Tuning 2D magnetism in Fe$_{3+x}$GeTe$_2$ films by element doping

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ABSTRACT

Two-dimensional (2D) ferromagnetic materials have been discovered with tunable magnetism and orbital-driven nodal-line features. Controlling the 2D magnetism in exfoliated nanoflakes via electric/magnetic fields enables a boosted Curie temperature ($T_C$) or phase transitions. One of the challenges, however, is the realization of high $T_C$ 2D magnets that are tunable, robust and suitable for large scale fabrication. Here, we report molecular-beam epitaxy growth of wafer-scale Fe$_{3+x}$GeTe$_2$ films with $T_C$ above room temperature. By controlling the Fe composition in Fe$_{3+x}$GeTe$_2$, a continuously modulated $T_C$ in a broad range of 185–320 K has been achieved. This widely tunable $T_C$ is attributed to the doped interlayer Fe that provides a 40% enhancement around the optimal composition X = 2. We further fabricated magnetic tunneling junction device arrays that exhibit clear tunneling signals. Our results show an effective and reliable approach, i.e. element doping, to producing robust and tunable ferromagnetism beyond room temperature in a large-scale 2D Fe$_{3+x}$GeTe$_2$ fashion.

Keywords: 2D ferromagnetic material, Fe$_{3+x}$GeTe$_2$ film, element doping, above room temperature, $T_C$ tunability

INTRODUCTION

Since the discovery of van der Waals two-dimensional (2D) materials, especially graphene [1], such 2D crystals have been widely extended to transition metal dichalcogenides [2] and 2D superconductors [3]. More recently, 2D magnets have attracted enormous attention because of the emergence of ferromagnetism in the monolayer limit [4,5]. Novel theoretical proposals and experiments in magnetic tunability and spintronic devices have been reported. Theoretically, moiré skyrmions [6], the nodal-line property [7], the quantum anomalous Hall effect [8] and the ‘magic angle’ effect on magnetism [9,10] have been proposed in 2D magnets and their heterostructures. Magneto-band-structure effect [11], described as the electronic band structure modified by magnetization directions, has also been predicted in 2D van der Waals ferromagnetic materials for the realization of giant magnetoresistance. Experimentally, the rapid exploration of new 2D ferromagnets provides a fertile ground for exotic magnetic properties, for instance, Curie temperature ($T_C$) and coercive field ($H_C$) tunability via gate voltage [12,13], magnon-assisted tunneling [14] and giant magnetoresistance [15–17]. In spite of the tremendous progress made in the CrX$_3$ system, its $T_C$ remains below 60 K and the exploration of high $T_C$ materials becomes particularly appealing. Fe$_2$GeTe$_2$ exhibits a relatively high $T_C$ of ~220 K in the bulk state with a strong perpendicular magnetic anisotropy [18]. In exfoliated Fe$_2$GeTe$_2$ nanoflakes with a sample...
size in the order of micrometers, $T_C$ achieves a high modulation even up to room temperature via ionic liquid gating [19]. Characterized by magnetotransport and angle-resolved-photoemission spectroscopy, the bulk Fe$_3$GeTe$_2$ is proposed to be a ferromagnetic nodal-line semimetal [7] that promises more exotic properties like magnetically tunable nodes [20,21]. An intriguing proposal, with regard to such materials, is to realize the quantized anomalous Hall effect at significantly higher temperatures in the monolayer limit [22,23]. However, the approach to achieving controllable growth with large-scale functioning devices and high-$T_C$ ferromagnetic order remains elusive to date.

Chemical doping, via intentionally introducing impurities into parent materials, has been established as a direct yet effective approach to modulating and functionalizing the intrinsic electronic properties of 2D materials [24,25]. Doped transition metal dichalcogenides exhibit tunable electronic and optoelectronic properties [26–29]. Through Cr doping, the quantized anomalous Hall effect at millikelvin temperatures was discovered in Cr-doped (Bi, Sb)$_2$Te$_3$ films [30]. Dilute magnetic semiconductors, such as (Ga, Mn)As, yield a large modulation of $T_C$ with different Mn compositions [31,32]. Scenarios of nitrogen-decorated NbSe$_2$ nanosheets show the coexistence of ferromagnetism and superconductivity [33]. In Fe$_{3−x}$Ge$_{1+y}$Te$_2$ bulk crystals [34] and films made by molecular-beam epitaxy (MBE) [35], the ferromagnetic behavior of $T_C$ undergoes a monotonically decreasing trend with the reduction of the Fe composition. Nevertheless, the atom-doping-engineered $T_C$ in 2D materials remains lower than 250 K, and further effective methods for magnetism modulation and the investigation into the underlying mechanism are indispensable.

