Nearly room temperature ferromagnetism in a magnetic metal-rich van der Waals metal

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In spintronics, two-dimensional van der Waals crystals constitute a most promising material class for long-distance spin transport or effective spin manipulation at room temperature. To realize all-vdW-material–based spintronic devices, however, vdW materials with itinerant ferromagnetism at room temperature are needed for spin current generation and thereby serve as an effective spin source. We report theoretical design and experimental realization of a iron-based vdW material, Fe4GeTe2, showing a nearly room temperature ferromagnetic order, together with a large magnetization and high conductivity. These properties are well retained even in cleaved crystals down to seven layers, with notable improvement in perpendicular magnetic anisotropy. Our findings highlight Fe4GeTe2 and its nanometer-thick crystals as a promising candidate for spin source operation at nearly room temperature and hold promise to further increase Tc in vdW ferromagnets by theory-guided material discovery.

INTRODUCTION
The isolation of various two-dimensional (2D) van der Waals (vdW) crystals has triggered intensive research on exploring new phenomena in the 2D limit and designing novel devices with tailored functionalities in their heterostructures. Particularly in spintronics, 2D vdW materials often surpass many known 3D materials because of their exceptional transport-, optical-, and spin-related properties. For example, graphene, the first 2D vdW crystal, turns out to be the best-performing spin channel material with the longest spin diffusion length at room temperature due to its high mobility and low spin-orbit coupling (1–4). For spin manipulation, spin-valley locking in transition metal dichalcogenides (TMDCs) (5, 6) or spin-momentum locking in the surface state of bismuth chalcogenide–based topological insulators (7–10) provides unprecedented electrical/optical spin control by their strong spin-orbit coupling (5, 6, 11–13). One missing component is a metallic vdW ferromagnet for spin source, which can generate highly spin-polarized current at room temperature. Despite recent developments on magnetic vdW materials (14–25), most of the bulk vdW ferromagnets such as Cr(Si,Ge)Te3 (17, 18), Cr(Br,I)3 (19, 20), and Fe3GeTe2 (22, 23) have relatively low critical temperatures (Tc), well below the room temperature, which poses a challenge for using magnetic vdW materials in spintronic applications. Recently, the nearly room temperature ferromagnetism was induced in a few-layers-thick Fe3GeTe2 crystal by the sophisticated electrolyte gating (21). This may not be suitable for real spintronic applications but suggests that with proper material design, the room temperature ferromagnetism can be stabilized in a bulk vdW ferromagnet. Very recently, a vdW ferromagnet, Fe5Fe3GeTe2, has been synthesized, showing Tc ~ 300 K, while its crystal structure and the underlying mechanism of high-Tc ferromagnetism have remained as an open question (26, 27). If a stable vdW ferromagnet exists and also has a high conductivity and a large magnetization at room temperature, it can be used as a key component in all-vdW-material–based spintronic applications.

The relatively low Tc of vdW ferromagnets is a consequence of their 2D nature (see Fig. 1, A and B). In the typical TMDC-like structure, each layer of transition metal atoms is encapsulated by chalcogen or halogen atoms (Fig. 1A) and forms a 2D magnetic system with a weak magnetic interlayer coupling across the vdW gap. The pair-exchange interaction is mostly between the neighboring magnetic atoms in the 2D plane and is much weaker than in the 3D magnets. Furthermore, in the 2D limit, the Mermin-Wagner theorem (28) states that any continuous symmetry breaking similar to ferromagnetism cannot be spontaneous at a finite temperature. The ferromagnetic (FM) order is therefore stabilized against thermal fluctuations by the uniaxial magnetic anisotropy, and its energy scale K, together with spin-exchange interaction J, determines Tc as Tc ~ J/ln(3π/4 K) in the 2D limit (29). Usually, the magnetic anisotropy is set by the magnetocrystalline anisotropy, due to the spin-orbit coupling, and thus is much smaller in energy than exchange interaction, suppressing Tc in vdW ferromagnets. This strongly contrasts to the cases of 3D ferromagnets, in which the spin-exchange interaction J alone determines Tc, as found in, e.g., a bulk iron with Tc ~ 1000 K (30), much higher than found in vdW ferromagnets.

Our approach to achieve high Tc in vdW ferromagnets is to design a material having a 3D-like network of magnetic elements with enhanced exchange interaction while keeping the vdW structure. This design can be possible if several layers of closely linked magnetic atoms, experiencing 3D-like spin-pair interactions, form the
several-atom-thick Fe building blocks, which are stacked by vdW interaction. In such a case, $T_c$ is expected to be increased by enhancing $J$ with larger spin-pair interaction and also by suppressing the $K$ dependence of $T_c$. To realize this material design scheme, we propose Fe₄GeTe₂ ($n \geq 3$) as a model system, including two existing metallic ferromagnets, Fe₃GeTe₂ ($T_c = 220$ K) (22, 23) and Fe ($T_c = 1043$ K) (30), as the extreme cases. In this material class, magnetically active $n$ Fe atoms are linked and stacked with one Ge atom in the unit cell to form a multiple-layered metal-rich slab. This slab is then sandwiched by two Te layers, one above and one below, and becomes suitable for the vdW stacking. Using ab initio calculations, we identified the stable Fe₄GeTe₂ compounds, consisting of Fe-rich thick slabs stacked by vdW coupling. We successfully synthesize a newly designed vdW material Fe₄GeTe₂ that exhibits room temperature ferromagnetism with $T_c = 270$ K and has a large conductivity, a large magnetic moment, and a low magnetic anisotropy. Fe₄GeTe₂ is therefore a promising spin-source candidate for 2D spintronics.

