Effects of Fe Deficiency and Co Substitution in Polycrystalline and Single Crystals of Fe₃GeTe₂

Daniel A. Mayoh,* George D. A. Wood, Samuel J. R. Holt, Grady Beckett, Emily J. L. Dekker, Martin R. Lees, and Geetha Balakrishnan*

ABSTRACT: Fe₃GeTe₂ is a two-dimensional van der Waals material with a ferromagnetic ground state and a maximum transition temperature \( T_c \sim 225 \text{ K} \). However, when Fe₃GeTe₂ is synthesized, lower values of \( T_c \) are often reported. This is attributed to a deficiency in the Fe at the 2c site in the crystal structure. Here, we investigate the effect of Fe deficiency and the substitution of Co for Fe on the magnetic properties of this system. We have synthesized both polycrystalline material and single crystals by chemical vapor transport and the flux method, with the largest crystals obtained using the flux method. Cobalt substitution at the Fe site is found to significantly reduce the magnetic transition temperature. Crystals of Fe₃GeTe₂ grown by chemical vapor transport with \( \sim 8\% \) excess Fe in the starting materials display an optimum Fe content and magnetic transition temperature.

INTRODUCTION

Van der Waals (vdW) bonded magnetic materials are currently shaping the field of two-dimensional (2D) materials science.¹ The presence of van der Waals bonding in these materials allows them to be cleaved down to monolayers and combined with other 2D materials to create novel heterostructures without concern for lattice matching. By modifying these heterostructures, the electrical, optical, and magnetic properties can be fine-tuned, and in some cases, unique magnetic phases can be realized.² Many magnetic vdW materials have been discovered to host an assortment of magnetic orders such as ferromagnetism (e.g., CrBr₃,³³ CrI₃,⁴ CrGeTe₃,⁶,⁷ and CrSiTe₃⁸), antiferromagnetism (e.g., MnBi₂Te₄,¹⁰ MnP(S/Se)₃,¹¹ and CrCl₃,¹²), helimagnetism (e.g., NiBr₂,¹³ and NiI₂,¹⁴), and frustrated magnetism (e.g., RuCl₃).³⁵

Fe₃GeTe₂ is a 2D magnetic material that has been generating significant attention as it was the first vdW material found to be both magnetic and metallic. It also offers a significant step up in Curie temperature (\( T_c \sim 225 \text{ K} \)) from previous magnetic vdW materials.¹⁶−¹⁸ Much research has been directed toward tuning the magnetic properties of this material by layer thickness dependence studies,¹⁹ varying the Fe content,²⁰ Co substitution,²¹,²² and the investigation of the anomalous Hall effect,²³ planar topological Hall effect,²⁴ Kondo lattice physics,²⁵ anisotropy magnetostriiction effect,²⁶ and ionic liquid voltage gating.²⁷ In bulk Fe₃GeTe₂, there have been some conflicting reports over whether the ground state of Fe₃GeTe₂ should be antiferromagnetic or ferromagnetic.²⁸−³⁰ In its stoichiometric form, there should be interlayer antiferromagnetism in Fe₃GeTe₂; however, Fe vacancies in this system, which correspond to more hole charge carriers, produce a ferromagnetic ground state.³⁰ This observation agrees with the majority of the literature, in which samples are frequently reported to be Fe-deficient and ferromagnetic.³⁰ It has also been suggested that an antiferromagnetic to ferromagnetic transition in Fe₃GeTe₂ can be induced by electron doping.³⁰

In addition to the highly tunable nature of the magnetic properties of Fe₃GeTe₂, there have been several studies concentrating on skyrmions and the spin textures that have been observed in this material. Magnetic bubble-like formations were first observed in Fe₃GeTe₂ when a magnetic Ni tip of a scanning tunneling microscope (STM) was held close to a freshly cleaved surface of Fe₃GeTe₂.³¹ Lorentz transmission electron microscopy (TEM) measurements further revealed magnetic bubble-like textures in Fe₃GeTe₂.

Received: June 14, 2021
Revised: September 16, 2021
which were claimed to be skyrmions. These bubbles could be tuned in size with applied magnetic field. The presence of a topological Hall effect has recently been observed in Fe₃GeTe₂; this signal is frequently taken as the hallmark of skyrmions. Since Fe₃GeTe₂ crystallizes in the centrosymmetric hexagonal space group P6₃/mmc (No. 194) as shown in Figure 1, the mechanism for the stabilization of skyrmions in bulk Fe₃GeTe₂ is currently unclear. Skyrmion-like magnetic bubbles have only been observed in Fe₃GeTe₂ in a thin-film regime or at the interface of the material, as is the case for the STM study, where it is conceivable that inversion symmetry can be broken, leading to a Dzyaloshinskii–Moriya (DM) interaction. The observation of Néel-type skyrmions at an oxide interface in Fe₃GeTe₂ gives further confirmation that the DM interaction is allowing the stabilization of skyrmions in this material. Should skyrmions be realized in bulk Fe₃GeTe₂, the interactions stabilizing them cannot include the DM interaction due to the centrosymmetric nature of the crystal structure.