Here, we employ a precise control of element flux in MBE to directly accomplish a $T_C$ of 320 K in wafer-scale Fe$_{3+1.86}$GeTe$_2$ films. Aberration-corrected scanning transmission electron microscopy (STEM) investigations confirm the well-preserved layered structure in Fe-rich films. The angle-dependent anomalous Hall effect (AHE) evidences the persistent perpendicular magnetic anisotropy up to its $T_C$ of 320 K, which is consistent with that deduced from zero-field-cooled (ZFC) and field-cooled (FC) susceptibility results ($T_C \sim 316.1$ K) and X-ray magnetic circular dichroism results (XMCD, $T_C \sim 313.3$ K). The $T_C$ of the Fe$_{3+X}$GeTe$_2$ films is found to be strongly dependent on the $X$ value, which continuously increases from $\sim$185 K ($X = −0.25$) to 320 K ($X = 1.80$) followed by the decreasing behavior to 290 K at $X = 2.80$. Density functional theory (DFT) calculations confirm the ferromagnetic ground state of the bulk Fe$_3$GeTe$_2$ via a comparison with different antiferromagnetic states. Moreover, the calculations find that the doped interlayer Fe atoms contribute significantly to the $T_C$ enhancement. Based on these high-quality thin films, Fe$_{3+0.76}$GeTe$_2$/MgO/Fe$_3$GeTe$_2$ magnetic tunneling junction (MTJ) arrays are fabricated and clear tunneling signals are distinguished with a low-temperature tunneling magnetoresistance (TMR) ratio of $\sim$0.25%.

**Fe$_{3+X}$GeTe$_2$ FILM SYNTHESIS**

The layered Fe$_3$GeTe$_2$ compound has a hexagonal structure with the lattice parameters of $a = 3.991(1)$ Å, $c = 16.33(3)$ Å and a space group of P6$_3$/mmc [36]. Figure 1a shows the projection view of the Fe$_3$GeTe$_2$ atomic structure along the [01–10] zone-axis, in which each layer consists of five sub-layers [36] with a Fe$_3$Ge slab sandwiched between two neighboring Te layers with the corresponding nominal valence state of (Te$^2$)$^2$(Fe$^{2+}$)(Fe$^{2+}$)(Ge$^{4+}$)(Fe$^{3+}$)(Te$^{2−}$). By controlling the growth temperature and the flux of each element, high-crystalline Fe$_{3+X}$GeTe$_2$ films can be successfully grown by MBE. Figure 1b is an X-ray diffraction (XRD) pattern taken from a representative film, from which diffraction peaks can be ascribed to a series of {0002} planes (PDF# 75–5620). Its inset displays a streaky in-situ reflection high-energy electron diffraction (RHEED) pattern, indicative of a layer-by-layer growth mode for Fe-doped Fe$_{3+X}$GeTe$_2$ films (also displayed in Fig. S1). Figure 1c is a STEM-high angle annular dark-field (HAADF) image taken from a typical cross section of the film and shows the layered structure with an interlayer distance of $\sim$0.8 nm (close to the determined value for the stoichiometric Fe$_3$GeTe$_2$ films [35,37]). Therefore, the layered structure and high crystalline quality in Fe-rich Fe$_{3+X}$GeTe$_2$ thin films are well preserved. Figure 1d shows the corresponding X-ray energy dispersive spectrometry (EDS) profile of the film, and the quantitative analysis suggests the composition of the epitaxial Fe$_{3+X}$GeTe$_2$ is Fe$_{3+1.06}$GeTe$_2$. The left inset is a photograph of a 2-inch Fe$_{3+1.06}$GeTe$_2$ film, and the right inset shows an average surface roughness of 0.32 nm in the area of $10 \mu m \times 10 \mu m$ detected by atomic force microscopy.
Figure 1. 2D layered structure in Fe$_3$GeTe$_2$ thin films. (a) Fe$_3$GeTe$_2$ structure geometry. (b) XRD spectrum from Fe$_{3+1.10}$GeTe$_2$, with the peaks ascribed to (0002), (0004), (0006), (00010), (00012) and (00014) according to PDF # 75-5620. Inset, an RHEED pattern. (c) A cross section HAADF image of Fe$_{3+1.06}$GeTe$_2$. Labeled structure with an interlayer distance of 0.8 nm is well-preserved in such Fe-rich films. The scale bar is 1 nm. (d) EDS for Fe$_{3+1.06}$GeTe$_2$. Left inset, a photograph of a 2-inch Fe$_3$GeTe$_2$ film. Right inset, an atomic force microscopy image taken from a 10 µm x 10 µm surface, showing the average surface roughness of 0.32 nm. The scale bar is 3 µm.

