

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

Shanshan Liu^{1,2#}, Zihan Li^{1,2#}, Ke Yang^{1,3#}, Enze Zhang^{1,2}, Awadhesh Narayan⁴, Xiaoqian Zhang⁵, Jiayi Zhu⁶, Wenqing Liu⁷, Zhiming Liao^{8,9}, Masaki Kudo¹⁰, Takaaki Toriyama¹⁰, Yunkun Yang^{1,2}, Qiang Li^{1,2}, Linfeng Ai^{1,2}, Ce Huang^{1,2}, Jiabao Sun,⁷ Xiaojiao Guo¹¹, Wenzhong Bao¹¹, Qingsong Deng⁹, Yanhui Chen⁹, Lifeng Yin^{1,2,12}, Jian Shen^{1,2,12}, Xiaodong Han⁹, Syo Matsumura^{10,13}, Jin Zou^{8,14}, Yongbing Xu⁵, Xiaodong Xu⁶, Hua Wu^{1,3,12*}, Faxian Xiu^{1,2,12,15*}

¹State Key Laboratory of Surface Physics and Department of Physics, Fudan University, Shanghai 200433, China

²Institute for Nanoelectronic Devices and Quantum Computing, Fudan University, Shanghai 200433, China

³Laboratory for Computational Physical Sciences (MOE), Fudan University, Shanghai 200433, China

⁴Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

⁵School of Electronic Science and Engineering, Nanjing University, Nanjing 210093, China

⁶Department of Physics, University of Washington, Seattle, WA 98195-1560, USA.

⁷Department of Electronic Engineering, Royal Holloway University of London, Egham TW20 0EX, UK

⁸Materials Engineering, The University of Queensland, Brisbane QLD 4072, Australia

⁹Beijing Key Lab of Microstructure and Property of Advanced Material, Institute of Microstructure and Properties of Advanced Materials, Beijing University of Technology, Beijing 100124, China

¹⁰The Ultramicroscopy Research Center, Kyushu University, Fukuoka 819-0395, Japan

¹¹State Key Laboratory of ASIC and System, School of Microelectronics, Fudan University, Shanghai 200433, China

¹²Collaborative Innovation Center of Advanced Microstructures, Nanjing 210093, China

¹³Department of Applied Quantum Physics and Nuclear Engineering, Kyushu University, Fukuoka 819-0395, Japan

¹⁴Centre for Microscopy and Microanalysis, The University of Queensland, Brisbane QLD 4072, Australia

¹⁵Shanghai Research Center for Quantum Sciences, Shanghai 201315, China

These authors contributed equally to this work

*Correspondence and requests for materials should be addressed to F.X. (E-mail: Faxian@fudan.edu.cn) and H.W. (wuh@fudan.edu.cn).

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 the 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 $\text{Fe}_{3+X}\text{GeTe}_2$ films with T_C above-room-temperature. By controlling the Fe composition in $\text{Fe}_{3+X}\text{GeTe}_2$, 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 provide 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 produce robust and tunable ferromagnetism beyond room temperature in a large-scale 2D $\text{Fe}_{3+X}\text{GeTe}_2$ fashion.

Keywords

2D ferromagnetic material, $\text{Fe}_{3+X}\text{GeTe}_2$ film, element doping, above-room-temperature, T_C tunability

INTRODUCTION

Since the discovery of van der Waals 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], nodal-line property[7], quantum anomalous Hall effect[8], and ‘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, the 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_3GeTe_2 exhibits a relatively high T_C of ~220 K in the bulk state with a strong perpendicular magnetic anisotropy[18]. In exfoliated Fe_3GeTe_2 nanoflakes with the 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_3GeTe_2 is proposed to be a

ferromagnetic nodal-line semimetal[7] which promises more exotic properties like magnetically tunable nodes[20,21]. An intriguing proposal in 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 a 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 modulate and functionalize 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 $(\text{Bi,Sb})_2\text{Te}_3$ films[30]. Dilute magnetic semiconductors, such as $(\text{Ga,Mn})\text{As}$, 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 $\text{Fe}_{3-x}\text{GeTe}_2$ 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 the 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 $\text{Fe}_{3+1.80}\text{GeTe}_2$ 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 $\text{Fe}_{3+x}\text{GeTe}_2$ films is found to be strongly dependent on the X value, in which it continuously increases from ~ 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_3GeTe_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, $\text{Fe}_{3+0.76}\text{GeTe}_2/\text{MgO}/\text{Fe}_3\text{GeTe}_2$ magnetic tunneling junction (MTJ) arrays are fabricated and clear tunneling signals are distinguished with a low-temperature tunneling magnetoresistance (TMR) ratio of $\sim 0.25\%$.