RESULTS

Searching for stable crystal structures of FeₓGeTe₂ ($0 \leq n \leq 5$) was carried out using the ab initio random structure searching (AIRSS) (31) method based on density functional theory (DFT) calculations to predict possible Fe-rich compounds over the existing Fe₃GeTe₂ (22, 23). For the stoichiometry of Fe:Ge:Te = $n$:1:2, we first compare the formation enthalpy ($\Delta H$) of various possible crystal structures and identify the structure with the lowest $\Delta H$.

For $n = 3$, we obtained Fe₃GeTe₂ in the hexagonal vdW structure (P6₃/mmc), in excellent agreement with the experimental structure, which confirms the validity of our structural searching approach. The results obtained using the same procedure for $n = 4,5$ are summarized in a convex hull plot, referenced by the decomposition line into Fe and GeTe₂ (Fig. 1C). We found that the lowest energy structure in Fe₅GeTe₂ and Fe₄GeTe₂ is close to the convex hull line by $\sim 36$ and $\sim 86$ meV/atom, respectively. The extended structure prediction on various Fe:Ge:Te compositions in the ternary convex hull surface (Fig. 1D) provides a more general aspect of the energy landscape, revealing that these vdW-type Fe₅GeTe₂ ($n = 4,5$) phases are more stable than the neighboring ones. The proximity to the convex hull surface of each predicted compound, displayed by the symbol size and color, shows a valley-like feature along the stoichiometry line of Fe:Ge:Te = $n$:1:2 ($n \leq 3$) in the ternary phase diagram. This suggests that the predicted vdW-type Fe₅GeTe₂ ($n \geq 4$) can be dynamically stabilized while Fe₄GeTe₂ being an energetically stable one. The formation energy of the vdW-type Fe₅GeTe₂ gradually increases with

Fig. 1. Material design of Fe-rich van der Waals ferromagnets. (A) Schematic illustration of combining two structural motifs of transition metal dichalcogenides $MCh₂$ ($M$, transition metal; $Ch$, chalcogen) and body-centered cubic iron for Fe-rich vdW ferromagnets Fe₅MCh₂. (B) Three stable vdW structures in the series of FeₓGeTe₂ identified for $n = 3,4,5$ by ab initio calculations. The common structural units of Fe-Fe dumbbells form multiple-layer Fe-rich slabs, which are stacked by vdW coupling. The number of nearest Fe neighbors per Fe atom gradually increases with Fe content $n$, which is expected to be essential to enhance the pair exchange interaction and, thus, $T_c$. (C) Convex hull plot for FeₓGeTe₂ ($1 \leq n \leq 5$) with the horizontal decomposition line into Fe and GeTe₂. In addition to the thermodynamically stable vdW structure of Fe₅GeTe₂, two additional vdW structures of FeₓGeTe₂ ($n = 4,5$) have the low-enough total energy, albeit not on the convex hull line, indicating their possible dynamical stability. (D) Ternary phase diagram for various iron-rich compositions, together with the stoichiometry line of Fe:Ge:Te = $n$:1:2. The symbol size and color indicate the proximity to the convex hull plane, and the shape of symbols represents the structure types, including the known stable phases (diamond), vdW type (square), and others (circle). This ternary phase diagram clearly shows relatively stronger stability of the vdW-type FeₓGeTe₂ phases ($n = 3,4,5$) than their neighbors.
increasing iron concentration and eventually becomes too close to those of the neighboring compounds above \( n = 6 \), setting up the theoretical limit of the vdW-type \( \text{Fe}_4\text{GeTe}_2 \).

Our predicted \( \text{Fe}_4\text{GeTe}_2 \) has a rhombohedral structure (space group \( R3m \)) with vdW gap between the layers as shown in Fig. 1B. Similar to \( \text{Fe}_2\text{GeTe}_2 \), \( \text{Fe}_4\text{GeTe}_2 \) has similar structural units of Fe-Fe dumbbells, which are alternatingly off from the plane of Ge atoms and bonded with Te atoms directly. The calculated phonon dispersion of \( \text{Fe}_4\text{GeTe}_2 \) confirms the dynamic stability without any imaginary phonon modes (fig. S1). For \( \text{Fe}_2\text{GeTe}_2 \), the most stable structure also exhibits a vdW structure (space group \( P3m1 \)), which is similar to \( \text{Fe}_4\text{GeTe}_2 \) except that one additional Fe atom is inserted right above the Ge atom (fig. S1D). Its phonon dispersion is also confirmed to be stable (fig. S1). This case, however, includes another non–vdW-type structure (space group \( R3m \)) with a similar formation energy and dynamic stability, in which additional Fe atoms are inserted within the vdW gap of \( \text{Fe}_4\text{GeTe}_2 \) (fig. S1D). Therefore, we expect that in terms of the phase stability, the vdW structure competes with the other structures, including the intercalated one, as the Fe content \( n \) increases in the \( \text{Fe}_n\text{GeTe}_2 \) series. Nevertheless, our calculations clearly show that various types of multiple Fe stacking within a \( \text{GeTe}_2 \) layer are possible in the vdW structure, at least for \( 3 \leq n \leq 5 \) (Fig. 1B).

