Gate-Controlled Magnetic Phase Transition in a van der Waals Magnet Fe$_5$GeTe$_2$

Cheng Tan, Wen-Qiang Xie, Guolin Zheng, Nuriyah Aloufi, Sultan Albarakati, Meri Algarni, Junbo Li, James Partridge, Dimitrie Culcer, Xiaolin Wang, Jia Bao Yi, Mingliang Tian, Yimin Xiong, Yu-Jun Zhao, and Lan Wang

**Cite This:** Nano Lett. 2021, 21, 5599–5605

**ABSTRACT:** Magnetic van der Waals (vdW) materials are poised to enable all-electrical control of magnetism in the two-dimensional limit. However, tuning the magnetic ground state in vdW itinerant ferromagnets by voltage-induced charge doping remains a significant challenge, due to the extremely large carrier densities in these materials. Here, by cleaving the vdW itinerant ferromagnet Fe$_5$GeTe$_2$ (FSGT) into 5.4 nm (around two unit cells), we find that the ferromagnetism (FM) in FSGT can be substantially tuned by the thickness. Moreover, by utilizing a solid protonic gate, an electron doping concentration of above 10$^{21}$ cm$^{-3}$ has been exhibited in FSGT nanosheets. Such a high carrier accumulation exceeds that possible in widely used electric double-layer transistors (EDLTs) and surpasses the intrinsic carrier density of FSGT. Importantly, it is accompanied by a magnetic phase transition from FM to antiferromagnetism (AFM). The realization of an antiferromagnetic phase in nanosheet FSGT suggests the promise of applications in high-temperature antiferromagnetic vdW devices and heterostructures.

**KEYWORDS:** Fe$_5$GeTe$_2$, van der Waals ferromagnetism, magnetic phase transition, solid protonic gating

Control of magnetism and magnetic properties by voltage is vital to modern low-energy nanoelectronic devices.\textsuperscript{2–3} In traditional FM metals, tuning of magnetism by voltage-induced charge doping is limited to the surface,\textsuperscript{4} due to the strong electric-field screening effect in FM metals. The emergence of vdW magnetic materials\textsuperscript{5–7} has greatly expedited the development of vdW spintronic devices\textsuperscript{8–14} and, thanks to the extreme large surface-to-bulk ratio in atomically thin layers, provided an unrivalled opportunity to manipulate magnetism in the two-dimensional (2D) limit by all-electrical means.\textsuperscript{7,15–18} However, voltage-control of the magnetic ground state in vdW itinerant FM$^*$ has remained elusive. This is because the high carrier concentrations in vdW itinerant FM$^*$ exceed those in any traditional field-effect transistors or widely used electric double-layer transistors (EDLTs).\textsuperscript{19}

Here, we report a systematic investigation of the anomalous Hall effect in vdW itinerant FM Fe$_5$GeTe$_2$ (FSGT). Both the coercivity and the critical temperature of the ferrimagnetic transition of Fe$^*$ sites depend strongly on the thickness of the FSGT. Furthermore, we fabricate a solid proton field-effect transistor (SP-FET) and demonstrate that an electron doping concentration of above 10$^{21}$ cm$^{-3}$ (or 10$^{16}$ cm$^{-2}$ in 2D) can be achieved with just a few volts applied to the gate. This is an order of magnitude increase over doping concentrations achievable in EDLTs.\textsuperscript{19} In the FSGT nanosheets, the high gate voltage-induced doping suppresses the hysteresis of the FM state, leading to a magnetic phase transition from FM to AFM. This ability to control the magnetic phase in FSGT via gate voltages suggests the possibility of antiferromagnetic spintronic devices that operate at high temperatures and a new pathway in the search for vdW itinerant AFMs.

