Interlayer engineering of Fe$_3$GeTe$_2$: From 3D superlattice to 2D monolayer

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The discoveries of ferromagnetism down to the atomically thin limit in van der Waals (vdW) crystals by mechanical exfoliation have enriched the family of magnetic thin films [C. Gong et al., Nature 546, 265–269 (2017) and B. Huang et al., Nature 546, 270–273 (2017)]. However, compared to the study of traditional magnetic thin films by physical deposition methods, the toolbox of the vdW crystals based on mechanical exfoliation and transfer suffers from low yield and ambient corrosion problem and now is facing new challenges to study magnetism. For example, the formation of magnetic superlattice is difficult in vdW crystals, which limits the study of the interlayer interaction in vdW crystals [M. Gibertini, M. Koperski, A. F. Morpurgo, K. S. Novoselov, Nat. Nanotechnol. 14, 408–419 (2019)]. Here, we report a strategy of interlayer engineering of the magnetic vdW crystal Fe$_3$GeTe$_2$ (FGT) by intercalating quaternary ammonium cations into the vdW spacing. Both three-dimensional (3D) vdW superlattice and two-dimensional (2D) vdW monolayer can be formed by using this method based on the amount of intercalant. On the one hand, the FGT superlattice shows a strong 3D critical behavior with a decreased coercivity and increased domain wall size, attributed to the co-engineering of the anisotropy, exchange interaction, and electron doping by intercalation. On the other hand, the 2D vdW few layers obtained by over-intercalation are capped with organic molecules from the bulk crystal, which not only enhances the ferromagnetic transition temperature ($T_\text{c}$), but also substantially protects the thin samples from degradation, thus allowing the preparation of large-scale FGT ink in ambient environment.

van der Waals magnet | intercalation | exfoliation

Thin film magnetism has been one of the most important topics over a century since the first study of magnetic thin films (1–4). The development of ultra-high vacuum deposition technologies allowed the synthesis of magnetic superlattice structures with periodic non-magnetic buffer layers in between the magnetic layers (Fig. 1A). This enabled study and manipulation of the interlayer exchange interaction, which led to remarkable discoveries and device applications such as the oscillations in exchange interaction (5) and giant magnetoresistance (6, 7). In parallel, the epitaxial growth of atomically thin monolayer sheet of magnetic atoms (e.g., Fe, Co, Ni, etc.) enabled the investigation of monolayer 2D magnetic behavior (Fig. 1B) (8, 9).

The recently discovered atomically thin vdW (van der Waals) magnetic materials have reinvigorated the field of 2D magnetism with an entirely new library of intrinsic 2D magnetic compounds by removing the neighboring layers through mechanical exfoliation (Fig. 1D) (10, 11). However, the vdW material’s version of magnetic/nonmagnetic superlattice, in analogy to the study of magnetic thin films, is still missing, leaving the intermediate anisotropy and exchange regime relatively unexplored.

Although in vdW materials, it is theoretically feasible to form quasi-superlattices by sandwiching non-magnetic 2D materials with magnetic 2D materials through the exfoliation and transfer method, there are still practical challenges due to the low yield of these transfer methods, particularly when constructing multi-period (>3) superlattice structures. Although recent developments in epitaxial growth have shown progress in synthesizing quasi-vdW superlattice structures (12, 13), the choice of species is highly limited, and the structures are not dynamically controllable and tunable. In parallel, the study of 2D superconductivity in vdW crystals has given hints for how to modulate the interlayer coupling through intercalation of large organic molecules (14–16). During the intercalation process, interlayer distances are expanded to accommodate large organic molecules between them (14).

Here, we electrochemically intercalate the organic quaternary ammonium cations in the vdW gaps of FGT (Fe$_3$GeTe$_2$). By controlling the intercalation time, voltage, or current, either a 3D superlattice (Fig. 1C) or 2D monolayer (Fig. 1D) magnet can be constructed. Here, the quaternary ammonium ions are hexadecyltrimethylammonium cation ($[(\text{CH}_3\text{CH}_2)_4\text{N}]^+$, 10, 11) and intercalated Fe$_3$GeTe$_2$ monolayer (Fig. 1D) magnet can be constructed. Here, the quaternary ammonium ions are hexadecyltrimethylammonium cation ($[(\text{CH}_3\text{CH}_2)_4\text{N}]^+$, 10, 11).