Guided by the material design, we successfully synthesized \( \text{Fe}_4\text{GeTe}_2 \) as a new member in the series of \( \text{Fe}_n\text{GeTe}_2 \) (see Fig. 2). From the systematic synthesis of \( \text{Fe}_4\text{GeTe}_2 \) in a wide range of the Fe content \( x \) (1.5 \( \leq x \leq 7 \)), we identified \( \text{Fe}_4\text{GeTe}_2 \) being stable in the vdW structure (fig. S3). High-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) clearly visualized the vdW gap between the layers and the atomic structure of \( \text{Fe}_4\text{GeTe}_2 \) (Fig. 2, C to E). The thickness of a single layer reaches \( d \sim 10 \) Å, which is consistent with the results of X-ray diffraction (fig. S3) and of electron beam diffraction (fig. S4). This is much thicker than observed in other magnetic vdW materials, typically \( d = 7 \) to 8 Å in \( \text{CrI}_3 \) (20) or \( \text{Fe}_2\text{GeTe}_2 \) (22, 23). This difference occurs because Fe and Ge atoms in \( \text{Fe}_4\text{GeTe}_2 \) form a five-atom-thick network, sandwiched by two Te layers, as explained in the plane views of each sublayer of a \( \text{Fe}_4\text{GeTe}_2 \) single layer (Fig. 2A). The weak interlayer vdW coupling in \( \text{Fe}_4\text{GeTe}_2 \) is further confirmed by the fact that it can be easily cleaved using the mechanical exfoliation method and has an atomically flat surface, as seen by scanning tunneling microscopy and atomic force microscopy (figs. S5 and S6).

Between the Te layers, distinctly contrasted in the cross-sectional images (Fig. 2, C and D), the interior Fe atoms are neighbored closest along the \( c \) axis in the identical Fe layers (Fe1 or Fe2) and form Fe-Fe dumbbells with a spacing of 2.47 Å. The neighboring Fe atoms between the Fe1 and Fe2 sublayers are also linked with a similar spacing of 2.52 Å. Besides the Fe network, the slightly stronger contrast appears at the Ge sites in the cross-sectional views along \( [110] \) (Fig. 2C) and along \( [120] \) (Fig. 2D), consistent with the larger Z-contrast effect of Ge \( (Z_{\text{Ge}} = 32) \) atoms than of Fe \( (Z_{\text{Fe}} = 26) \) atoms. These multilayer building blocks are stacked in the so called ABC configuration in a hexagonal structure (Fig. 2B), yielding a triangular pattern with almost the same contrast in the cross-sectional view along the \( [001] \) direction (Fig. 2E). The atomic structure from ab initio calculations (Fig. 2, C to E, inset) and, accordingly, its simulated HAADF STEM images perfectly match with the projection images along the \( [001] \), \( [120] \), and, particularly, \( [110] \) directions (Fig. 2, C to E). We, thus, conclude that the crystal structure of \( \text{Fe}_4\text{GeTe}_2 \) is rhombohedral (space group \( R3m \)) with lattice parameters \( a = 9.97(2) \) Å and \( c = 23.3(2) \) Å, consistent with the x-ray diffraction and x-ray photoelectron diffraction results (figs. S3 and S5), confirming that \( \text{Fe}_4\text{GeTe}_2 \) has the predicted vdW structure. We note that the recently discovered \( \text{Fe}_{5−x}\text{Ge}_{2+x} \), although its precise crystal structure is yet to be identified (26, 27), contains the similar structural motif predicted in our calculations on \( \text{Fe}_4\text{GeTe}_2 \), as discussed in fig. S4.

Now, we focus on the magnetic and transport properties of \( \text{Fe}_4\text{GeTe}_2 \) (Fig. 3). The high-\( T_c \) ferromagnetic ordering in \( \text{Fe}_4\text{GeTe}_2 \) was observed by measurements of magnetization \( M(T) \) and in-plane resistivity \( \rho(T) \) as a function of temperature (Fig. 3A). A clear upturn in the \( X(T) \) curves for \( H||c \) and \( H||ab \) indicates an FM transition...
at $T_c \approx 270$ K, followed by another transition at $T_{SR} = 110$ K, related to the spin reorientation as discussed below. Anomalies in $\rho(T)$ were consistently observed at $T_c$ and $T_{SR}$ but were more clearly visible in its temperature derivative curve $d\rho(T)/dT$ (Fig. 3A). We also obtained $T_c = 270$ K from the Arrott’s plot of the anomalous Hall effect (AHE) shown in fig. S8. The conductivity $\sigma$ at $T_c$, of Fe$_4$GeTe$_2$ is $\sim 5 \times 10^5$ ohm$^{-1}$m$^{-1}$, much larger than those of insulating vdW ferromagnets with $\sigma \sim 10^{-2} - 10^{-3}$ ohm$^{-1}$m$^{-1}$ (20, 24), comparable with that of Fe$_2$GeTe$_2$ (23, 25). The saturation magnetization is $M_{sat} = 1.8$ $\mu_B$/Fe atom, which corresponds to a volume magnetization of $\sim 500$ electromagnetic unit (emu)/cm$^3$, larger than $M_{sat} = 200$ to 340 emu/cm$^3$ of other vdW ferromagnets (17, 20, 23, 32). The high $T_c$ close to room temperature, high conductivity, and large magnetic moment of Fe$_4$GeTe$_2$ are obviously strong merits for spin-source materials.

