC. [22] For example, famous MO transition metal alloys such as FePt, CoPt and PtMnSb have Kerr rotation angles ranging from 0.4° to 0.5° [21, 60]. Nevertheless, thin film MnBi has a record-high Kerr rotation of 2.3° at 1.84 eV [62], which is comparable to or smaller than that of TL, FL and QL Fe₃GeTe₂ in the infra-red frequency range (within 1.0 eV) (see Fig. S).

For further comparison, let us examine famous magnetic semiconductors with good MO properties. Ferromagnetic semiconductors Y₃Fe₂O₁₂ and Bi₃Fe₅O₁₂, which have been widely used in spintronic research, have Kerr rotation angle of -0.12° at 4.8 eV and -1.21° at 2.4 eV, respectively [59, 61]. For diluted magnetic semiconductors Ga₁₋ₓMnₓAs, a Kerr rotation of ~0.4° near 1.8 eV was reported [62]. Excitingly, layered ferromagnetic semiconductors Cr₁₃ and Cr₂Ge₂Te₆ were recently thinned down to just one or two monolayer with the ferromagnetic order retained at low temperatures [21, 60]. Moreover, TL Cr₂Ge₂Te₆ and TL Cr₁₃ were predicted to have large Kerr rotation of 0.7° near 2.8 eV and ~1.0° at 1.3 eV, respectively [15, 30]. Overall, in comparison to these famous MO semiconductors, the MOKE in bulk and ML Fe₃GeTe₂ are comparable and in particular, TL, FL and QL Fe₃GeTe₂ exhibit stronger MOKE.

Figure S also shows that bulk and few-layer Fe₃GeTe₂ all exhibit large negative Kerr rotations above 1.0° in the low energy region below ~0.4 eV. In particular, the Kerr angles of FL and QL Fe₃GeTe₂ are larger than 3.0° at ~0.3 eV. As photon energy further increases, the negative Kerr rotations decrease monotonically and become positive between 0.6 eV and 1.0 eV. Then they all peak at around 1.0 eV and stay positive until photon energy of around 2.0 eV. The positive peaks near 1.0 eV are rather prominent and can reach 1.0° in TL, FL and QL Fe₃GeTe₂ (Fig. S). The Kerr rotation spectra then have a negative peak at -1.0° again at around 2.5 eV and become positive again as photon energy increases beyond ~2.6 eV. They all have a positive pronounced peak at around 3.0 eV except bulk and ML Fe₃GeTe₂ which have the positive peak at 3.2 eV and 2.8 eV, respectively. Interestingly, the Kerr ellipticity spectra of all the structures have two large negative peaks at around 0.5 eV and 2.6 eV, respectively. MOKE experiments were carried out on a 340-nm thick sample using 633 nm HeNe laser (photon energy 1.96 eV). We note that the measured Kerr angle of ~0.33° is compared well with our calculated Kerr angle of bulk Fe₃GeTe₂ [see Fig. S(a)].

To investigate the potential applications of the...
data-storage devices.

Finally, we notice that MO Faraday rotation spectra of bulk and 2D Fe$_3$GeTe$_2$ (Fig. 2) are similar to their MO Kerr rotation spectra (Fig. 3). This may be expected since Eqs. (7), (8) and (10) indicate that all these MO spectra are more or less proportional to the MO conductivity ($\sigma_{xy}$). Indeed, the large MOKE and MOFE in bulk and few-layer Fe$_3$GeTe$_2$ stem from their large MO conductivity (i.e., strong magnetic circular dichroism). For example, overall, the MO conductivity of bulk and 2D Fe$_3$GeTe$_2$ (Fig. 5 as well as Figs. S4 and S5 in the SM [28]) is about 20 times larger than Y$_3$Fe$_5$O$_{12}$ and also 2 times larger than Bi$_3$Fe$_5$O$_{12}$ [29]. They are also around 2 times larger than bulk and 2D CrI$_3$ [30].

IV. CONCLUSIONS

Summarizing, we have investigated two relativity-induced properties, namely, magnetic anisotropy energy (MAE) and magneto-optical (MO) effects, of ML, BL, TL, FL and QL as well as bulk Fe$_3$GeTe$_2$, and also their connections with the underlying electronic structures of the materials, based on systematic first-principle DFT calculations. First of all, we find that all the considered Fe$_3$GeTe$_2$ structures prefer the out-of-plane magnetization and have gigantic MAEs of $\sim$3.0 meV/f.u., being about 20 and 6 times larger than 2D ferromagnetic semiconductors Cr$_2$Ge$_2$Te$_6$ and CrI$_3$, respectively. These MAE values are also comparable to that of FePt, which is known to have the largest MAE among the magnetic transition metals and their alloys. This gigantic perpendicular anisotropy results from the large relativity-induced MCE of $\sim$3.32 meV/f.u., which is ten times larger than the competing classical MDE of $\sim$0.3 meV/f.u., which favors an in-plane magnetization (Table II).