RESULTS

The layered Fe_3GeTe_2 compound has a hexagonal structure with the lattice parameters of $a = 3.991(1)$ Å and $c = 16.33(3)$ Å and a space group of $P6_3/mmc$. [36] Figure 1a shows the projection of the Fe_3GeTe_2 atomic structure along the $[01-10]$ zone-axis, in which each layer consists of five sub-layers[36] with a Fe_3Ge slab sandwiched between two neighboring Te layers with the corresponding nominal

valence state of $(\text{Te}^{2-})(\text{Fe}^{3+})[(\text{Fe}^{2+})(\text{Ge}^{4+})](\text{Fe}^{3+})(\text{Te}^{2-})$. By controlling the growth temperature and the flux of each element, high-crystalline $\text{Fe}_{3+x}\text{GeTe}_2$ 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 $\text{Fe}_{3+x}\text{GeTe}_2$ 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 ~ 0.8 nm (close to the determined value for the stoichiometric Fe_3GeTe_2 films [35,37]). Therefore, the layered structure and high crystalline quality in Fe-rich $\text{Fe}_{3+x}\text{GeTe}_2$ 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 $\text{Fe}_{3+x}\text{GeTe}_2$ as $\text{Fe}_{3+1.06}\text{GeTe}_2$. The left inset is a photograph of a 2-inch $\text{Fe}_{3+1.06}\text{GeTe}_2$ film, and the right inset shows the average surface roughness of 0.32 nm in the area of $10 \mu\text{m} \times 10 \mu\text{m}$ detected by atomic force microscopy.

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

To experimentally probe the high- T_C ferromagnetism in $\text{Fe}_{3+1.80}\text{GeTe}_2$ films, we carried out magnetotransport and M - H measurements. Unless specifically mentioned, hereafter, the thicknesses of Fe_3GeTe_2 films are ~ 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_3GeTe_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 θ 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 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_3GeTe_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 Stoner–Wohlfarth

model[19,38], the perpendicular magneto-crystalline anisotropy energy density (K_u) is estimated to be $\sim 1.08 \times 10^7$ erg/cm³ (Note S2), which is comparable to that of the Fe₃GeTe₂ bulk crystals[38]. We have further explored the zero-field-cooled/field-cooled (ZFC-FC) magnetization curves for Fe_{3+1.80}GeTe₂ film (Fig. 2c, Details in Note S3), which exhibit different trends as the temperature decreases; and they start to separate at ~ 320 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 χ_0 is a temperature-independent parameter resulted from the density of states at the Fermi energy, 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 that 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 SQUID. We further carried out the surface-sensitive polar reflective magnetic circular dichroism (RMCD) measurement where the focused laser spot is ~ 3 μ m 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. 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_{3+1.80}GeTe₂ films can be confirmed and the presence of either Fe films or magnetic clusters can be unambiguously excluded[39–41] (Note S2). In addition, XMCD results are also next presented to safely exclude these extrinsic effects.

X-ray magnetic circular dichroism (XMCD) is a powerful technique that is element- and site-sensitive to probe the localized ferromagnetism. Left (blue) and right (red) circularly polarized X-rays, denoted as μ^+ and μ^- , were used parallel to the external magnetic field and at 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.*, $XMCD = \mu^- - \mu^+$. Two pairs of XAS using total-fluorescence yield mode are 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 Fe₃GeTe₂ bulk crystals[43] in the spectra shape further confirms its intrinsic high T_C ferromagnetism of the doped films, possessing the similar two sites of Fe with such crystals[44–47]. The lower temperature, the stronger XMCD intensity was observed (Fig. 3b). Here, to estimate the magnetic order, the XMCD percentage β , 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 $(10.9 \pm 1.0) \%$ and

$(1.5 \pm 0.1) \%$ 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 ± 9.5 K. These results confirm our findings of the above-room-temperature ferromagnetism in $\text{Fe}_{3+1.80}\text{GeTe}_2$. In addition, solid ferromagnetism can be identified with a strong remanent XMCD percentage of 26.4% under zero magnetic field (Fig. 3d).