Itinerant ferromagnetism is clearly revealed by the AHE. As found in typical FM metals, the field-dependent magnetization $M(H)$ (Fig. 3C) matches well with the field-dependent transverse conductivity $\sigma_{xy}$ (Fig. 3D), given as $\sigma_{xy} = \rho_{xx}/(\rho_{xx}^2 + \rho_{xy}^2)$, where $\rho_{xx}$ and $\rho_{xy}$ are the longitudinal and transverse resistivities, respectively. This indicates that the observed AHE is dominantly determined by the anomalous term $\sigma^A_{xy} = S_H M$, where $S_H$ is the anomalous Hall coefficient, quantifying the strength of the AHE. At high temperatures, $S_H \sim 0.02$ is nearly independent of temperature above $T_{SR}$ but drops significantly below $T_{SR}$. Accordingly, the anomalous Hall angle $\Theta_{AH} = \sigma^A_{xy}/\sigma_{xx}$ shows a maximum near $T_{SR}$ and decreases to $\sim 0.004$ at low temperatures (Fig. 3E). The sensitive response of the AHE to the magnetic transitions at $T_c$ and $T_{SR}$ unambiguously confirms the itinerant nature of the observed ferromagnetism, consistent with electronic structure calculations (fig. S2).

The contrasting properties of Fe$_4$GeTe$_2$ to other vdW ferromagnets are manifested by the low-temperature transition at $T_{SR}$. Comparison of the field-dependent magnetization curves $M(H)$ under $H||c$ and $H||ab$ (Fig. 3C) shows that the magnetic easy axis lies in the $ab$-plane at high temperatures ($T_{SR} < T < T_c$) but is rotated to the $c$ axis at temperatures below $T_{SR}$. Such a spin reorientation transition, without modifying the magnitude of magnetization, is the consequence of the small effective uniaxial magnetic anisotropy ($K_{eff}$), which originates from two competing contributions, the magnetocrystalline anisotropy ($K_m$), favoring the easy-axis anisotropy, and the shape anisotropy ($K_{sh}$), favoring the easy-plane anisotropy. They usually follow different temperature dependences, roughly $K_m \sim M_s^2$ and $K_{sh} \sim M_s$, which leads to the temperature-driven spin reorientation transition (Fig. 3B). From the saturation field $H_{sat}$ along the hard axis at low temperatures and the relation of $H_{sat} = 2K_{eff}/M_{sat}$, we estimate that $K_{eff}$ of Fe$_4$GeTe$_2$ is $\sim 0.23$ J/cm$^3$, mainly determined by the magnetocrystalline anisotropy of $K_m \sim 0.39$ J/cm$^3$ with a smaller shape anisotropy of $K_{sh} \sim 0.16$ J/cm$^3$. This is an order of magnitude smaller than that of Fe$_3$GeTe$_2$, showing a strong uniaxial magnetic anisotropy of $K_{eff} = 1.03$ J/cm$^3$. The small magnetic anisotropy, together with the high $T_c$, in Fe$_4$GeTe$_2$ is clearly off from the trend of other vdW ferromagnets, in which $T_c$ has a positive correlation with the uniaxial

![Fig. 3. Magnetotransport properties of Fe$_4$GeTe$_2$ single crystal. (A) Temperature dependence of the magnetic susceptibility $\chi$ (green) at $H = 1$ kOe for different field directions, $H||c$ and $H||ab$, and the electrical resistivity $\rho$ (black, solid symbol) with its temperature derivative $d\rho/dT$ (black, open symbol) with the in-plane current. Both $\chi(T)$ and $d\rho/dT$ show anomalies at $T_c = 270$ K, corresponding to the ferromagnetic transition, and at $T_{SR} = 110$ K for the spin-reorientation transition, indicated by red arrows. (B) Temperature dependence of the magnetic saturation field $H_{sat}$ for $H||ab$ (open symbols) and $H||c$ (solid symbols). The spin orientation changes from the easy axis ($||c$) to the easy plane (lelab) around $T_{SR} = 110$ K. (C) Magnetic field–dependent magnetization $M(H)$ at various temperatures for $H||ab$ (open symbols) and $H||c$ (solid symbols). At temperatures below $T_{SR} = 110$ K, the saturation of $M(H)$ occurs at lower magnetic field for $H||c$ than for $H||ab$, but this relation reverses at higher temperatures below $T_c = 270$ K. (D) Magnetic field–dependent Hall conductivity $\sigma_{xy}(H)$ (open symbols) at various temperatures for $H||c$. The magnetic field–dependent magnetization $M(H)$ (solid lines), scaled using the anomalous Hall factor $S_H = \sigma^A_{xy}(H)/M(H)$, matches well with the curves of $\sigma_{xy}(H)$. (E) Temperature dependence of the anomalous Hall angle $\Theta_{AH} = \sigma^A_{xy}/\sigma_{xx}$ and the anomalous Hall factor $S_H = \sigma^A_{xy}/M$, showing anomalies at $T_{SR}$. (F) Uniaxial magnetic anisotropy energy $K_{sat}$ and the FM transition temperature $T_c$ for various vdW ferromagnets, CrSiTe$_3$ ($X = Br, I$) (19, 20), CrMTe$_2$ ($M = Si, Ge$) (17, 32), and Fe$_4$GeTe$_2$ (23, 25) ($n = 3, 4$). The positive correlation between $T_c$ and $K$ in vdW ferromagnets is indicated by the shaded line.