ROOM-TEMPERATURE FERROMAGNETISM IN Fe$_{3+1.80}$GeTe$_2$ FILM

To experimentally probe the high-$T_C$ ferromagnetism in Fe$_{3+1.80}$GeTe$_2$ films, we carried out magnetotransport and $M$-$H$ measurements. Unless specifically mentioned, hereafter, the thickness of Fe$_3$GeTe$_2$ films is ~10 nm. The Hall effect for general ferromagnetic materials can be described as

$$R_{xy} = R_H B + R_{AH} M,$$

where the Hall coefficient $R_H$ stands for the ordinary Hall effect that is linearly dependent on the magnetic field ($B$), and the anomalous Hall effect $R_{AH}M$ comes from the magnetization ($M$) contribution. The AHE component can be obtained by subtracting the linear Hall resistance from the total Hall effect data, as illustrated in Fig. 2a. By increasing the temperature, the coercive field ($H_C$) decreases correspondingly. Up to 300 K, the anomalous Hall resistance ($R_{XY}$) still shows a hysteresis as the magnetic field scans back and forth; and eventually $H_C$ vanishes at 330 K (Fig. 2a inset), based on which $T_C$ is estimated to be ~320 K. It should be noted that in exfoliated Fe$_3$GeTe$_2$, perpendicular magneto-crystalline anisotropy persists to monolayer even though $T_C$ has been largely suppressed [19].

To characterize the Fe-doping effect on its magnetic anisotropy, the angle-dependent AHE at different temperatures is investigated. Here, the angle $\theta$ is defined as the angle between the magnetic field and the normal vector of the sample surface, as illustrated in the inset of Fig. 2b. At 2.5 K, the easy axis is confirmed to be along the out-of-plane direction with a perpendicular magnetic anisotropy due to the fact that the $H_C$ increases simultaneously with the angle rotating from 0° to 90°, thus sharing the same anisotropy property as the stoichiometric Fe$_3$GeTe$_2$ [35]. This perpendicular anisotropy persists up to 320 K, as verified by the angle-dependent AHE at 270 K, 300 K and 320 K, shown in Fig. S7. Analyzed with the Stoner-Wohlfarth model [19,38], the perpendicular magneto-crystalline anisotropy energy density ($K_v$) is estimated to be $\sim1.08 \times 10^7$ erg/cm$^3$ (Supplementary Note S2), which is comparable to that of the Fe$_3$GeTe$_2$ bulk crystals [38]. We have further explored the zero-field-cooled/field-cooled (ZFC-FC) magnetization curves for Fe$_{3+1.80}$GeTe$_2$ film (Fig. 2c, details in Supplementary Note S3), which exhibit different trends as the temperature decreases; they start to separate at $\sim320$ K. The variation of magnetization as a function of temperature is positively proportional to the magnetic susceptibility, which can be fitted by the Curie-Weiss law

$$\chi = \chi_0 + C/(T - T_C),$$

where $\chi_0$ is a temperature-independent parameter resulting from the density of states at the Fermi energy level, and $C$ is the Curie constant. The best fit to the experimental FC curve yields a $T_C$ of 316.1 ± 2.6 K (Fig. 2c inset), consistent with the value tracked from the temperature-dependent AHE (Fig. 2a). The $M$-$H$ curves at different temperatures are illustrated in Fig. S12a, where the coercive field of 40 Oe can be distinguished at 300 K.