TUNABLE MAGNETISM AND THEORETICAL CALCULATION

In stark contrast to the continuously-decreased T_C in Fe-deficient $\text{Fe}_{3-\delta}\text{GeTe}_2$ samples[34,35] where the Fe composition is in a negative deviation ($\delta < 0.3$) from Fe_3GeTe_2 , here we present a large enhancement of the ferromagnetic order in $\text{Fe}_{3+x}\text{GeTe}_2$ 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 $\text{Fe}_{3+2.80}\text{GeTe}_2$. This T_C behavior is a prominent extension to that of the Fe-deficient $\text{Fe}_{3-\delta}\text{GeTe}_2$ samples. Utilizing the high- T_C and large-scale thin films, we have built MTJ device arrays (Fig. 4a inset) with a $\text{Fe}_{3+0.76}\text{GeTe}_2/\text{MgO}/\text{Fe}_3\text{GeTe}_2$ device structure (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 an insight into the observed room-temperature ferromagnetic behavior in $\text{Fe}_{3+x}\text{GeTe}_2$ films, we performed DFT calculations within the LSDA+U framework to understand the bulk Fe_3GeTe_2 and its doping effect (Note S5 and Fig. S17). We chose four different magnetic states, namely, the FM, AFM1, AFM2, and the 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_3GeTe_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 as 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 vdW layered structure of Fe_3GeTe_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 1×1 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 $\text{Fe}_{3+X}\text{GeTe}_2$ can experimentally be largely enhanced.

To study the impact of the doped interlayer Fe atoms on the magnetism of $\text{Fe}_{3+X}\text{GeTe}_2$, we first compare the two cases of $\text{Fe}_{3+0.5}\text{GeTe}_2$ with one doped Fe atom either on $(0,0)$ or on $(1/3,2/3)$ 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 in $\text{Fe}_{3+0.5}\text{GeTe}_2$ on the interlayer Fe positions. We then simulate $\text{Fe}_{3+X}\text{GeTe}_2$ ($X=0.5-3$) by adding the interlayer Fe atoms in the AB stacking Fe_3GeTe_2 unit cell one by one, at A $(1/3,2/3)$, B $(2/3,1/3)$, A $(2/3,1/3)$, B $(1/3,2/3)$, A $(0,0)$, and B $(0,0)$, to minimize the interlayer Fe-Fe coordinations in each case. As seen in Fig. 4a, upon increasing the interlayer Fe concentrations, the calculated AFM1-FM energy difference increases from 470 meV/f.u. (after atomic relaxation) for the stoichiometric Fe_3GeTe_2 to the maximal 670 meV/f.u. for $X=2$ and then drops to 600 meV/f.u. for $X=3$. The maximal enhancement of the FM strength by $\sim 40\%$ at the optimal concentration $X=2$ agrees well with our experimental findings. This composition-dependent T_C in $\text{Fe}_{3+X}\text{GeTe}_2$ films correlates with the electron doping effect which enhances the itinerant FM up to an optimal doping level (Supplementary Note S6).

CONCLUSION

In summary, we have demonstrated a direct doping approach in MBE growth to achieve high- T_C 2D ferromagnetic $\text{Fe}_{3+X}\text{GeTe}_2$ films beyond room temperature. Through systematically tuning the Fe composition, T_C acquires an efficient modulation from 185 K to 320 K, which arrives at the peak value of 320 K at $\text{Fe}_{3+1.80}\text{GeTe}_2$ validated by the temperature-dependent XMCD measurements. We further demonstrate the large-scale MTJ device arrays based on $\text{Fe}_{3+X}\text{GeTe}_2$ films. Moreover, our DFT study suggests that the doped interlayer Fe atoms provide a strong tunability to the magnetic order, achieving the optimal enhancement of FM strength by 40% at $X=2$. Therefore, this study opens an avenue to a significant enhancement of the T_C in the emerging 2D ferromagnetic $\text{Fe}_{3+X}\text{GeTe}_2$ films, which may facilitate their practical applications in spintronic devices.