FSGT is a newly synthesized vdW ferromagnet\textsuperscript{20–24} which is noteworthy due to its high Curie temperature ($T_c$). This $T_c$ approaches room temperature and exceeds the Curie temperature of up to 230 K exhibited by the widely investigated itinerant vdW FM Fe$_3$GeTe$_2$ (FGT).\textsuperscript{7,25–26} Figure 1a illustrates a schematic diagram of the Fe$_5$GeTe$_2$ crystal structure projected along the [100] direction. Like FGT, the FSGT crystal is formed from thicker Fe–Ge slabs sandwiched by Te layers. The crystal structure of FSGT has a space group R$\bar{3}$m with lattice parameters $a = 4.04$ Å and $c = 29.19$ Å.\textsuperscript{20} In each unit cell, there are 3 Fe sites, and the Fe$^*$ site is regarded as a split site located either above or below the Ge site, leading to the complex crystal structure. Figure 1b shows optical and atomic force microscope images of an ultrathin FSGT...
nanosheet supported on a SiO2 substrate. Figure 1c illustrates the lateral distance-dependent height (corresponding to the dashed blue line in Figure 1b) of a thin F5GT nanosheet, indicating a thickness of 6.8 nm. The normalized resistance vs temperature (RT) curves of F5GT devices with various thicknesses are shown in Figure 1d. In samples with thicknesses exceeding 6.8 nm, the RT curves exhibit a kink around \( T \approx 145 \) K. This resistance anomaly is attributed to the gradual magnetic transition of the Fe1 site with decreasing temperature,\(^{20}\) as discussed later. A small response near 115 K is observed in the magnetization data collected from the bulk crystal at 1 T (Figure S1a), which is also indicative of a first-order transition of the magneto-structure.\(^{20,21}\)

Figure 2a illustrates the magnetic field-dependent anomalous Hall resistivity (\( \rho_{xy} \)) of F5GT nanosheets with different thicknesses. All measurements were performed with the magnetic field oriented perpendicular to the planes of the nanosheets. The 113 nm nanosheet exhibits a hard magnetic property with two magnetic phases and a small coercive field (\( H_c \)) of 65.5 mT. These attributes agree well with the magnetic measurements taken from the single crystal (Figure S1). Reducing the thickness from 113 to 40 nm, \( \rho_{xy}(0 \text{ T})/\rho_{xy}^{\text{SAT}} \) (with \( \rho_{xy}^{\text{SAT}} \) being the saturated anomalous Hall resistivity) increases from 0.24 to 0.73, and the coercive field correspondingly increases to 93.8 mT in the 40 nm thick nanosheet. Furthermore, the magnetic loops from the samples of thickness 17 and 12 nm exhibit larger \( H_c \) and are nearly square-shaped with \( \rho_{xy}(0 \text{ T})/\rho_{xy}^{\text{SAT}} \) values approaching unity. Further lowering the thickness to 5.4 nm results in a single, hard magnetic phase with a large \( H_c \) of 1.7 T and a \( \rho_{xy}(0 \text{ T})/\rho_{xy}^{\text{SAT}} \) ratio of 1. The larger \( \rho_{xy}(0 \text{ T})/\rho_{xy}^{\text{SAT}} \) ratios indicate the magnetic moments align perpendicular to the plane of the nanosheet at the remanence point in thinner F5GT nanosheets, implying a strong magnetic perpendicular anisotropy. Interestingly, few-layer F5GT nanoflakes exhibit a much larger (around 4 times) coercivity than FGT nanoflakes of similar thicknesses. In the absence of defects, the coercivity is mainly determined by the magnetic anisotropic energy (MAE).

However, the MAE of F5GT is much smaller than that of FGT nanoflakes (see Table S3), revealing that the pinning effect induced by defects might play a pivotal role in the coercivity mechanism, given that FGT usually has much more Fe-deficiency-induced defects in a comparison with FGT. While the theoretically calculated interlayer depinning field is only \( \sim 3.7 \) kOe (see Supporting Information), this is still considerably smaller than the measured coercivity (\( \sim 20 \) kOe) in few-layer FSGT. Therefore, the defect-induced intralayer pinning effect possibly contributes to the large coercivity in
few-layer F5GT. In thicker F5GT nanoflakes, the chance of domain expansion along the interlayer direction can be largely enhanced. Accordingly, the interlayer depinning field and the MAE will gradually dominate the mechanism of coercivity and result in much smaller coercivity in thicker F5GT.