Now the global room-temperature ferromagnetism in the millimeter-level flakes has been verified both by AHE and magnetization measurement. We further carried out the surface-sensitive polar reflective magnetic circular dichroism (RMCD) measurement where the focused laser spot was $\sim3$ µm to investigate its local magnetism. Figure 2d displays temperature-dependent RMCD measurement as a function of $B$. Consistent with the decreasing $H_C$ and $R_{XY}$ in the AHE measurements, the $H_C$ and remanent magnetization decrease with the increasing temperature.
Figure 2. Out-of-plane ferromagnetic anisotropy of Fe\textsubscript{3+1.80}GeTe\textsubscript{2} film with \( T_C \) of \( \sim 320 \) K. (a) Temperature-dependent AHE under the perpendicular measurement geometry. Top inset, a schematic configuration of the perpendicular geometry between the sample surface and the magnetic field. Bottom inset, coercive field tracked from AHE. Up to 320 K, visible hysteresis can be distinguished, and vanishes at 330 K. \( T_C \) can be determined to be \( \sim 320 \) K. (b) Angle-dependent AHE at 2.5 K. Because \( H_C \) increases with \( \theta \) tilting from 0° to 90°, the easy axis is determined to be out-of-plane. Inset, the schematic geometry that defines the angle \( \theta \). (c) Zero-field-cooled (ZFC) and field-cooled (FC) susceptibility curves under a magnetic field of 200 Oe. \( T_C \) is determined to be \( 316.1 \pm 2.6 \) K by the Curie-Weiss law as shown in the inset. The detailed estimation process is described in Supplementary Note S3. (d) Temperature-dependent polar RMCD curves. \( H_C \) and remanent magnetization decrease as the temperature increases, while ferromagnetic order still exists at 287 K.

It remains visible at 287 K and therefore confirms the enhanced ferromagnetism and the film uniformity. Combined with the persistent perpendicular magneto-crystalline anisotropy at various temperatures (Figs 2b and S7), this high \( T_C \) behavior in Fe\textsubscript{3+1.80}GeTe\textsubscript{2} films can be confirmed and the presence of either Fe films or magnetic clusters can be unambiguously excluded [39–41] (Supplementary Note S2). In addition, XMCD results are also presented next to safely exclude these extrinsic effects.

The element-specific XMCD was further performed to probe the localized magnetism. Left (blue) and right (red) circularly polarized X-rays, denoted as \( \mu^+ \) and \( \mu^- \), were used to resolve the XMCD signals, which was in parallel to the external magnetic field and in the normal incidence with respect to the sample surface (Fig. 3a inset). The XMCD signals were obtained by taking the difference of the X-ray absorption spectroscopy (XAS) spectra, i.e. \( \text{XMCD} = \mu^- - \mu^+ \). The XAS spectra obtained in total-fluorescence yield mode were subtracted by a two-step function [42] and a strong XMCD signal was acquired at 300 K, as shown in Fig. 3a. The agreement with the XAS of Fe\textsubscript{2}GeTe\textsubscript{2} bulk crystals [43] in the spectra shape further confirms its intrinsic high \( T_C \) ferromagnetism in the doped films, possessing two similar sites of Fe with such crystals [44–47]. The lower the temperature, the stronger the observed XMCD intensity (Fig. 3b). Here, to estimate the magnetic order, the XMCD percentage \( \beta \), defined as the intensity ratio of XMCD to XAS in the equation \( \beta = \frac{(\mu^- - \mu^+)}{(\mu^- + \mu^+)} \), is utilized as a parameter, which is calculated to be (10.9 ± 1.0)\% and (1.5 ± 0.1)\% for the two peaks at \( L_3 \) edge. As the critical peak on the left side of Fe \( L_3 \) edge (marked as P1) gives the strongest dichroism, which suggests a larger magnetic contribution, we focus on P1 during the XMCD analyses. As shown in Fig. 3c, the temperature-dependent XMCD percentages can be fitted with an empirical function (1 − \( T/T_C \))^\gamma to extract the Curie temperature \([48,49]\), based on which \( T_C \) is determined to be \( 313.3 \pm 9.5 \) K. These results confirm our findings regarding the above-room-temperature ferromagnetism in Fe\textsubscript{3+1.80}GeTe\textsubscript{2}.
In stark contrast to the continuously-decreased $T_C$ in Fe-deficient Fe$_{3-x}$GeTe$_2$ samples [34,35] where the Fe composition deviates negatively ($\delta < 0.3$) from Fe$_3$GeTe$_2$, here we present a large enhancement of the ferromagnetic order in Fe$_{3+x}$GeTe$_2$ films by systematically tuning the X value from $-0.25$ (Fe-deficient) to 2.80 (Fe-rich). As illustrated in Fig. 4a, $T_C$ initially increases with the increasing Fe doping, reaches a maximum value of 320 K at $X = 1.80$ and finally drops to 290 K in Fe$_{3+2.80}$GeTe$_2$. This $T_C$ behavior is a prominent extension to that of the Fe-deficient Fe$_{3-x}$GeTe$_2$ samples. Utilizing the high-$T_C$ and large-scale thin films, we have built MTJ device arrays (Fig. 4a inset) with an Fe$_{3+0.75}$GeTe$_2$/MgO/Fe$_3$GeTe$_2$ device structure (Supplementary Note S4). Clear tunneling magnetoresistance signals can be detected as the magnetic field scans back and forth. However, the tunneling magnetoresistance ratio is still low ($\sim 0.25\%$), which calls for further improvements on the crystalline quality of MgO.