Significance

Magnetic van der Waals (vdW) crystals are highly anticipated as an analogy to deposited magnetic thin films. However, challenges remain in achieving ultrathin layers and forming superlattice structures. Here, three-dimensional superlattice and two-dimensional monolayer vdW magnets are achieved by intercalation-based interlayer engineering. Robust 3D critical behavior and enhanced ferromagnetic transition temperature are observed in three-dimensional superlattice and two-dimensional few layers, respectively. Our work provides a technique to fill the gap in the study of magnetic vdW crystal compared to the study of traditional magnetic thin film, offering new opportunities for magnetoelectronics.


The authors declare no competing interest.

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or CTA\(^+\)) and tetaoctylammonium cation (\([\text{[C}_{18}\text{H}_{37}]\text{N}]^+\), or TOA\(^+\)) from their bromide salts. CTA\(^+\) contains one long hydrophobic alkyl chain with 16 carbon atoms, with a maximum length of ~2 nm, while TOA\(^+\) is a bulkier molecule that contains four branches of long hydrophobic alkyl chain with eight carbon atoms, and has a maximum length for each branch of ~1 nm (17).

Results

To perform the electrochemical intercalation of quaternary ammonium cations into FGT, an on-chip design is used. Thick FGT flakes (±15 nm) are exfoliated and transferred onto SiO\(_2\)/Si substrate by polydimethylsiloxane (PDMS)-assisted exfoliation process (18). Standard electron beam lithography and metal evaporation are used to define and deposit 5/150 nm Cr/Au electrical contacts on FGT flakes. A 3/60 nm Ti/Pt electrode is pre-patterned on the other end of the chip as a counter electrode. To perform an in situ observation of the intercalation process, the FGT flakes, Cr/Au working electrodes, Pt counter electrode, and the liquid electrolyte (~5 mg/mL quaternary ammonium bromide salt in acetonitrile or n-methyl-2-pyrrolidone (NMP) are assembled in an argon-filled glovebox and sealed by a thermoplastic film and a transparent glass coverslip cover, as schematically and photographically shown in the *Inset* of Fig. 2 A. The intercalation reaction is conducted by applying a constant current through the negative working and positive counter electrodes. During the intercalation process, FGT contacted by the negative Cr/Au electrode is reduced and accompanied by intercalation of the quaternary ammonium cations into the FGT vdW spacing; the bromide anions are oxidized to bromine on the positive Pt electrodes, which is similar to the intercalation process in other transition metal dichalcogenides (19, 20).