Figure 2b shows the temperature-dependent remanence of F5GT nanosheets with different thicknesses. In the nanosheets with a thickness above 5.4 nm, the remanence first increases with decreasing temperature and reaches a maximum at around 120−150 K, before declining sharply. This behavior indicates that the phase in thicker F5GT nanosheets is ferrimagnetic rather than ferromagnetic. However, for the 5.4 nm F5GT device, the lack of the “peak” in the temperature-dependent remanence curve indicates that the first-order magnetic transition of the Fe1 sites disappears, and the curve shows a typical ferromagnetic behavior. Note that the remanence of the 5.4 nm thick F5GT nanosheet decreases to zero at around 220 K, revealing a lower \( T_c \). This lower \( T_c \) may result from weaker interlayer magnetic coupling due to the reduced number of layers, as reported to be the case in other vdW magnets.

As discussed above (Figure S1a), the magnetic transition on the Fe1 site results in a first-order transition on the temperature-dependent magnetization curve of the bulk crystal. In F5GT nanosheets, the temperature-dependent magnetization curves correspond to the temperature-dependent remanence curves, and we define the temperature at which the remanence is at a maximum as the critical temperature \( (T_c) \) of the ferrimagnetic transition on the Fe1 sites. Figure 2c shows the thickness-dependent \( \rho_{xy}^{\rm{AFM}}/\rho_{xy}^{\rm{FM}} \) and \( T_c \). \( T_c \) gradually increases with decreasing thickness and eventually disappears in the 5.4 nm thick nanosheet. The abrupt disappearance of a ferrimagnetic transition of Fe1 sites in the 5.4 nm thick F5GT reveals a magnetic phase transition between the thicknesses of 12 and 5.4 nm, again possibly due to the increased intralayer pinning effect discussed above.

In vdW materials, controlling the magnetism by the application of voltage would enable a greater number of applications in spintronics and memory devices. For vdW itinerant magnets, however, conventional field-effect transistors or EDLTs are insufficient for electrical control of the magnetic order, due to their limited capacities. To date, protonic intercalation induced by a protonic gate has proved effective in tuning the magnetism and interlayer coupling in vdW itinerant FM FGT. Using the same protonic gate technique, as illustrated in Figure 3a, we fabricate a SP-FET and find that the FM in F5GT nanosheets can be significantly modulated. Figure 3b shows the magnetic field-dependent anomalous Hall resistivity \( \rho_{yx} \) at various gate voltages in the 40 nm thick F5GT at 2 K. In the pristine nanosheet, the hysteresis loop shows a large AHE value, with \( \rho_{xy} \) defined by \( \rho_{xy} = |\rho_{xy}| (1 T) = \rho_{yx} (-1 T) \). Sweeping the voltage from 0 V to \( V_g = -3.1 \) V and \( -3.6 \) V, we find the \( \rho_{xy} \) decreases accordingly. The anomalous Hall resistivity can usually be written as \( \rho_{xy} = R_{xy} H + \rho_{xy}^{\rm{fM}} = R_{xy} + R_{xy} M_E \), where \( M_E \) represents the magnetization. As the normal Hall section \( R_{xy} \) is small compared with the whole anomalous Hall resistance, the hysteresis loop here is proportional to the magnetization loop, so the decrease of \( \rho_{xy} \) indicates a decrease in the magnetization. If the magnitude of the gate voltage is increased, the anomalous Hall resistivities are further suppressed and exhibit a sign reversal at \( -4.2 \) and \( -4.5 \) V, as discussed later. At \( V_g = -5 \) V, the anomalous Hall loop eventually disappears, implying the possibility of a magnetic phase transition. Note that the transport properties of F5GT nanoflakes are almost unchanged under the positive voltages and the gate-induced proton intercalation/deintercalation process mainly occurs in the negative voltage range.