In order to provide insight into the observed room-temperature ferromagnetic behavior in Fe$_{3+x}$GeTe$_2$ films, we performed DFT calculations within the LSDA + U framework to understand the bulk Fe$_3$GeTe$_2$ and its doping effect (Supplementary Note S5 and Fig. S17). We chose four different magnetic states, namely, the FM, AFM1, AFM2 and inter- AFM states, as illustrated in Fig. 4b. For the bulk, the LSDA + U calculations using the experimental lattice parameters confirm the FM ground state as summarized in Table 1. It is more stable than the inter-AFM state by 18 meV per formula unit (f.u.), indicating a relatively weak ferromagnetic interlayer coupling associated with the van der Waals bonding of the 2D material. However, due to the metallic behavior of Fe$_3$GeTe$_2$, the intralayer itinerant FM is quite strong. Compared with the FM ground state, the AFM1 state lies much higher in energy (by 300 meV/f.u.). This energy cost is due to the suppressed electron itinerancy in the AFM1 state (with one AFM Fe1-Fe3-Fe1 zigzag channel, see Fig. 4b) and the corresponding reduced kinetic energy gain. If two AFM zigzag channels (Fe1-Fe3-Fe1 and Fe2-Fe3-Fe2, see Fig. 4b) appear as in the AFM2 state, the energy cost is calculated to be 624 meV/f.u., being nearly doubled compared with the AFM1-FM energy difference with the change of one magnetic channel. Therefore, in our calculations, we employed the AFM1-FM energy difference to characterize the stability of the FM ground state and to trace the varying FM stability with the changing Fe concentrations.

Owing to the van der Waals layered structure of Fe$_3$GeTe$_2$, the additional Fe atoms most probably lie in the interlayer interstitial region. We use LSDA + U calculations to search the stable interlayer interstitial positions by optimizing the $c$-axis lattice parameter and atomic $z$ coordinates. Our calculations find that, for a doped Fe atom, there are three most stable interlayer occupation positions on the $1 \times 1$ plane, $(0,0)$, $(1/3,2/3)$ and $(2/3,1/3)$, which have almost the same potential well depth, as seen in Fig. 4c. This finding explains why the Fe concentration in Fe$_{3+x}$GeTe$_2$ can experimentally be largely enhanced.
To study the impact of the doped interlayer Fe atoms on the magnetism of Fe$_{3-x}$GeTe$_2$, we first compare the two cases of Fe$_{3+0.5}$GeTe$_2$ with one doped Fe atom on either the (0,0) or (1/3,2/3) position (Fig. 4d), using the LSDA + U calculations including a full atomic relaxation. The AFM1-FM energy difference is calculated to be 530 and 521 meV/f.u., respectively, showing insignificant site dependence of the FM strength by 40% at the optimal concentration $X = 2$. Therefore, this study opens an avenue to a significant enhancement of the $T_C$ in emerging 2D ferromagnetic Fe$_{3-x}$GeTe$_2$ films, which may facilitate their practical application in spintronic devices.

**METHODS**

**Thin film synthesis and characterization**

Fe$_{3-x}$GeTe$_2$ thin films were synthesized on (0001)-sapphire in a Perkin Elmer 430 MBE system (base vacuum: $\sim 2.5 \times 10^{-9}$ Torr). The substrates were firstly cleaned using a standard process, and before the growth, substrates were annealed at 600°C for 30 minutes, which was then cooled to the target temperature of 340°C. The growth temperatures for Ge-cell and Te-cell were 1020°C and 285°C, and the Fe composition was tuned via varying the Fe-cell temperature. The crystal oscillator was used to measure each element’s flux. XRD results were measured in a Bruker D8 Discover facility and transmission electron microscope measurements were performed using JEOL JEM-ARM 200F and FEI Titan G2 systems.