Fig. 2A plots the voltage profile of an FGT flake intercalated with CTA\(^+\) in NMP solvent, and Fig. 2B shows the corresponding in situ optical microscopy images at different times. The in situ video of the intercalation process is shown in Movie S1. Before intercalation, the device exhibits an open circuit voltage (OCV) of ~200 mV, this OCV is related to the concentration of the electrolyte and is also affected by the area and relative position of gold and Pt electrodes, which varies from sample to sample. At intercalation time \(t = 10\) s, a constant current of ~150 nA is applied through the FGT to Pt. A sharp voltage drop to about ~3.2 V is observed immediately after the current is applied. The intercalation starts at \(t = 30\) s from the edge, as shown by the color change. The intercalation front moves from one side of the FGT to the other at this voltage plateau. Multiple stages are observed by the color change under optical microscopy, indicating a staging effect during the intercalation process (21). The color of the flake becomes darker during intercalation, and surface wrinkling is also observed, which is likely due to the spatially non-uniform intercalation. At \(t = 105\) s, when the ~150 nA current is stopped, the OCV shows a steep increase. Soon after that, the FGT sample gradually stabilizes: the color of the FGT flake progressively becomes lighter, and the surface wrinkling is steadily flattened. Two possible reasons can account for these phenomena after the voltage is off: 1) Some of the intercalated molecules diffuse out of the flake; 2) the orientation of the intercalated molecules changes. Sometimes intermediate voltage plateaus can be observed in the voltage profile when the voltage is released (e.g., \(t = 110\) s), which is related to the lag in the movement of the organic molecules that can be seen from the Movie S1. After sufficient time (~30 min, see SI Appendix, Fig. S1), the flake is stable. Our following measurements are performed on the final state (CTA\(^+\))\_FGT at the stable OCV. A more detailed study about the dynamics of the molecules in FGT is beyond the scope of this work. Another larger size cation TOA\(^+\) is also intercalated into FGT flakes. The intercalation process is similar to that for CTA\(^+\) intercalation but requires careful current control and strict sample storage conditions: while (CTA\(^+\))\_FGT is stable in the ambient environment, a thickness reduction of some of the (TOA\(^+\))\_FGT samples is observed when the sample is removed from the solvent. Directly drying the solvent in a vacuum or freezing the sample at cryogenic temperatures can preserve the TOA\(^+\) inside the FGT.

In situ liquid-phase atomic force microscopy (AFM) is used to characterize the thickness change due to intercalation. As shown in Fig. 2C, the thickness is expanded by ~2.09 times as a result of CTA\(^+\) intercalation. Ex situ AFM of six FGT flakes with different initial thickness is performed before and after intercalation.
(SI Appendix, Fig. S2D). The results of ex situ AFM are consistent with the in situ AFM, where the thickness is enlarged by ~2.1 times. The X-ray diffraction of (CTA)\textsuperscript{+} FGT also confirms the interlayer expansion (SI Appendix, Fig. S2E). Similarly, another flake with TOA\textsuperscript{+} intercalation is characterized in liquid-phase AFM showing that the thickness is ~4.5 times larger than before (Fig. 2D). In fact, among different samples with TOA\textsuperscript{+} intercalation, we observe a thickness increase by a factor ranging from 4 to 6. This is likely because the large size of TOA\textsuperscript{+} can easily cause exfoliation of the FGT, especially in the fully intercalated state. To obtain a stable sample, our (TOA)\textsuperscript{+} FGT is at an intermediate level of intercalation, thus showing some variations of the thickness change. The in situ liquid-phase AFM during intercalation and the ex situ AFM in air after removing the solvent, are shown in SI Appendix, Fig. S2. Transmission electron microscopy (TEM) electron diffraction shows a small in-plane strain of ~0.36\% after intercalation (SI Appendix, Fig. S3).

We start to study the magnetic properties of the FGT 3D superlattice through magnetotransport measurements. The temperature-dependent longitudinal resistances (r\textsubscript{xx}) of FGT and 3D FGT superlattices are plotted in Fig. 3A. The intrinsic FGT exhibits metallic behavior down to low temperatures of 20 to 50 K, below which a weak insulating behavior is observed. A kink in the r\textsubscript{xx}–T curve is also seen at ~200 K, indicating the ferromagnetic phase transition which is consistent with literature reports of bulk flakes (22, 23). The samples with larger interlayer spacing became more insulating, which in closer similarity to the r\textsubscript{xx} behavior of pristine thin flakes (22). The magnetism is studied by probing the Hall resistance, R\textsubscript{yx}, under an external magnetic field (μ\textsubscript{B}H) parallel to the easy axis (c-axis, which is perpendicular to the layered planes) of FGT (22). Both the normal Hall effect (R\textsubscript{NH}) and the anomalous Hall effect (R\textsubscript{AH}) contribute to R\textsubscript{yx}, but the R\textsubscript{NH} contribution is negligible compared to R\textsubscript{AH} at low field in FGT. The temperature dependence of the R\textsubscript{yx} hysteresis loops in SI Appendix, Fig. S4 shows a negligible change of T\textsubscript{C} in 3D FGT superlattice. Fig. 3B plots the R\textsubscript{yx} hysteresis loops of FGT and 3D FGT superlattices at 2 K, and Fig. 3C summarizes the temperature dependence of the coercive fields (H\textsubscript{C}) of different types of samples. Both the (CTA)\textsuperscript{+} FGT and (TOA)\textsuperscript{+} FGT maintain a ferromagnetic ground state but with a reduction of coercivity. Coercivity is strongly dependent on the saturation magnetization and the domain wall energy which is a function of the anisotropy constant (A) (24). Hence, a reduced coercivity in 3D FGT superlattice could emerge from a reduction of anisotropy, although the easy axis is still maintained to c-axis in 3D FGT superlattice (SI Appendix, Fig. S5). The tensile strain in FGT will increase the coercive field (25), which is contradictory to our observation. Thus, the reduction of the coercivity is not caused by the observed ~0.36\% strain.