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magnetic anisotropy energy $K_{\text{eff}}$ (Fig. 3F). This suggests that the enhanced $J$ is responsible for the high $T_c$ in Fe$_4$GeTe$_2$, where a large spin-pair interaction is expected in the network of Fe atoms.

The observed high-$T_c$ ferromagnetism and high conductivity are well retained in nanometer-thick Fe$_4$GeTe$_2$ flakes, as confirmed by magnetic circular dichroism (MCD) and AHE measurements (Fig. 4). The MCD signal, obtained in the seven-layer-thick (7L) flake with a small external field $H = 0.5$ T, clearly exhibits the FM transition at $T_c \sim 270$ K. With a zero external field, however, the MCD is nearly zero above $T_{\text{SR}} \sim 200$ K but becomes finite below $T_{\text{SR}}$ with a magnetic domain structure with a typical size of a few micrometers. Since MCD probes the out-of-plane component of magnetization, this confirms the spin-reorientation transition. The high $T_c$ and the high conductivity for nanoflakes are confirmed by the magnetotransport measurements, $\rho(T)$ (Fig. 4D) and $\sigma_{xy}^A(H)$ (Fig. 4E). The spontaneous component of $\sigma_{xy}^A(T)$, estimated from the Arrrott plot of $\sigma_{xy}^A(H)$ at different temperatures for nanoflakes with various thicknesses (fig. S8), shows a clear onset at $T_c \sim 270$ K (Fig. 4F), indicating that $T_c$ remains almost the same or slightly increased with lowering the thickness (Fig. 4G).

Unlike high $T_c$ and conductivity, the magnetic anisotropy and the magnetic coercivity are more significantly controlled by reducing the thickness. As shown in Fig. 4E and fig. S9, magnetic hysteresis curves of $\sigma_{xy}^A(H)$ become square shaped with a large coercive field $H_c \sim 1000$ Oe. The remnant magnetization ($M_R$) with respect to $M_{\text{sat}}$, estimated from $\sigma_{xy}^A(H = 0)/\sigma_{xy}^A(H_{\text{sat}})$, approaches to $\sim 1$ in nanoflakes at low temperatures, but it is suppressed above $T_{\text{SR}}$ (fig. S9). The spin-reorientation temperature $T_{\text{SR}}$ is significantly enhanced up to $\sim 200$ K with lowering the thickness down to 7L, extending the temperature range of perpendicular magnetic anisotropy (PMA).

Consistently, the saturation field $H_{\text{sat}}$ along the in plane, i.e., the magnetic hard axis, estimated from the angle-dependent AHE experiments (fig. S10) is almost six times larger than the bulk value. This implies that the surface magnetic anisotropy becomes dominant in nanoflakes, inducing strong enhancement of PMA, which is known to be critical to thermal stability and magnetic remanence. Although the observed increase in PMA is not sufficient to maintain magnetic remanence close to $T_c$, our findings strongly suggest that the magnetic anisotropy of Fe$_4$GeTe$_2$ nanoflakes can be further controlled with proper surface modification while keeping high-$T_c$ ferromagnetism.

**DISCUSSION**

One of the most critical questions is the origin of the observed increase in $T_c$ in Fe$_4$GeTe$_2$ with respect to Fe$_3$GeTe$_2$. To theoretically understand this question, we used DFT calculations, combined with dynamic mean field theory (DMFT) on the series of Fe$_x$GeTe$_2$ ($3 \leq x \leq 5$). Since the calculations based on the mean field theory are known to overestimate $T_c$ and the saturation magnetization $M_{\text{sat}}$, we scaled them against those of Fe$_3$GeTe$_2$ ($T_c = 220$ K) and compared their relative changes, as shown in Fig. 5A. The resulting saturation magnetic moment as a function of temperature shows that $T_c$ and $M_{\text{sat}}$ increase in Fe$_4$GeTe$_2$ by $\sim 21$ and $\sim 16\%$, respectively. These