**Electrical and magnetization measurement**

Magnetotransport results were collected by SR830 in the Physical Properties Measurement System (PPMS) and the devices were in the six-Hall-bar
geometry. The magnetization measurements were accomplished by DC-Superconducting-Quantum-Interface-Devices (SQUID) by Quantum Design.

**RMCD and XMCD measurements**

RMCD measurements were performed in a closed-cycle helium cryostat with measurable temperature ranges from 15 to 287 K. A 633 nm HeNe laser with the power of ~0.3 μW and the focused beam spot of 3 μm was in the normal incidence onto the sample. A lock-in amplifier was utilized to acquire the RMCD signals. XMCD measurements at Fe $L_{2,3}$ edge were performed on beamline 110 at the Diamond Light Source.

**DFT calculation**

DFT calculations were processed using the Vienna 
*ab initio* Simulation Package (VASP) [50,51]. Local density approximation to the exchange-correlation function was used [52], which has previously been shown to describe the structural properties of Fe$_3$GeTe$_2$ well [53]. A plane wave cut-off of at least 400 eV was employed. The Brillouin zone was sampled using an $8 \times 8 \times 3$ k-point mesh. The ionic potentials, including the effect of core electrons, were described by the projector augmented wave method [54]. The atomic relaxations were implemented until the Hellmann-Feynman force on each atom was smaller than 0.01 eV/Å. We used the experimental lattice constants with atomic relaxations to study the smaller than 0.01 eV/Å. We used the experimental [54]. The atomic relaxations were implemented undescribed by the projector augmented wave method potentials, including the effect of core electrons, were described by the projector augmented wave method [54]. The atomic relaxations were implemented until the Hellmann-Feynman force on each atom was smaller than 0.01 eV/Å. We used the experimental lattice constants with atomic relaxations to study the smaller than 0.01 eV/Å. We used the experimental [54]. The atomic relaxations were implemented undescribed by the projector augmented wave method.

**SUPPLEMENTARY DATA**

Supplementary data are available at NSR online.

**ACKNOWLEDGEMENTS**

We acknowledge the Diamond Light Source for the XMCD measurements (Proposal SI20748). Part of the sample fabrication was performed at Fudan Nano-Fabrication Laboratory.

**FUNDING**

This work was supported by the National Key Research and Development Program of China (2017YFA0303302, 2018YFA0305601, 2016YFA0300700 and 2017YFA0206304), the National Natural Science Foundation of China (11934006, 61322407, 11874116, 11747059, 11674064, 61427812 and 11774160), the Science and Technology Commission of Shanghai (19511120300), the Shanghai Municipal Science and Technology Major Project (2019SHZDZX01), the Program of Shanghai Academic/Technology Research Leader (20XD1400200), the Beijing Natural Science Foundation (1780014), the National Basic Research Program of China (2014CB921101 and 2016YFA0300803), the UK EPSRC (EP/S010246/1), the Australian Research Council, the Progress 100 program to encourage the UQ-KU collaboration and the Japanese Nanotechnology Platform Project for advanced nanotechnology characterization (JPMPF09-A-19-KU-0312).

E.Z. acknowledges support from the China Postdoctoral Innovative Talents Support Program (BX20190085) and the China Postdoctoral Science Foundation (2019M661331). S.L. acknowledges support from the China Postdoctoral Science Foundation (2020TQ0080 and 2020M681138). A.N. acknowledges support from the startup grant (SG/MHRD-19–0001) of the Indian Institute of Science. The work at the University of Washington is supported by the Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division (DE-SC0018171).

**AUTHOR CONTRIBUTIONS**

F.X. and H.W. conceived the ideas and F.X. supervised the overall research. S.L., Z.L., X.G. and W.B. synthesized high-quality Fe$_3$GeTe$_2$ thin films and fabricated the devices. S.L., Z.L., E.Z., Y.Y., L.A. and C.H. performed the PPMS measurements. S.L., E.Z., Q.L., L.Y. and J.S. processed the transport and SQUID data. J.Z. and X.X. carried out the RMCD measurement and analysis. A.N., W.L. and J.S. performed the XMCD measurement and analyzed the XMCD data. K.Y. and H.W. carried out DFT calculations and theoretical analyses of different magnetic states. Z.L., M.K., T.T., Q.D., Y.C., X.H., S.M. and J.Z. did the transmission electron microscopy characterizations and analysis. J.Z., Z.L., K.Y., A.N., H.W. and F.X. wrote the paper with assistance from all other authors.

**Conflict of interest statement.** None declared.

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