Note that the anomalous Hall resistivities exhibited by nanosheets thinner than 40 nm are nearly “flat” at high magnetic fields. In order to qualitatively determine the doping concentrations during the gating process, we tested more samples with different thicknesses (Figure S3). In a 78 nm thick nanosheet, we found that negative gate voltages led to electron-type doping (Figure S3a) which suppressed the anomalous Hall resistivity. A similar suppression of anomalous Hall resistivity has also been identified in other samples at negative gate voltages, indicating the same n-type doping at negative gate voltages. We can rule out the possibility of the magnetic anisotropy changing from out-of-plane to in-plane, because there is no magnetic hysteresis loop at \( V_g = -5 \) V. An in-plane magnetization should be rotated to the perpendicular direction gradually under an increasing perpendicular magnetic field, and this is not shown in our results. Therefore, the absence of a hysteresis loop at \( V_g = -5 \) V is attributed to the formation of an AFM state. Figure 3c shows the \( V_g \)-dependent carrier density of a 78 nm thick nanosheet as well as the \( \rho_{xy} \) of 40 and 78 nm thick nanosheets, respectively. Sweeping the voltage \( V_g \) from 0 to \(-5 \) V, \( \rho_{xy} \) values in both the 40 and 78 nm thick nanosheets decrease while the electron density in the 78 nm thick nanosheet increases by \( 0.8 \times 10^{22} \) cm\(^{-3}\). As discussed above, since \( \rho_{xy} \) (\( V_g \)) values of the 40 nm thick nanosheet exhibits a similar tendency under negative gate voltages, we speculate that an electron doping concentration of above \( 10^{21} \) cm\(^{-3}\) could totally suppress ferromagnetism and give rise to a magnetic phase transition from FM to AFM in F5GT nanosheets. Generally, the maximal carrier accumulation in widely used EDLTs is less than \( 10^{15} \) cm\(^{-2}\), which is at least one order smaller than present solid protonic gates (above \( 10^{16} \))
The ochre region indicates AFM coupling, while the blue region indicates FM coupling.

As mentioned above, the anomalous Hall loops exhibit sign reversal during the gate process (at $V_g = -4.2$ V and $-4.5$ V); this reversal in the hysteresis loops indicates the reversal of $\rho_{xy}^\sigma$ (see Figure S2), indicating a large energy gap (>20 meV) between the FM state and the paramagnetic state at 2 K, which is much larger than $\Delta E$ calculated from both LDA+U and PBE methods. In pristine F5GT, $\Delta E$ should be negative due to its FM ground state. As shown in Figure 4c, electron doping applied in both PBE and LDA+U functionals can narrow the energy discrepancy between FM and AFM and eventually lead to a positive $\Delta E$ or an AFM ground state. This tunable magnetism for F5GT is mainly due to the evolution of interlayer coupling under various charge dopings (Figure S6a).

To further assess the experimental results above, additional DFT calculations with PBE and LDA+U functionals were carried out. Figure 4c shows the doping-dependent energy difference between FM and AFM. Here, $\Delta E = E_{\text{FM}} - E_{\text{AFM}}$, where $E_{\text{FM}}$ and $E_{\text{AFM}}$ represent the energy of antiferromagnetic and ferromagnetic F5GT, respectively. Both PBE and LDA+U functionals exhibit a doping-dependent $\Delta E$. Moreover, $\Delta E$ values of LDA+U and PBE are only $-1.42$ and $1.45$ meV, respectively. This may explain the highly tunable hysteresis loop as well as the magnetic order in F5GT under various gate voltages. We first rule out the possibility of a paramagnetic phase in electron-doped F5GT. This is because the pristine F5GT nanosheets have a high Curie temperature ($T_C \geq 250$ K, Figure S2), indicating a large energy gap (>20 meV) between the FM state and the paramagnetic state at 2 K, which is much larger than $\Delta E$ calculated from both LDA+U and PBE methods. In pristine F5GT, $\Delta E$ should be negative due to its FM ground state. As shown in Figure 4c, electron doping applied in both PBE and LDA+U functionals can narrow the energy discrepancy between FM and AFM and eventually lead to a positive $\Delta E$ or an AFM ground state. This tunable magnetism for F5GT is mainly due to the evolution of interlayer coupling under various charge dopings (Figure S6a).