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**Fig. 4. Thickness-dependent magnetic properties and phase diagram of Fe$_4$GeTe$_2$ nanoflakes.** (A and B) Magnetic circular dichroism (MCD) image of a seven-layer-thick (7L) Fe$_4$GeTe$_2$ crystal at $B = 0$ T (A) and $B = 0.5$ T (B). (C) The corresponding temperature-dependent MCD signal with $B = 0$ T (red) and $B = 0.5$ T (black), showing both ferromagnetic and spin-reorientation temperatures $T_c$ and $T_{\text{SR}}$. The inset shows the optical image of the 7L Fe$_4$GeTe$_2$ crystal and the circular polarizations for MCD measurements. (D) Temperature dependence of the normalized in-plane resistivity $\rho(T)$ for cleaved Fe$_4$GeTe$_2$ crystals with various thicknesses, indicated by numbers of the layers. The optical image of a typical device of BN-covered Fe$_4$GeTe$_2$ crystals. (E) Field-dependent Hall conductivity ($\sigma_{xy}$) for a 11-layer-thick Fe$_4$GeTe$_2$ crystal, revealing AHE with a clear hysteresis. (F) Temperature dependence of the spontaneous anomalous Hall conductivity ($\sigma_{xy}^A$), normalized by $\sigma_{xy}^A(150$ K), indicating its clear onset at $T_c$ for all cleaved crystals. (G) Thickness-dependent phase diagram of Fe$_4$GeTe$_2$ crystal with $T_c$ and $T_{\text{SR}}$ estimated from resistivity, AHE, MCD, and magneto-optical Kerr effect (MOKE) measurements. Significant enhancement of $T_{\text{SR}}$ with lowering thickness contrasts to the nearly constant $T_c \sim 270$ K and is consistent with a strong enhancement of perpendicular magnetic anisotropy.
M 27% in the relative increases of with Fe₃GeTe₂. The similar increase in (fig. S2). This corroborates that the dominant mechanism determining bonds (the inset of Fig. 5B) despite the different electronic structures m magnets. Calculated magnetization for Fe₄GeTe₂ to show their relative changes. (The temperature and the magnetization per Fe atom are normalized by those of T sat (Fig. 5B) and, thus, is a candidate, satisfying the most of requirements, except the PMA condition. The weak PMA property and a small magnetic remanence of bulk Fe₄GeTe₂ can be further tailored by reducing its thickness down to a few layers, leading to strong increase in both PMA and Tₜₜ, together with a hard magnet–type hysteresis. These results clearly demonstrate the synergetic combination of material design and thickness control on vdW magnets, which improves the magnetic properties more suitable for realistic spintronic applications. Furthermore, the not-yet-synthesized stoichiometric compound Fe₅GeTe₂ (26, 27, 33) or Fe₅GeTe₂ nanoflakes with proper surface modification using, e.g., electrolyte gating (21), are expected to exhibit better ferromagnetic properties with even higher T c or stronger magnetic remanence. We therefore envision that the heterostructures of Fe₅GeTe₂ and other vdW materials with surpassing spin-related properties at room temperatures, including graphene as an effective spin channel, TMDCs as optical or electrical control of spin dynamics, or bismuth chalcogenide–based topological insulators for spin-orbit torque operation, will open a new avenue for realizing all-vdW-material-based spintronic devices at room temperature.

Fig. 5. Magnetic properties of Fe₄GeTe₂ in comparison with other vdW ferromagnets. (A) Calculated magnetization for Fe₄GeTe₂ as a function of temperature. The temperature and the magnetization per Fe atom are normalized by those of Fe₅GeTe₂ to show their relative changes. (B) Ferromagnetic transition temperature T c and saturation magnetization M sat for various vdW-type ferromagnets, including Cr-based insulating vdW ferromagnets (open symbols) (17, 20, 32), Fe-based metallic vdW ferromagnets (solid symbols) (23, 25–27, 40–42), and the ferromagnetic TMDC compounds (crosses) with intercalation of magnetic transition metal atoms (M = Fe, Cr, and Mn) (43–46). Among them, Fe₄GeTe₂ compounds exhibit high T c and high M sat. The inset shows that calculated (open) and measured (cross) T c’s of Fe₄GeTe₂, normalized by that of Fe₅GeTe₂, increase almost linearly with the number of the nearest Fe neighbors (NN) per Fe atom. The results are in good agreement with experiments for Fe₅GeTe₂, showing the relative increases of ~27% in T c and ~29% in M sat, compared with Fe₅GeTe₂. The similar increase in T c with increasing n is also predicted for hypothetical Fe₅GeTe₂ (n = 5), as shown in Fig. 5A. In the recently discovered Fe₅₋ₓGe₄-xTe₂, T c for bulk samples is enhanced up to ~310 K (26, 27), which is less than our prediction, presumably due to Fe deficiency, but consistently follows the expected trend. This systematic increase in T c with n is consistent with the enhancement of FM spin-pair interaction, which is usually proportional to the number of the nearest neighbor (NN) Fe–Fe bonds. We found that T c of Fe₅GeTe₂ depends almost linearly on the number of NN Fe atoms (the inset of Fig. 5B) despite the different electronic structures (fig. S2). This corroborates that the dominant mechanism determining T c is the FM spin-pair interaction in the network of Fe atoms within the relatively thick layers.