Further investigation of the domain structure of 3D FGT superlattice is conducted by using the cryogenic Lorentz TEM (cryo-LEEM). By tilting the sample to a certain angle (31.5°) at 100 K, the domain wall can be visualized by the bright and dark contrast at the defocused lens. Fig. 3D and E show the magnetic domain structure of FGT and (CTA)\textsuperscript{+} FGT by zero magnetic field.
cooling under the same imaging condition. The variation of the domain structure under an external magnetic field is shown in SI Appendix, Fig. S6. A parallel stripe domain (or labyrinth) structure is observed in pristine FGT, consistent with previous reports (26, 27), indicating the dominant role of dipolar interaction over anisotropy and exchange interaction in FGT (28–31). In (CTA⁺)₂FGT, the domain structure is strikingly different from the domain structure of FGT. The domain structure of the (CTA⁺)₂FGT is different from that of the FGT, with an around 2 times enlargement of the domain width. The domain width is a balance between the exchange energy and anisotropy (32); an increase in domain width suggests a reduced anisotropy or enhanced exchange energy (Fig. 3F).

To investigate the critical behavior of FGT 3D superlattice, both magnetotransport measurement and polar reflective magnetic circular dichroism (RMCD) microscopy are employed. The temperature dependence of the remanent $R_{yx}^{R}$ and RMCD signal are plotted in Fig. 4A and B, respectively. $R_{yx}^{R} = R_{xy} M_0 M_p$, where the anomalous Hall coefficients $R_{xy}$ is related to the longitudinal resistance (33) but can be approximated as a constant in a narrow temperature range. In comparison, the RMCD signals are linearly proportional to the magnetization of the sample. It is worth noting that an objective under the magnetic field will produce a Faraday rotation in the light transmitted in the objective. This effect is essentially the same as a magneto-optic Kerr effect that would be measured from the reflected light from the surface of a magnetized sample, as is the case in this work. Thus, in this work, we chose to measure the RMCD signal, which suffers less interference from Faraday rotation.

To further validate the enhanced magnetic coupling, we turn our attention to the critical exponent $\beta$ (34). Critical exponents play a vital role in describing the behavior of physical quantities near continuous phase transitions. In ferromagnetic systems, the relationship between magnetization and temperature follows the pattern (35):