METHODS

Thin-film synthesis and characterization

$\text{Fe}_{3+x}\text{GeTe}_2$ 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 and then decreased to the aimed temperature of 340°C. The growth temperatures for Ge-cell and Te-cell are 1020°C and 285°C, and the Fe composition is tuned via varying the Fe-cell temperature. The crystal oscillator is used to measure each element's flux. X-Ray Diffraction results were measured through 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 and the devices are in the six-Hall-bar geometry. The magnetization measurements were accomplished in DC-Superconducting-Quantum-Interface-Devices by Quantum Design.

RMCD and XMCD measurements

Reflective magnetic circular dichroism (RMCD) measurements were performed in a closed-cycle helium cryostat with the measurable temperature ranges from 15 to 287 K. A 633 nm HeNe laser with the power of $\sim 0.3 \mu\text{W}$ and focused beam spot of 3 μm incident normally on the sample. A lock-in amplifier is utilized to acquire the RMCD signals. X-ray magnetic circular dichroism (XMCD) measurements at Fe $L_{2,3}$ edge were performed on beamline I10 at the Diamond Light Source.

Density functional theory 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_3GeTe_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 are described by the projector augmented wave method[54]. The atomic relaxations are implemented until the Hellmann-Feynman force on each atom is smaller than 0.01 eV/Å. We use the experimental lattice constants with atomic relaxations to study the magnetism of $\text{Fe}_{3+x}\text{GeTe}_2$. In addition to LSDA, the LSDA plus Hubbard U (LSDA+U) method is employed [51], and we have chosen $U=3.5$ eV (and Hund exchange $J=0.9$ eV) for the Fe 3d electrons to calculate the magnetic properties. The calculation details were shown in Supplementary Note S6.

SUPPLEMENTARY MATERIALS

Supplementary data are available at NSR online.

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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 $\text{Fe}_{3+x}\text{GeTe}_2$ 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. X.Z., W.L., J.S. and Y.X. 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 TEM characterizations and analysis. S.L., 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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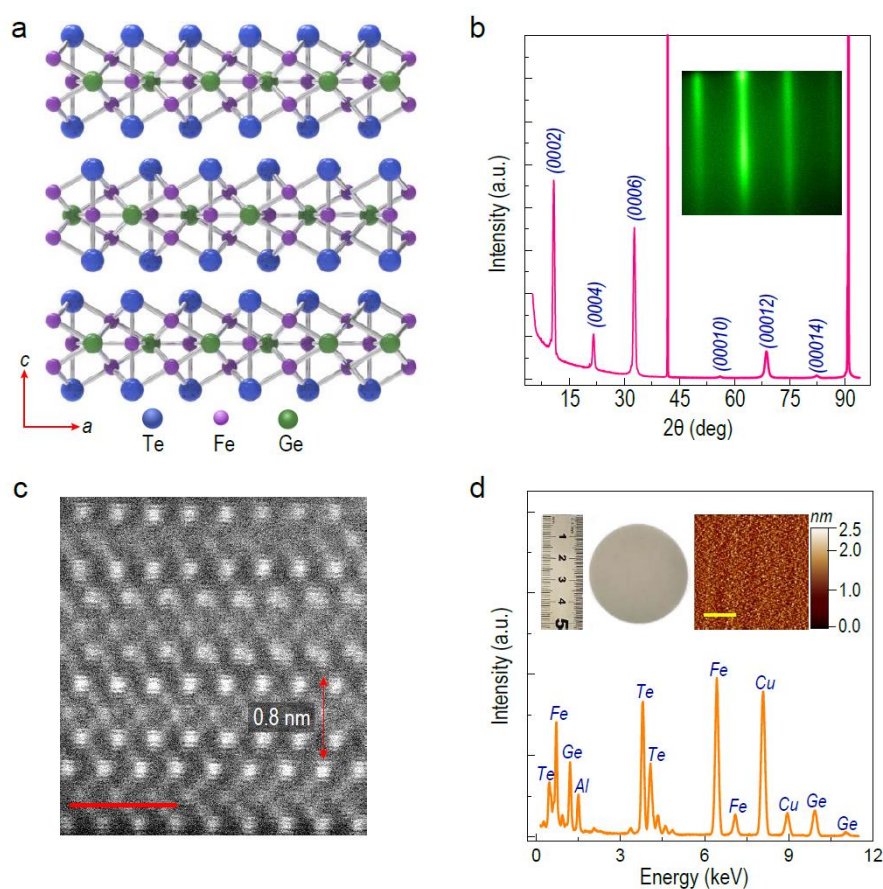