On the other hand, the intralayer magnetism almost stays unchanged with the doping (Figure S6b). The doping amount (at $V_g = -4.5$ V) is close to the saturation of electron doping (Figure S6c). Moreover, the intralayer coupling energy (see Figures S6 and S7) and results in a possible in situ magnetic phase transition in nanodevices, potentially enabling greater applications in vdW spintronics.

As mentioned above, the anomalous Hall loops exhibit sign reversal during the gate process (at $V_g = -4.2$ V and $-4.5$ V); this reversal in the hysteresis loops indicates the reversal of $\rho_{xy}^\sigma$ (see Figures S6 and S7) and results in a possible in situ magnetic phase transition in nanodevices, potentially enabling greater applications in vdW spintronics. The charge density differences observed in F5GT can be ascribed to the high mobility of protons which are easily intercalated into vdW materials under modest gate voltages. This leads to a dramatic change of carrier density within the F5GT. Recent experiments have revealed that the cobalt substitution can change the intralayer local configuration and interlayer stacking configuration of F5GT (or Fe$_x$GeTe$_2$) and result in AFM states. In addition, the gate-controlled charge doping here mainly changes the magnetic interaction in F5GT by affecting the interlayer coupling energy (see Figures S6 and S7) and results in a possible in situ magnetic phase transition in nanodevices, potentially enabling greater applications in vdW spintronics.
voltage. An electron doping concentration of above $10^{21}$ cm$^{-3}$ induced in FSGT by a protonic gate can trigger a magnetic phase transition from FM to AFM. Theoretical calculations based on DFT support the experimental observations and demonstrate that the FSGT can be modulated from an FM state to an AFM ground state by electron doping. Realizing an AFM phase in vdW FM FSGT nanosheets by protonic gating may constitute an important step toward vdW antiferromagnetic devices and heterostructures that operate at high temperatures.

### ASSOCIATED CONTENT

- **Supporting Information**
  The Supporting Information is available free of charge at [https://pubs.acs.org/doi/10.1021/acs.nanolett.1c01108](https://pubs.acs.org/doi/10.1021/acs.nanolett.1c01108).

Methods, magnetic measurements, detailed hysteresis behaviors of 113 and 6.8 nm FSGT devices, protonic gating modulation of other 3 devices at 2 K, angle-dependent anomalous Hall measurement of 6.8 and 17 nm devices, basic properties of FSGT calculated by density functional theory with various functionals, density functional theory calculations of $\Delta E$ based on thickness of FSGT, Hartree–Fock band structures without SOC and corresponding Hall conductivity, calculated interlayer and intralayer magnetic couplings of FSGT, charge density difference of electron doping FSGT, coercivity in few-layer FSGT and FGT, and decrease of coercivity with the increase of thickness in FGT and FSGT nanoflakes (PDF)

### AUTHOR INFORMATION

- **Corresponding Authors**
  Guolin Zheng — School of Science, RMIT University, Melbourne, Victoria 3001, Australia; Email: guolin.zheng@rmit.edu.au
  Yu-Jun Zhao — Department of Physics, South China University of Technology, Guangzhou 510640, China; orcid.org/0000-0002-6923-1099; Email: zhaoyj@scut.edu.cn
  Lan Wang — School of Science, RMIT University, Melbourne, Victoria 3001, Australia; orcid.org/0000-0001-7124-2718; Email: lan.wang@rmit.edu.au