We have undertaken a detailed investigation into the dependence of the magnetic properties on the Fe content in the Fe₃GeTe₂ materials. We have synthesized both polycrystalline and single crystals of Fe₃GeTe₂ and Co-substituted materials, Feₓ₋₀.₃ₐ₀GeTe₂ for y = 0.3, 0.6, 0.9, 1.2, and 1.5. Investigations of the structure and properties of the polycrystalline and single crystals produced have been undertaken using X-ray diffraction and magnetic measurement techniques. Composition analysis, including estimates of the Fe content in these materials, reveal a direct correlation with the observed magnetic transitions. We also find that an excess of Fe is necessary for the synthesis of Fe₃GeTe₂ to optimize the Fe content and therefore achieve the highest T_c.

EXPERIMENTAL DETAILS

Polycrystalline materials were synthesized by solid-state reaction. Single-crystal growths were carried out by either chemical vapor transport (CVT) or the flux method using Te flux. All of the sample preparation techniques are discussed in more detail in the following section. To determine the phase purity and crystal structure of the synthesized polycrystalline materials, powder X-ray diffraction was performed at room temperature using a Panalytical Empyrean diffractometer (Bragg–Brentano geometry) with a Cu Kα1 and Kα2 source and a solid-state PIXcel detector. Rietveld refinements were carried out on the observed diffraction patterns using the TOPAS academic v6.0 software suite. The quality of the single crystals obtained was investigated by Laue X-ray imaging using a Photonic Science Laue camera.

The chemical composition was determined using a ZEISS GeminiSEM 500, which was used to perform energy-dispersive X-ray spectroscopy (EDX). The magnetic properties of both the single crystals and the polycrystalline materials were measured using a Quantum Design Magnetic Property Measurement System (MPMS) superconducting quantum interference device (SQUID) magnetometer. Measurements were made in the temperature range of 2–300 K in various applied magnetic fields in the zero-field-cooled (ZFC) and field-cooled (FC) modes.

MATERIAL SYNTHESIS

Polycrystalline Synthesis. Polycrystalline materials of Fe₃GeTe₂ and Feₓ₋₀.₃ₐ₀GeTe₂ (y = 0.3, 0.6, 0.9, 1.2, 1.5) were synthesized by the solid-state reaction. Stoichiometric quantities of high-purity elements in powder form, Fe (STREM Chemicals, Inc., 99.99%), Co (Alfa Aesar, 99.99%), Ge (Acros Organics, 99.999%), and Te (Alfa Aesar, 99.99%) were ground together inside an argon-filled glovebox and transferred into quartz ampoules. The evacuated quartz ampoules were held at 675 °C for 10 days with heating/cooling rates of ca. 60–100 °C/h. The resulting gray/black powders were ground and investigated for phase formation.

Single-Crystal Growth. Two different techniques were employed to obtain single crystals of the various compositions listed: chemical vapor transport and the flux method using excess Te.

For the CVT process, growth was attempted using two different transport agents, I₂ and TeCl₄. Quantities of Fe, Ge, Co, and Te powders (see Table 1) along with 5 mg/cm² of the transport agent were sealed in quartz ampoules. The growth of crystals was carried out by holding the source and the sink ends of each tube at different temperatures in a two-zone furnace for 2 weeks, before cooling to room temperature. Several different temperature profiles were used, 750–675 °C for the hot end and 700–650 °C for the cold end. In some of the CVT growth processes, in addition to the platelets that have been identified as corresponding to the desired Fe₃GeTe₂ crystals, other needle-like and pyramidal-shaped structures
Table 1. Nominal Starting Compositions along with the Eventual Compositions Determined by EDX Analysis for Single Crystals of Fe–Ge–Te and Fe–Co–Ge–Te Grown by either CVT or the Flux Method

| nominal composition | composition from EDX | growth technique |
|---------------------|----------------------|------------------|
| Fe$_{2.0}$GeTe$_2$  | Fe$_{2.12}$GeTe$_{2.08}$ | flux             |
| Fe$_{2.5}$GeTe$_2$  | Fe$_{2.44}$GeTe$_{2.08}$ | CVT              |
| Fe$_{2.7}$GeTe$_2$  | Fe$_{2.68}$GeTe$_{2.08}$ | CVT              |
| Fe$_{2.8}$GeTe$_2$  | Fe$_{2.68}$GeTe$_{2.08}$ | CVT              |
| Fe$_{2.9}$GeTe$_2$  | Fe$_{2.66}$GeTe$_{2.08}$ | CVT              |
| Fe$_{3.0}$GeTe$_2$  | Fe$_{2.64}$GeTe$_{2.08}$ | CVT              |
| Fe$_{3.1}$Co$_{0.8}$GeTe$_2$ | Fe$_{3.10}$Co$_{0.8}$GeTe$_{2.08}$ | CVT |
| Fe$_{3.2}$Co$_{0.6}$GeTe$_2$ | Fe$_{3.0}$Co$_{0.6}$GeTe$_{2.08}$ | CVT |
| Fe$_{3.2}$Co$_{0.5}$GeTe$_2$ | Fe$_{3.0}$Co$_{0.5}$GeTe$_{2.08}$ | CVT |
| Fe$_{3.2}$Co$_{0.4}$GeTe$_2$ | Fe$_{3.0}$Co$_{0.4}$GeTe$_{2.08}$ | CVT |
| Fe$_{3.2}$Co$_{0.3}$GeTe$_2$ | Fe$_{3.0}$Co$_{0.3}$GeTe$_{2.08}$ | CVT |