Figure 1. 2D layered structure in $\text{Fe}_{3+x}\text{GeTe}_2$ thin films. (a) Fe_3GeTe_2 structure geometry. (b) XRD spectrum from $\text{Fe}_{3+0.18}\text{GeTe}_2$, with the peaks ascribed to be (0002), (0004), (0006), (00010), (00012) and (00014) according to PDF# 75-5620. Inset, an RHED pattern. (c) A cross-section HAADF image of $\text{Fe}_{3+1.06}\text{GeTe}_2$. Layered structure with the inter-layer distance of 0.8 nm is well-preserved in such Fe-rich films. The scale bar is 1 nm. (d) EDS for $\text{Fe}_{3+1.06}\text{GeTe}_2$. Left inset, a photograph of a 2-inch $\text{Fe}_{3+1.06}\text{GeTe}_2$ film. Right inset, an atomic force microscopy image taken from a $10\ \mu\text{m} \times 10\ \mu\text{m}$ surface, showing the average surface roughness of 0.32 nm. The scale bar is $3\ \mu\text{m}$.

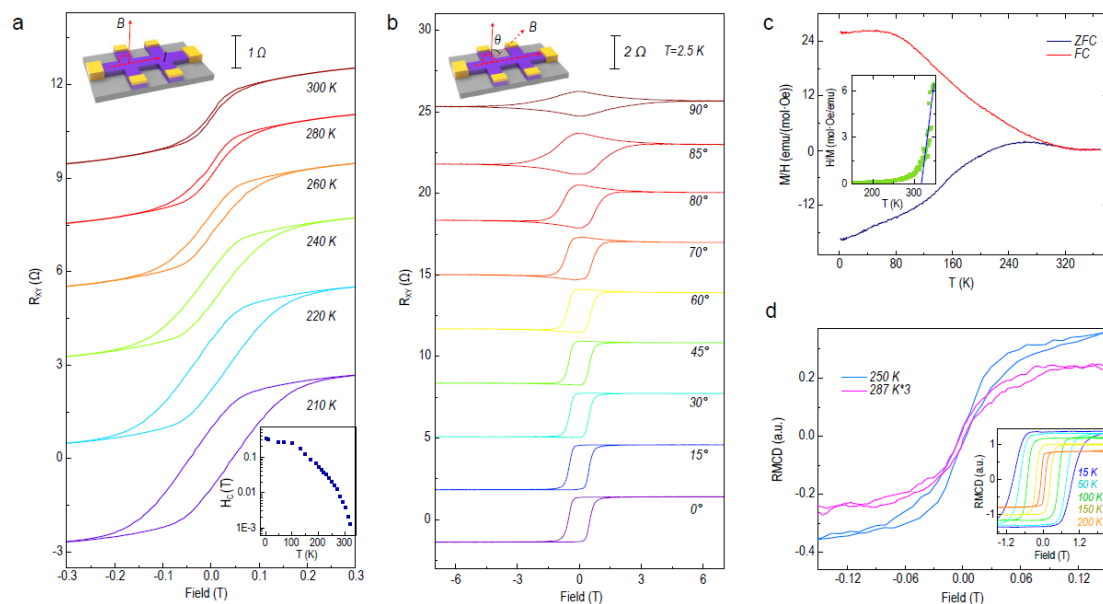


Figure 2. Out-of-plane ferromagnetic anisotropy of Fe_{3+1.80}GeTe₂ film with T_C of ~ 320 K. (a) Temperature-dependent AHE under the perpendicular measurement geometry. Top inset, a schematic configuration of the perpendicular geometry between the sample surface and the magnetic field. Bottom inset, coercive field tracked from AHE. Up to 320 K, visible hysteresis can be distinguished and it vanishes at 330 K. T_C can be determined to be ~ 320 K. (b) Angle-dependent AHE at 2.5 K. Because H_C increases with θ tilting from 0° to 90° , the easy axis is determined to be out-of-plane. Inset, the schematic geometry that defines the angle θ . (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 ± 2.6 K by the Curie-Weiss law as shown in the inset. The detailed estimation process is described in 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.