### Authors
  - Cheng Tan — School of Science, RMIT University, Melbourne, Victoria 3001, Australia
  - Wen-Qiang Xie — Department of Physics, South China University of Technology, Guangzhou 510640, China
  - Nuriyah Aloufi — School of Science, RMIT University, Melbourne, Victoria 3001, Australia
  - Sultan Albarakati — School of Science, RMIT University, Melbourne, Victoria 3001, Australia
  - Meri Algarni — School of Science, RMIT University, Melbourne, Victoria 3001, Australia
  - Junbo Li — Anhui Province Key Laboratory of Condensed Matter Physics at Extreme Conditions, High Magnetic Field Laboratory, Chinese Academy of Sciences (CAS), Hefei 230031, Anhui, China
  - James Partridge — School of Science, RMIT University, Melbourne, Victoria 3001, Australia
  - Dimitri Culcer — School of Physics and ARC Centre of Excellence in Future Low-Energy Electronics Technologies, UNSW Node, University of New South Wales, Sydney, New South Wales 2052, Australia
  - Xiaolin Wang — Institute for Superconducting & Electronic Materials, Australian Institute of Innovative Materials and ARC Centre for Future Low-Energy Electronics Technologies (FLEET), University of Wollongong, Wollongong, New South Wales 2500, Australia; orcid.org/0000-0003-4150-0848
  - Jia Liao Yi — Global Innovative Center for Advanced Nanomaterials, School of Engineering, University of Newcastle, Callaghan, New South Wales 2308, Australia; orcid.org/0000-0001-5299-9897
  - Mingliang Tian — Anhui Province Key Laboratory of Condensed Matter Physics at Extreme Conditions, High Magnetic Field Laboratory, Chinese Academy of Sciences (CAS), Hefei 230031, Anhui, China; Department of Physics, School of Physics and Materials Science, Anhui University, Hefei 230601, Anhui, China; Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, China; orcid.org/0000-0002-0870-995X
  - Yimin Xiong — Anhui Province Key Laboratory of Condensed Matter Physics at Extreme Conditions, High Magnetic Field Laboratory, Chinese Academy of Sciences (CAS), Hefei 230031, Anhui, China

Complete contact information is available at: [https://pubs.acs.org/10.1021/acs.nanolett.1c01108](https://pubs.acs.org/10.1021/acs.nanolett.1c01108)

### Author Contributions
  †C.T. and W.-Q.X contributed equally. G.Z. and L.W. conceived and designed the research. C.T., S.A. and M.A. fabricated the solid proton gate. C.T., N.A. and G.Z. did the device fabrication. C.T. and G.Z. performed the electron transport measurements. W.-Q. X. and Y.-J. Z. did the theoretical calculation. J.L. and Y.X. synthesized the material. X.W., J.B.Y., M.T., Y.X., D.C., Y.-J. Z. and L.W. did the data analysis and modeling. C.T., W.-Q.X., G.Z., J.P., D.C., Y.-J. Z. and L.W. wrote the paper with the help from all of the other coauthors. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes
  The authors declare no competing financial interest. All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supporting Information. Additional data related to this paper may be requested from the authors.

### ACKNOWLEDGMENTS

This research was performed in part at the RMIT Micro Nano Research Facility (MNRF) in the Victorian Node of the Australian National Fabrication Facility (ANFF) and the RMIT Microscopy and Microanalysis Facility (RMMF). This research was supported by the Australian Research Council Centre of Excellence in Future Low-Energy Electronics Technologies (CE170100039), the Natural Science Foundation of China (12071426), the National Key Research and Development Program of China (2016YFA0300404), the Fundamental Research Funds for the Central Universities (2020ZYGXZ076), the Collaborative Innovation Program of Hefei Science Center, CAS (Grant 2019HSC-CIP007), and the High Magnetic Field Laboratory of Anhui Province.
**ABSTRACT**

vdW, van der Waals; FSGT, Fe₅GeTe₂; FM, ferromagnetism; AFM, antiferromagnetism; FGT, Fe₄GeTe₂; Tₚ, Curie temperature; EDLTs, electric double-layer transistors; SP-FET, solid proton field-effect transistor; MAE, magnetic anisotropic energy; DFT, density functional theory; PBE, Perdew–Burke–Ernzerhof; LDA+U, local density approximation plus Hubbard U; SOC, spin–orbit coupling

**REFERENCES**

(1) Ohno, H.; Chiba, A. D.; Matsukura, A. F.; Omiya, T.; Abe, E.; Dietl, T.; Ohno, Y.; Ohtani, K. Electric-field control of ferromagnetism. Nature 2000, 408, 944–946.