$$M(T < T_C) \propto |T / T_C - 1|^\beta.$$  

The values of critical exponent $\beta$ are fitted from the temperature dependence of the magnetization (i.e., $R_{yx}^{R}$ or RMCD signal) in the near-$T_C$ region as shown by solid lines in Fig. 4A and B are summarized in Fig. 4C. Generally, a larger $\beta$ value signifies a more robust magnetic interaction and a higher spin dimension. For instance, the $\beta$ values for the idealized 2D Ising, 3D Ising, and 3D Heisenberg models are 0.125, 0.3265, and 0.369, respectively (34). For intrinsic FGT, $\beta \approx 0.2$ is obtained, which is slightly smaller than the reported values of bulk FGT ($\approx 0.25$) (25, 36). This smaller fitting result is caused by the intermediate magnetic states at elevated temperature in thick FGT flakes, which can be compensated by changing the remanent $R_{yx}^{R}$ and RMCD extraction method (SI Appendix, Fig. S7). The discussion regarding the distinction between using hall resistance and RMCD for fitting is shown in SI Appendix, Supporting Text 2. Usually, the interlayer distance expansion in vdW crystals leads to a dimensional crossover behavior and forms monolayer atomic crystal molecular superlattices due to the reduced interlayer coupling (29). On the contrary, the $\beta$ of 3D FGT superlattice (CTA⁺)₂FGT and
Fig. 4. Dimensionality of 3D FGT superlattice. (A) $R_{\text{cc}}^f$ of the FGT (−50 nm), (CTA$^+$), FGT (−30 nm before intercalation), and (TOA$^+$), FGT (−20 nm before intercalation) as a function of temperature. The solid lines are least-squares criticality fits of the form $\alpha(1 - T/T_c)$. Only the solid dots are used for fitting, and the hollow dots are not included in the fitting. (B) Remanent RMCD signal as a function of temperature for FGT and (CTA$^+$), FGT, and the corresponding fitting lines. (C) Fitted values of the exponent $\beta$ for FGT, (CTA$^+$), FGT, and (TOA$^+$), FGT by using remanent $R_{\text{cc}}^f$ and RMCD signal in panel A and B. The dash line indicates the $\beta$ values for idealized models. The error bar represents 95% CI of the fitting.

(TOA$^+$), FGT increase to −0.27 and −0.44, respectively, revealing a strong 3D critical behavior of the 3D FGT superlattice and consistent with the change of coercivity and domain structure as discussed above. The modified Arrott plots further confirm the 3D behavior of the FGT superlattice (SI Appendix, Fig. S8). The large value of $\beta$ suggests a decrease of the anisotropy (34) or an increase of the exchange interaction through intercalation.

The observed enhancement in magnetism might appear counterintuitive at first glance. In traditional magnetic multilayer thin films, interlayer coupling can be explained through quantum interferences due to reflections at spacer boundaries. The nature of this coupling is intricately tied to the characteristics of the complex Fermi surface (37). Consequently, the relationship between interlayer coupling and spacer thickness may exhibit either oscillatory behavior as seen in Ruderman– Kittel–Kasuya–Yosida interactions or exhibit exponential decay patterns with insulating spacers. Notably, the envelopes of these patterns decay with increasing spacer thickness due to their inverse correlation (38).

In our 3D superlattice, apart from interlayer distance, electron doping is another critical factor affecting the magnetic properties. Each introduction of a cationic molecule results in the incorporation of an additional electron into the parent FGT. The doping electrons not only fill the sub-bands originating from the Fe 3d orbital but also facilitate interlayer hopping carriers, thereby promoting interlayer exchange coupling (39, 40).

Therefore, the interlayer magnetic exchange coupling in our 3D superlattice arises from the interplay between interlayer spacing and doping. Assuming a positive correlation between doping concentration and interlayer distance, it is reasonable to expect an initial boost in exchange coupling as intercalation progresses within the 3D superlattice. However, as the interlayer spacing expands to an exceptionally large extent, the distance factor will dominate the interlayer coupling, and eventually lead to exfoliation and the formation of a 2D monolayer, causing a decline in the decoupling strength. Some extrinsic factors, such as iron content, disorder, and thickness, have negligible effects on the conclusion, as discussed in SI Appendix, Supplementary Text S1.