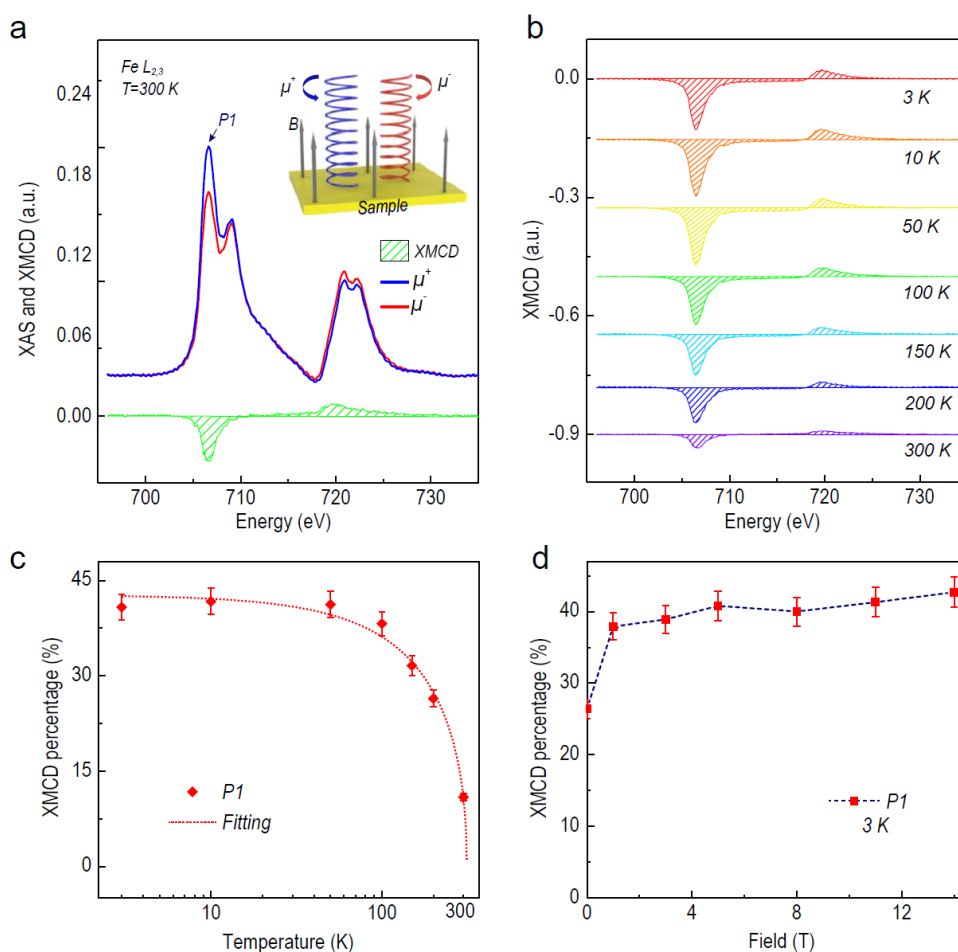


Figure 3. XAS spectra and XMCD signals of Fe_{3+1.80}GeTe₂ sample at Fe L_{2,3} edges. (a) Room-temperature XAS and XMCD spectra of Fe L_{2,3} edges at the field of 5T. The agreement with the XAS of Fe₃GeTe₂ bulks[43] in the spectra shape further confirms the intrinsic room-temperature ferromagnetism. The two peaks at Fe L₃ edge suggest two sites of Fe, with the XMCD percentages calculated to be $(10.90 \pm 1.0)\%$ and $(1.47 \pm 0.1)\%$, respectively. The XMCD results are discussed on the strongest-signal peak at the left side of Fe L₃ edge (marked as P1). Inset, schematic of the XMCD experiments. (b) Temperature-dependent XMCD of Fe L_{2,3} edges where the spectra at different temperatures have vertical offsets for clarity. The magnetic field is fixed at 5T. (c) XMCD percentage versus temperature. As the temperature rises, the XMCD percentage decreases continuously. The dashed lines represent the XMCD percentages fitting to the empirical equation $(1 - T/T_C)^{\gamma}$. T_C values are determined to be 313.3 ± 9.5 K, which further confirms the above-room-temperature ferromagnetism in Fe_{3+1.80}GeTe₂. (d) Field-dependent XMCD percentage, showing a large remanent XMCD percentage of 26.7% at zero-field.