The giant MCEs can be attributed to the presence of significant Te $p_{x,y}$ orbital DOS in the vicinity the Fermi level and also to some extent, to the topological nodal point just below the Fermi level at the K points in the Brillouin zone in these materials. This strong PMA thus stabilizes the long-range ferromagnetic order in 2D Fe$_3$GeTe$_2$ at temperatures higher than that in 2D Cr$_2$Ge$_2$Te$_6$ and CrI$_3$. Secondly, we also find that 2D and bulk Fe$_3$GeTe$_2$ exhibit strong MO effects with the calculated Kerr and Faraday rotation angles being comparable or even larger than that of best-known bulk MO materials such as PtMnSb, Y$_3$Fe$_5$O$_{12}$ and Bi$_3$Fe$_5$O$_{12}$. In particular, all the Fe$_3$GeTe$_2$ structure are predicted to have large Kerr rotation angles of $\sim$1.0° at $\sim$3.0 eV and FL and QL Fe$_3$GeTe$_2$ have Kerr rotation angles as large as $\sim$3.0° at $\sim$0.25 eV (Fig. 8). Furthermore, ML Fe$_3$GeTe$_2$ has a Faraday rotation angle of -156 deg/µm, which is three times larger than that of famous MO oxide Bi$_3$Fe$_5$O$_{12}$. The shape and position of the features in the Kerr and Faraday rotation spectra are almost thickness-independent though the Kerr rotation angles increase slightly with the film thickness. The strong MO Kerr and Faraday effects are found to result from the large MO conductivity (i.e., strong magnetic circular dichroism) in these ferromagnetic materials. In particular, the calculated MO conductivity spectra are one order of magnitude larger than that of Y$_3$Fe$_5$O$_{12}$. The calculated MO conductivity spectra are analysed in terms of the symmetry of the band states and dipole-allowed optical transitions at high symmetry Γ, K and K’ points, which also reveal that atomically thin Fe$_3$GeTe$_2$ films with odd layer-number would exhibit anomalous ferrovalley Hall effect. We notice that our calculated MAE values for bulk and ML Fe$_3$GeTe$_2$ agree well with the corresponding experimental values and our predicted Kerr angle of bulk Fe$_3$GeTe$_2$ at 1.96 eV is in good agreement with the measured one. Also, the DC-limit of the real part of the calculated MO conductivity of bulk Fe$_3$GeTe$_2$ agrees well with the measured AHC. ALL these interesting findings therefore indicate that 2D and bulk ferromagnetic Fe$_3$GeTe$_2$ may find valuable applications for high density MO and spintronic nanodevices.

ACKNOWLEDGMENTS

The authors acknowledge the support from the Ministry of Science and Technology and the National Center for Theoretical Sciences (NCTS) of The R.O.C. The authors are also grateful to the National Center for High-performance Computing (NCHC) for the computing time.

[1] C. Gong, L. Li, Z. Li, H. Ji, A. Stern, Y. Xia, T. Cao, W. Bao, C. Wang, Y. Wang, Z. Q. Qiu, R. J. Cava, S. G. Louie, J. Xia, and X. Zhang, Discovery of intrinsic ferromagnetism in two-dimensional van der Waals crystals, Nature 546, 265 (2017).

[2] B. Huang, G. Clark, E. Navarro-Moratalla, D. R. Klein, R. Cheng, K. L. Seyler, D. Zhong, E. Schmidgal, M. A. McGuire, D. H. Cobden, W. Yao, D. Xiao, P. Jarillo-Herrero, and X. Xu, Layer-dependent ferromagnetism in a van der Waals crystal down to monolayer limit, Nature 546, 270 (2017).

[3] Z. Fei1, B. Huang, P. Malinowski1, W. Wang, T. Song, J. Sanchez1, W. Yao, D. Xiao, X. Zhu, A. F. May, W. Wu, D. H. Cobden, J.-H. Chu, and X. Xu, Two-dimensional itinerant ferromagnetism atomically thin Fe$_3$GeTe$_2$, Nat. Mat. 17, 778 (2018).

[4] Y. Deng, Y. Yu1, Y. Song, J. Zhang, N. Z. Wang, Z. Sun, Y. Yi, Y. Z. Wu, S. Wu, J. Zhu, J. Wang, X. H. Chen, and Y. Zhang, Gate-tunable room-temperature ferromagnetism in two-dimensional Fe$_3$GeTe$_2$, Nature 563, 94 (2018).
Electronic correlation and magnetism in the ferromagnetic metal Fe$_3$GeTe$_2$, Phys. Rev. B 93, 144404 (2016).

[43] V. Y. Verchenko, A. A. Tsirlin, A. V. Sobolev, I. A. Presniakov, and A. V. Shevelkov, Ferromagnetic Order, Strong Magnetcocrystalline Anisotropy, and Magnetocaloric Effect in the Layered Telluride Fe$_{3-x}$GeTe$_2$, Inorg. Chem. 54, 8598 (2015).

[44] G. Y. Guo, Spin and Orbital Polarized Multiple Scattering Theory of Magneto-x-ray Effects in Fe, Co and Ni, Phys. Rev. B 55, 11619 (1997).

[45] P. M. Oppenner, Magneto-optical spectroscopy in the valence-band energy regime: relationship to the magnetocrystalline anisotropy, J. Magn. Magn. Mater. 188, 275 (1998).

[46] G.-Y. Guo, W. M. Temmerman, and H. Ebert, A relativistic spin-polarized band theoretical study of magnetic properties of nickel and iron, Physica B Condens. Matter 172, 61 (1991).

[47] P. Bruno, Tight-binding approach to the orbital magnetic moment and magnetocrystalline anisotropy of transition-metal monolayers, Phys. Rev. B 39, 865 (1989).

[48] See Supplemental Material at http://link.aps.org/supplemental/ for Figs. S1-S5, supplementary note 1 and Tables S1-S5, which include Refs. [49-54].

[49] J. Xu, W. A. Phelan, and C.-L. Chien, Large Anomalous Nernst Effect in a van der Waals Ferromagnet Fe$_3$GeTe$_2$, Nano Lett. 19, 8250 (2019).

[50] M. S. Dresselhaus, G. Dresselhaus, and A. Jorio, Group Theory Applications to the Physics of Condensed Matter (Springer-Verlag, Berlin, 2008).

[51] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, Properties of the thirty-two point groups (Cambridge, Mass.: M.I.T. Press., 1963).