Based on this, we serendipitously found that the intercalation could induce exfoliation of the FGT, thus enabling a scalable manufacture of 2D magnetic monolayers (41–44). Both CTA$^+$ and TOA$^+$ can cause exfoliation if the intercalation concentration is high enough. However, the larger size and faster intercalation dynamics of the TOA$^+$ lead to incomplete exfoliation and inhomogeneous exfoliated flake size (42). Therefore, CTA$^+$ are used to exfoliate the sample. As illustrated in Fig. 5A, without a contact lead on the top and edge to mechanically fix the FGT crystal, over-intercalation causes the exfoliation of FGT flakes. A series of in situ optical microscopy images in Fig. 5B demonstrates the release of the top few layers of an FGT flake. The in situ video and a monolayer release of a bottom-contacted sample are displayed in Movies S3 and S4. This over-intercalation-induced exfoliation is not only applicable to microscopic devices but also feasible for bulk crystals. By applying a large constant voltage (SI Appendix, Fig. S9 A–D) on a millimeter-size crystal, the strain and consequent fracture (due to the large volume expansion) of the intercalated area trigger the fracture of local flakes and release them from the crystal. The exfoliated flakes can be processed as liquid-phase chemically exfoliated flakes (45). These flakes are filtered, collected, and dispersed into dimethylformamide (DMF) or other organic polar solvents (such as isopropyl alcohol, acetonitrile, etc.) with mild sonication to form few-layer (CTA$^+$), FGT suspension ink (Fig. 5E).

AFM is used to characterize the thickness of these exfoliated flakes by drop-casting the ink on a SiO$_x$/Si substrate. The thickness of the as-deposited flakes ranges from 1.3 to 6.5 nm (Fig. 5 C and D). Fig. 5F shows an as-deposited flake of ~2.8 nm at room temperature. After annealing it at elevated temperature (300 °C) to remove the organic molecules (43), the thickness is reduced to ~0.9 nm (Fig. 5G), which is the thickness of a monolayer FGT, indicating that the exfoliated 2D FGT few layers are covered with organic molecules. The minimum thickness (~1.3 nm) is greater than the monolayer thickness (~0.8 nm) of FGT, suggesting a partially molecular-covered samples (e.g., only one surface of the FGT is covered with organic molecules). In addition, the morphology of the molecules on the FGT surface could also affect the thickness, especially for the monolayer samples. The surface capping also enhances the stability of atomically thin flakes, preventing any degradation in the ambient environment and allowing sample processing under ambient conditions. The magnetotransport properties of a ~4.8 nm exfoliated flake (bilayer) are studied. The sample resistance shows insulating behavior (Fig. 5H), which is due to the reduced sample dimension (22). Two stages are observed in the anomalous Hall resistance (Fig. 5I), which is likely due to multi-domain behavior. Surprisingly, ferromagnetism persists up to ~200 K, close to the $T_c$ of bulk samples. The elevated
Fig. 5. Formation and magnetic properties of 2D FGT few layers. (A) Schematic illustration of intercalation-induced exfoliation with contact on one end of the FGT flake. (B) A series of optical microscopy images demonstrating the exfoliation process by over-intercalation of CTAB into FGT (scale bar: 20 µm). (C) AFM characterization of the spin-coated (CTA‘), FGT from a high concentration ink (scale bar: 500 nm). (D) Histogram of the thickness distribution of the exfoliated (CTA‘), FGT flakes. (E) Photograph of a bottle of 100 ml (CTA‘), FGT ink. (F) AFM image of the exfoliated flakes deposited on SiO2/Si substrate. (G) AFM image of the same samples in (E) after annealing at 300 °C. (H) Temperature dependence of the normalized longitudinal resistance of an FGT and an exfoliated bilayer (CTA‘), FGT flake. (I) Temperature-dependent $R_{\text{p}}$ of the exfoliated bilayer (CTA‘), FGT flake.

$T_c$ of the ultrathin sample may be attributed to partial electron doping from the capping organic molecules (40). The FGT ink is compatible with spin coating and printing technology to fabricate wafer-scale FGT circuits (42).