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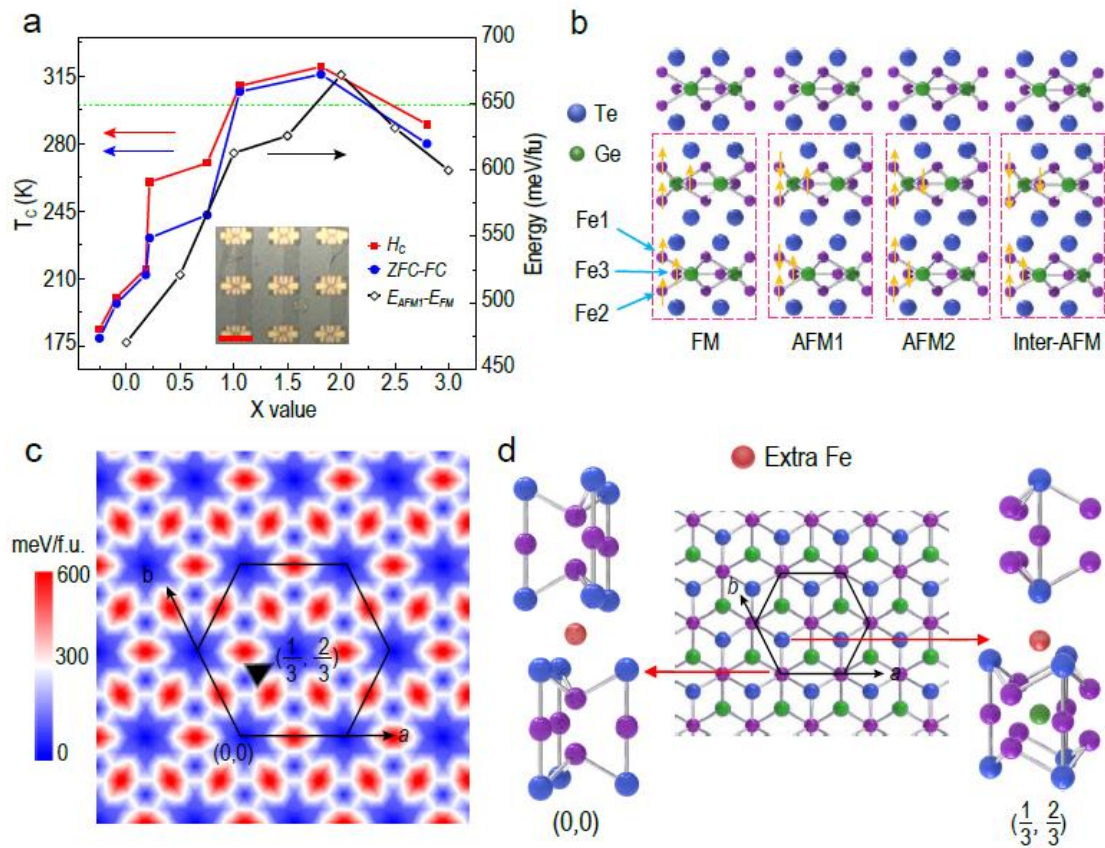


Figure 4. T_C modulation in $\text{Fe}_{3+X}\text{GeTe}_2$ film via Fe composition and DFT calculations. (a) T_C versus X ratio, reaching a peak value of 320 K at $X=1.80$. (b) Schematic diagrams for the four defined magnetic states, the orange arrows illustrating the spin direction of each Fe1, Fe2, and Fe3 atoms. (c) Relative total energies map of an extra Fe atom in the different interlayer positions of Fe_3GeTe_2 calculated by LSDA+U. There are three most stable sites at $(0,0)$, $(\frac{1}{3}, \frac{2}{3})$ and $(\frac{2}{3}, \frac{1}{3})$. (d) Local structure of an extra Fe at $(0,0)$ or $(\frac{1}{3}, \frac{2}{3})$ in bulk Fe_3GeTe_2 .

Table 1. Relative total energy (meV/f.u.) and local spin moments (μ_B) of different magnetic states calculated by LSDA+U for bulk Fe_3GeTe_2 .

Magnetic state	ΔE (meV/fu)	Fe1 (μ_B)	Fe2 (μ_B)	Fe3 (μ_B)
FM	0	2.74	2.74	1.96
AFM1	300	-2.74	2.62	1.77
AFM2	624	2.88	2.88	-1.64
Inter-AFM	18	2.72	2.72	1.95

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