(2) Matsukura, F.; Tokura, Y.; Ohno, H. Control of magnetism by electric fields. Nat. Nanotechnol. 2015, 10, 209–220.

(3) Manipatruni, S.; Nikonov, D. E.; Young, I. A. Beyond CMOS computing with spin and polarization. Nat. Phys. 2018, 14, 338–343.

(4) Weisheit, M.; Flahé, S.; Marty, A.; Souche, Y.; Poinssignon, C.; Givord, D. Electric field-induced modification of magnetism in thin-film ferromagnets. Science 2007, 315, 349–351.

(5) Gong, C.; Li, L.; Li, Z.; Ji, H.; Stern, A.; Xie, Y.; Cao, T.; Bao, W.; Wang, C.; Wang, Y.; Qiu, Z.; Cao, R. J.; Louie, S. G.; Xia, J.; Zhang, X. Discovery of intrinsic ferromagnetism in two-dimensional van der Waals crystals. Nature 2017, 546, 265–269.

(6) Huang, B.; Clark, G.; Navarro-Moratalla, E.; Klein, D. R.; Cheng, R.; Seyler, K. L.; Zhong, D.; Schmidgall, E.; McGuire, M. A.; Cobden, D. H.; Yao, W.; Xiao, D.; Jarillo-Herrero, P.; Xu, X. Layer-dependent ferromagnetism in a van der Waals crystal down to the monolayer limit. Nature 2017, 547, 270–273.

(7) Deng, Y.; Yu, Y.; Song, Y.; Zhang, J.; Wang, N. Z.; Sun, Z.; Yi, Y.; Wu, Y.; Wu, S.; Zhu, J.; Wang, J.; Chen, X. H.; Zhang, Y. Gate-tunable room-temperature ferromagnetism in two-dimensional Fe₅GeTe₂. Nature 2018, 563, 94–99.

(8) Wang, Z.; Sapkota, D.; Taniguchi, T.; Watanabe, K.; Mandrus, D.; Morpurgo, A. F. Tunneling spin valves based on Fe₅GeTe₂/hBN/Fe₅GeTe₂ van der Waals heterostructures. Nano Lett. 2018, 18, 4303–4308.

(9) Wang, Z.; Gutiérrez-Lezama, I.; Ubrig, N.; Kroner, M.; Gibertini, M.; Taniguchi, T.; Watanabe, K.; Amoglu, A.; Giannini, E.; Morpurgo, A. F. Very large tunneling magnetoresistance in layered magnetic semiconductor CrI₃. Nat. Commun. 2018, 9, 1–8.

(10) Klein, D. R.; MacNeill, D.; Lado, J. L.; Soriano, D.; Navarro-Moratalla, E.; Taniguchi, T.; Manni, S.; Canfield, P. E.; Fernández-Rossier, J.; Jarillo-Herrero, P. Probing magnetism in 2D van der Waals crystalline insulators via electron tunneling. Science 2018, 360, 1218–1222.

(11) Song, T.; Cai, X.; Tu, M. W.-Y.; Zhang, X.; Huang, B.; Wilson, N. P.; Seyler, K. L.; Zhu, L.; Taniguchi, T.; Watanabe, K.; McGuire, M. A.; Cobden, D. H.; Xiao, D.; Yao, W.; Xu, X. Giant tunneling magnetoresistance in spin-filter van der Waals heterostructures. Science 2018, 360, 1214–1218.