Our findings highlight that Fe-rich vdW ferromagnets are promising spin-source materials. To work well as a spin source, a candidate material should satisfy several conditions, including high T c for room temperature operation, high M sat for high spin polarization, metallic conductivity for relatively easy spin injection, and PMA for high density integration. In comparison with other vdW ferromagnets or intercalated vdW ferromagnets reported so far, Fe₅GeTe₂ shows high T c and high M sat (Fig. 5B) and, thus, is a candidate, satisfying the most of requirements, except the PMA condition. The weak PMA property and a small magnetic remanence of bulk Fe₄GeTe₂ can be improved by reducing its thickness down to a few layers, leading to strong increase in both PMA and Tₜₜ, together with a hard magnet–type hysteresis. These results clearly demonstrate the synergetic combination of material design and thickness control on vdW ferromagnets, which improves the magnetic properties more suitable for realistic spintronic applications. Furthermore, the not-yet-synthesized stoichiometric compound Fe₅GeTe₂ (26, 27, 33) or Fe₅GeTe₂ nanoflakes with proper surface modification using, e.g., electrolyte gating (21), are expected to exhibit better ferromagnetic properties with even higher T c or stronger magnetic remanence. We therefore envision that the heterostructures of Fe₅GeTe₂ and other vdW materials with surpassing spin-related properties at room temperatures, including graphene as an effective spin channel, TMDCs as optical or electrical control of spin dynamics, or bismuth chalcogenide–based topological insulators for spin-orbit torque operation, will open a new avenue for realizing all-vdW-material-based spintronic devices at room temperature.

MATERIALS AND METHODS

First principles calculations

To explore computationally the energy landscape of Fe₅GeTe₂ compounds, we performed crystal structure searching using AIRSS strategy (AIRSS, version 0.91) (31), combined with a plane wave–based DFT software. A plane wave basis set cutoff energy of 300 eV and k-points sampling of 0.06 Å⁻¹ were used. AIRSS generated ~11,000 trial structures to find the ground states of various stoichiometric compounds. Phonon dispersions were calculated using density functional perturbation theory (34), implemented in the VASP software and phonopy software (35). Electronic structure calculations within the DFT were performed by using the full-potential linearized augmented plane wave code WIEN2k (36). In the DFT + DMFT code, the DFT part was done by the WIEN2K software with Perdew-Burke-Ernzerhof exchange correlation potential (37). The DMFT part dealt with the correlation of d orbitals in Fe atoms. DFT + DMFT loops were operated in a charge self-consistent manner (38). For the impurity solver, a continuous time quantum Monte Carlo method was used with interaction parameters of Hubbard U = 5.0 eV and Hund J₁ = 1.2 eV (39). In these calculations, we used experimental lattice constants for Fe₅GeTe₂ and Fe₅GeTe₂, whereas we used for the hypothetical vdW structure (space group P3m1) from the AIRSS results for Fe₅GeTe₂.

Scanning transmission electron microscopy

Three kinds of samples having [120], [001], and [110] projections were prepared using dual-beam focused ion beam systems (Helios and Helios G3, FEI) to determine the 3D crystal structure. Because Fe₅GeTe₂ single crystal was formed in the shape of a thin hexagonal flake, the crystallographic directions can be easily determined. We used a Ga ion beam at 30 kV to make a thin specimen and then used different acceleration voltages from 5 to 1 kV for the sample cleaning process to reduce the Ga damage. The selected area diffraction pattern analysis and atomic structure observation were performed using a STEM (JEM-ARM200F, JEOL, Japan) at 200 kV equipped with an fifth-order probe corrector (ASCOR, CES GmbH, Germany). The optimum size of the electron probe for STEM observation was ~78 pm. The collection semiangles of the HAADF detector were adjusted from 68 to 280 mrad to collect scattered electrons in a large angle for clear Z-sensitive images. The annular bright field images
were obtained using a 6-mm aperture and a collection angle from 10 to 20 mrad. The obtained raw images were processed using a bandpass Wiener filter with a local window to reduce background noise (Filters Pro, HREM Research Inc., Japan). TEM diffraction pattern simulation was performed using SingleCrystal (CrystalMaker Software Ltd., UK). STEM image simulation was performed by using the multislice method implemented in the QSTEM software (shareware, http://qstem.org).

**Single crystal growth and bulk properties**

For single crystal growth, we used a presynthesized polycrystalline sample of Fe₄GeTe₂. A mixture of Fe (99.998%), Ge (99.999%), and Te (99.999%) in the molar ratio of x:1.2 (1.5 ≤ x ≤ 7) was placed in an evacuated quartz tube that was heated at 725°C for 10 days. The stoichiometry ratio of Fe:Ge:Te = 5:1:2 in the starting mixture was found to be optimal to produce single-phase polycrystalline Fe₄GeTe₂ samples (fig. S3A), which were then used for single crystal growth by a chemical vapor transport method using iodine as a transport agent. Polycrystalline Fe₄GeTe₂ was placed in an evacuated quartz tube together with iodine of 1.8 mg/cm³, which was heated at 800°C/750°C with a temperature gradient of 5°C/cm for 7 days. The obtained single crystals were in a plate shape with a typical size of ~1 × 1 × 0.04 mm³ as shown in the inset of fig. S3B. The x-ray diffraction confirms high crystallinity (fig. S3B), in good agreement with STEM experiments (fig. 2). The energy dispersive spectroscopy revealed that the stoichiometry of the single crystal was Fe:Ge:Te = 4.11:1.0:1.85, i.e., a slight Te deficiency of ~15%. The presence of Te deficiency was also confirmed by STM on the cleaved and mostly Te-terminated surface (fig. S5A). Magnetization was measured under a magnetic field along the c axis or ab-plane using a superconducting quantum interference device magnetometer (Magnetic Properties Measurement System, Quantum Design). The in-plane resistivity and Hall coefficient were measured in the standard six-probe configuration using a Physical Property Measurement System (PPMS-14T, Quantum Design).