**Conclusion**

In summary, both the 3D FGT superlattice and 2D FGT monolayer can be formed by intercalation. Our transport and cryo-LTEM study demonstrate a decreased coercivity and increased domain wall size of the 3D FGT superlattice. Fitting of critical behavior from transport and RMCD measurement shows a strong 3D dimensional behavior of the superlattice with an increased exponent $\beta$. Finally, over-intercalation induces exfoliation of FGT flakes, allowing for large-scale manufacture of 2D FGT few layers. The exfoliated samples are capped with organic molecules, which enables the possibility to process atomically thin samples in the ambient environment without degradation and enhances $T_c$ near the bulk value. In comparison to conventionally deposited magnetic thin films, while our current capabilities are limited to probing the steady state, intercalation offers greater versatility in selecting buffer layer materials, irrespective of the lattice mismatch concerns. This versatility not only allows adjustments in interlayer distance but also facilitates the introduction of doping into the system. Future advancements in voltage-controlled intercalation will undoubtedly enhance the study of intercalation-produced 3D superlattices and promote rapid prototyping of emerging magnetic devices. Our method supplements the toolbox of vdW magnetic crystals with a tuning knob of magnetic exchange interaction and anisotropy through interlayer engineering and provides opportunities for magnetic applications. More generally, they present an opportunity to induce and control novel spintronic phenomena using heterogeneous guest species environments.

**Materials and Methods**

**Fabrication of FGT Devices.** The FGT flakes are exfoliated from high-quality chemical vapor transport grown bulk crystal by using PDMS-assisted transfer onto 300 nm SiO2/Si wafers (prepatterned with Pt counter electrode) in an argon-filled glovebox with an oxygen concentration less than 0.1 ppm. Standard e-beam lithography is used to define the contact pattern by using a JEOL JBX-6300FS electron beam lithography system. 5/150 nm Cr/Au is deposited by using a KJ Lesker e-gun/beam evaporator. A mild argon ion mill is performed in the evaporator chamber before metal deposition to remove any organic residue and oxide layer on the top surface. Finally, the sample is lifted off by acetone, rinsing in IPA, and dried by argon gas in the argon glovebox. The electrochemical cell is assembled in the glovebox by sealing the cell with a top glass slide and thermoplastic film (Meltonx 1170-60, Solaronix), while leaving two small openings. After filling the cell with liquid electrolyte through the two openings, they are sealed by Epoxy glue.

**Intercalation.** The in situ electrochemical intercalation is performed with a Bio-Logic potentiostat and is imaged simultaneously using a light microscope.
(Olympus BX-51). The reactions on the working and counter electrodes for CTAB intercalation are:

\[
\text{Working: } x\text{CTA}^+ + xe^- \rightarrow (\text{CTA}^+)_x \text{FGT} \\
\text{Counter: } Br^- \rightarrow \frac{1}{2}Br + e^- 
\]

Either constant current or voltage sweeping can be used for intercalation. The voltage plateau for intercalation is ~3.4 V, but it varies from sample to sample due to the sample size, electrolyte concentration, and distance between working and counter electrodes. Side reactions occur on the gold electrodes (46). The side reactions on the gold have a negligible effect on the transport measurement. However, the side reactions make it difficult to calculate the number of intercalated molecules by integrating the time and current. The TOAB intercalation requires smaller current control to prevent over-rapid expansion (explosion) or contact exfoliation of the sample. After intercalation, it took tens of seconds to few minutes for the sample to stabilize. The (CTA)ₙFGT can be washed with acetonitrile without transport measurement. The (TOA)ₙFGT is dried in a vacuum or cooled down to the melting temperature of the electrolyte. The insulating dried electrolyte shows an insignificant effect on the transport measurement.

**AFM Characterization.** The AFM characterization in air is conducted using a Bruker Dimension Icon AFM. An Asylum MFP-3D AFM with a closed fluid cell is used for the liquid-phase AFM characterizations.

**Transport Measurement.** The longitudinal and Hall resistivities of the samples are measured using the van der Pauw geometry contacts sourcing 10 µA of AC. The angular dependence measurements are performed using a rotator probe.