(12) Albarakati, S.; Tan, C.; Chen, Z.-J.; Partridge, J. G.; Zheng, G.; Farrar, L.; Mayes, E. L.; Field, M. R.; Lee, C.; Wang, Y.; Xiong, Y.; Tian, M.; Xiang, F.; Hamilton, A. R.; Tretiakov, O. A.; Culcer, D.; Zhao, Y.-J.; Wang, L. Antisymmetric magnetoresistance in van der Waals Fe₅SeTe₅/graphite/Fe₅SeTe₅ triayer heterostructures. Sci. Adv. 2019, 5, No. eaaw0409.

(13) Wang, X.; Tang, J.; Xia, X.; He, C.; Zhang, J.; Liu, Y.; Yan, C.; Fang, C.; Guo, C.; Yang, W.; Zhang, X.; Xu, H.; Wei, J.; Liao, M.; Lu, X.; Feng, J.; Li, X.; Peng, Y.; Wei, H.; Yang, R.; Shi, D.; Zhang, X.; Han, Z.; Zhang, Z.; Gao, G.; Yu, G.; Han, X. Current-driven magnetization switching in a van der Waals ferromagnet Fe₅GeTe₂. Sci. Adv. 2019, 5, No. eaaw9904.

(14) Dolui, K.; Petrovich, M. D.; Zollner, K.; Plechac, P.; Fabian, J.; Nikolic, B. K. Proximity spin-orbit torque on a two-dimensional magnet within van der Waals heterostructure: current-driven antiferromagnet-to-ferromagnet reversible nonequilibrium phase transition in bilayer CrI₃, Nano Lett. 2020, 20, 2288–2295.
(32) May, A. F.; Du, M.-H.; Cooper, V. R.; McGuire, M. A. Tuning magnetic order in the van der Waals metal Fe₅GeTe₂ by cobalt substitution. Phys. Rev. Mater. 2020, 4, 074008.

(33) Seo, J.; An, E. S.; Park, T.; Hwang, S.-Y.; Kim, G.-Y.; Song, K.; Noh, W.-s.; Kim, J. Y.; Choi, G. S.; Choi, M.; Oh, E.; Watanabe, K.; Taniguchi, T.; Park, J.-H.; Jo, Y. J.; Yeom, H. W.; Choi, S.-Y.; Shim, J. H.; Kim, J. S. Tunable high-temperature itinerant antiferromagnetism in a van der Waals magnet. Nat. Commun. 2021, 12, 2811.

(34) Tian, C.; Pan, F.; Xu, S.; Ai, K.; Xia, T.; Cheng, P. Tunable magnetic properties in van der Waals crystals (Fe₁₋ₓCox)₅GeTe₂. Appl. Phys. Lett. 2020, 116, 202402.

(35) Nayak, A. K.; Fischer, J. E.; Sun, Y.; Yan, B.; Karel, J.; Komarek, A. C.; Shekhar, C.; Kumar, N.; Schnelle, W.; Kübler, J.; Felser, C.; Parkin, S. S. P. Large anomalous Hall effect driven by a nonvanishing Berry curvature in the noncolinear antiferromagnet Mn₃Ge. Sci. Adv. 2016, 2, No. e1501870.

(36) Blöchl, P. E. Projector augmented-wave method. Phys. Rev. B: Condens. Matter Mater. Phys. 1994, 50, 17953.

(37) Perdew, J. P.; Burke, K.; Emzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 1996, 77, 3865.

(38) Ferreira, L. G.; Marques, M.; Teles, L. K. Approximation to density functional theory for the calculation of band gaps of semiconductors. Phys. Rev. B: Condens. Matter Mater. Phys. 2008, 78, 125116.

(39) Tolba, S. A.; Gameel, K. M.; Ali, B. A.; Almossalami, H. A.; Alam, N. K. The DFT+U: Approaches, Accuracy, and Applications. In Density Functional Calculations; Yang, G., Ed.; IntechOpen: Rijeka, 2018, Chapter 1. DOI: 10.5772/intechopen.68548.

(40) Slater, J. C. Magnetic effects and the Hartree-Fock equation. Phys. Rev. 1951, 82, 538.