**Mechanical exfoliation and device fabrication**

Because of weak vdW coupling between the layers in Fe₄GeTe₂, we were able to obtain the thin flakes of Fe₄GeTe₂ using mechanical exfoliation. We used Si substrates terminated by a 270-nm-thick SiO₂ layer, which was cleaned in acetone, 2-propanol, and deionized water and then treated by oxygen plasma (O₂ = 10 sccm, P = 100 mtorr) for 5 min to remove adsorbates from the surface. Fe₄GeTe₂ single crystal was cleaved on the tape to make several flakes, which were brought into contact to the Si/SiO₂ substrate. All the cleaving and handling were done in the inert atmosphere with pure Ar [H₂O < 0.1 parts per million (ppm), O₂ < 0.1 ppm] gas, except the atomic force microscopy measurements. The obtained flakes were typically several micrometers squared in area and ~10 nm in thickness (~10 layers). Rarely, we found even a thinner flake with a thickness of ~7 nm (7 layers) but smaller in size. For device fabrication, thin exfoliated crystals of h-BN were subsequently transferred onto the ultrathin Fe₄GeTe₂ crystal in argon atmosphere. Electrodes for the transport measurements were fabricated by the electron beam lithography technique using poly(methyl methacrylate)-positive resist layer, which was spin coated and dried in vacuum. The patterned area on the ultrathin crystal was etched by ion milling, followed by deposition of Cr(10 nm)/Au(50 nm). We note that during device fabrication, ultrathin crystals were always in room temperature without postheating and not exposed to air, which was found to be critical to minimize the chemical degradation of the surface.

**Magneto-optical and magnetotransport property measurements for nanoflake devices**

For MCD measurements, a continuous-wave laser with wavelength at 664 nm (P = 60 μW) was focused onto the thin flakes of Fe₄GeTe₂. The polarization of the incident laser was altered between the right and left circular polarization at the frequency of 50 kHz using a photoelastic modulator, and lock-in detection was used to measure the absorption difference between two helicities of light. To obtain the 2D mapping of the MCD signal, we scanned the sample position using an xy piezo stage with the beam spot size of ~0.7 μm. For all measurements, we mounted samples in an optical cryostat with or without a magnet in Faraday geometry. For magneto-optical Kerr effect measurements, a continuous-wave laser with 532 nm (P = 100 μW) was linearly polarized at 45° to the photoelastic modulator fast axis. The linearly polarized light transmitted through the photoelastic modulator with phase modulation frequency of 50 kHz and phase retardation of π/2, and it was focused onto the sample at normal incidence. The reflected light from the sample was analyzed using Wollaston prism for splitting the orthogonal components of light, and the power difference was detected using balanced photodiode and lock-in amplifier. Permanent magnet in Faraday geometry with 0.1 T was adjusted, and the temperature of the sample was controlled in the optical cryostat. The in-plane resistivity and Hall resistivity of the Fe₄GeTe₂ nanoflakes were measured in standard six-probe configuration using a PPMS (PPMS-14T, Quantum Design). The alternating current with amplitude of a few microamperes and the frequency of ~13 Hz was used for lock-in measurements of longitudinal and Hall resistance. For the AHE measurements at various field orientations, a one-axis rotator was used in PPMS-14T with a typical angle resolution of ~1°.

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**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/6/5/eaay912/DC1

**Note S1. Material design for Fe₄GeTe₂.**

**Note S2. Material synthesis.**

**Note S3. TEM on Fe₄GeTe₂.**

**Note S4. Surface characterization on Fe₄GeTe₂ single crystal.**

**Note S5. Ultrathin Fe₄GeTe₂ nanoflakes and their magnetic properties.**

**Fig. S1. Material design for Fe₄GeTe₂.**

**Fig. S2. Electronic structures of Fe₄GeTe₂.**

**Fig. S3. Material synthesis of designed Fe₄GeTe₂.**

**Fig. S4. TEM on Fe₄GeTe₂.**

**Fig. S5. Surface characterization on Fe₄GeTe₂ single crystal.**

**Fig. S6. Ultrathin Fe₄GeTe₂ nanoflakes and their magneto-optical properties.**

**Fig. S7. Thickness dependence of resistivity for Fe₄GeTe₂ nanoflakes.**

**Fig. S8. Thickness-dependent AHE of Fe₄GeTe₂ nanoflakes.**

**Fig. S9. Thickness-dependent magnetic hysteresis behaviors of Fe₄GeTe₂ nanoflakes.**

**Fig. S10. Enhanced PMA of Fe₄GeTe₂ nanoflakes.**

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