**RMCD.** The temperature dependency RMCD signal is performed on a cryostat Attocube attoDRY2100, in which a magnetic field up to 9 T can be applied. The optical path is designed to be very similar to ref. 47, and it can be described and detailed as follows. A continuous-wave stabilized 532 nm laser, Verdi V5–Coherent coupled to a single mode fiber is collimated using a reflective collimator and chopped at 137 Hz. A wire-grid linear polarizer is placed just after the chopper. A half-wave plate, placed after the linear polarizer, is rotated to set the linear polarization at 45° with the fast axis of a photo-electric modulator (PEM). Hind Instruments-PEM series I, placed after the half-wave plate and before a 10T-90°-non-polarizing cube beam splitter. The retardation of the PEM is calibrated considering the wavelength used (532 nm) and set to oscillate at 50 kHz. The modulated light is now reflected inside the cryostat and focused on the surface of the sample using a cryogenic objective, Attocube LT-AP/ VISIR/0.82. The light, reflected from the sample mounted in a Faraday geometry, is now collimated back using the same focusing objective. The beam splitter will reflect the signal that will be focused and detected by a biased silicon photodiode DET36A-Thorlabs. The signal from the photodiode is divided into two different lock-in-amplifiers SR830. The different lock-ins are locked to the frequencies of the chopper and the PEM, which makes it possible to measure the intensity of the reflected light (Iₙ) and the RMCD (I₂/Iₙ) at the same time. For each data point in temperature, the laser is focused on the exact same position on the sample, and the data are acquired by setting the field to ramp from 0 T to –1 T and back to 0 T, measuring I₁ and I₂ at the end, and ramping the field from 0 T to +1 T and back to 0 T and measuring Iₙ and I₂ again at 0 T. The differential remanent magnetization is extracted by taking the difference between I₂/I₁ at 0 T but coming from the negative and positive fields for each temperature measured. Hysteresis loops are also measured when the temperature is above 200 K for the modified remanent RMCD signal extraction method.

**Extraction of Remnant \( R_m \) and RMCD Signals.** The standard remnant \( R_m \) or RMCD signals are performed by interpolating the hysteresis loops and extracting the values at \( \mu_0H = 0 \) (as shown by the \( R_m \) extraction in SI Appendix, Fig. S7A), which works well for the low-temperature data. However, thick FGT flakes have an additional ferromagnetic phase at elevated temperature near the \( T_c \) manifested through intermediate kinks in the hysteresis loop (SI Appendix, Fig. S7A) (23). Therefore, we proposed a modified extraction method by linearly fitting normal hall resistance (the orange dot lines in SI Appendix, Fig. S7A) the hysteresis loop beyond the coercive field and extracting the intercept as modified \( R_m \) or RMCD. As for the 3D FGT superlattice, the transition starts to become soft, and the intermediate level is almost absent. The fitting results based on the standard extraction method are shown in Fig. 4, with the modified extraction method applied to pristine FGT shown in SI Appendix, Fig. S7B.

**TEM Characterization.** The samples for TEM characterization are prepared by transferring exfoliated samples onto a silicon TEM grid with 25-nm silicon nitride film window. A shadow mask is used to deposit 200 Cu on one side of the flake as both electrical contact and thermal cooling contact (SI Appendix, Fig. S3). The samples are intercalated directly on the grid and washed with acetonitrile several times before loading to the TEM. The TEM characterization is conducted using a FEI Titan 80 to 300 aberration-corrected environmental TEM operated at 300 kV. The cryo-TEM is performed under Lorentz lens mode with a Gatan 626 cryo-transfer holder. The defocused images are taken by tilting the sample to 31.5°. The sample magnetic field in the cryo-TEM is controlled by adjusting the current of the objective lens.

**Exfoliation and Ink Formation.** The intercalation of bulk crystals is performed in a two-terminal electrochemical cell. The FGT crystal held by a conducting tweezer is used as the working electrode, and a platinum foil as the counter electrode. A high voltage (>3.4 V) between Pt and FGT is applied to realize rapid intercalation and exfoliation. The spikes in the current profile indicated the detachments of intercalated flakes from the bulk crystal (SI Appendix, Fig. S9). The exfoliated flakes are collected, washed with acetonitrile, and redispersed in DMF with mild sonication to form the FGT ink.

**Data, Materials, and Software Availability.** All study data are included in the article and/or supporting information.

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