Figure 2. Typical as-grown crystal of (a) Fe$_{1.5}$CoGeTe$_2$ prepared using CVT and (b) Fe$_{1.25}$CoGeTe$_2$ grown by the flux method. The compositions of the single crystals are those estimated by EDX analysis. Below each picture is a corresponding Laue diffractogram displaying the sixfold symmetry expected observing along the c axis of the crystal.

For the crystal growth by the flux method, using excess Te (powder) as the flux, mixtures of varying nominal compositions (see Table 1) were used. The mixtures were placed in an alumina crucible, which was then sealed in a quartz ampoule under vacuum. To enable the capture of the crystals during a subsequent centrifuging process, a small amount of quartz wool was placed over the alumina crucible inside the ampoule. The tubes were heated to 1000 °C and cooled at the rate of 3 °C/h to 675 °C, at which temperature, the tubes were removed from the furnace and centrifuged to remove the excess Te flux. An example of a crystal grown by the flux method is shown in Figure 2b.

In general, the thickness and size of the crystals grown by the flux method were found to be larger than those obtained by CVT. The average size of the CVT-grown crystals is 2 × 2 mm$^2$, while that obtained by the flux method is typically 7 × 5 mm$^2$.

## RESULTS AND DISCUSSION

### Laue Diffraction

X-ray back-reflection Laue patterns were taken on the crystals to check for crystalline quality. Typical Laue photographs of isolated platelets of Fe$_x$GeTe$_2$ and Fe$_{3-\delta}$Co$_{\delta}$GeTe$_2$ mounted with the ab plane perpendicular to the X-ray beam are shown in Figure 2a,b. They display the sixfold symmetry expected observing along the c axis of the crystals.

### Powder X-ray Diffraction

Phase purity and structural analysis were carried out using powder X-ray diffraction on the polycrystalline materials synthesized. The diffraction patterns obtained could be indexed to the hexagonal space group $P6_3/mmc$ (No. 194). Figure 3 shows the observed diffraction patterns for the various nominal starting compositions of the Fe–Ge–Te and Fe–Co–Ge–Te powders and the Rietveld refinements of the observed patterns obtained using the TOPAS software suite. The typical physical and crystallographic parameters obtained for Fe$_{3.0}$GeTe$_2$ are given in Table 2. Impurity peaks are denoted by a red asterisk.

Figure 3. Room-temperature powder X-ray diffraction patterns of polycrystalline samples with the nominal compositions (a) Fe$_{3.0}$GeTe$_2$, (b) Fe$_{1.5}$Co$_{0.5}$GeTe$_2$, (c) Fe$_{3.0}$Co$_{0.6}$GeTe$_2$, (d) Fe$_{3.0}$Co$_{0.5}$GeTe$_2$, (e) Fe$_{3.0}$Co$_{1.5}$GeTe$_2$, and (f) Fe$_{3.0}$Co$_{1.0}$GeTe$_2$. Shown are the experimental profiles (green circles) and the Rietveld refinement (red solid line) made using the hexagonal $P6_3/mmc$ space group with the calculated difference (orange solid line). The purple bars indicate the expected positions of the Bragg peaks. The physical and crystallographic parameters obtained for Fe$_{3.0}$GeTe$_2$ are given in Table 2. Impurity peaks are denoted by a red asterisk.
that Fe deficiency results in a decrease in α, while c increases. We find that both the a and c lattice parameters decrease with increasing Co substitution at the Fe site, consistent with that reported earlier. It was not possible to determine the actual occupancy levels of the Fe/Co in the Co-substituted samples using X-ray diffraction, due to the similar atomic numbers and hence X-ray scattering factors of the Fe and Co atoms. Therefore, the decrease observed in the lattice parameters can only be indirectly attributed to the preferential substitution of Co at the 2c (Fe2) sites.

X-ray diffraction patterns were also obtained on single-crystal platelets mounted with the ab plane parallel to the X-ray beam when the scattering angle is zero, to obtain a series of (00l) reflections. Figure 5 shows the diffraction patterns obtained from two different crystal platelets, exhibiting the (00l) reflections typical of the Fe3GeTe2 structure.

**Energy-Dispersive X-ray Analysis.** Composition analysis of the crystals obtained was carried out by EDX analysis. Estimates of the relative Fe, Co, Ge, and Te contents in the crystals are given in Table 1. Examples of the EDX spectra and scanning electron microscope images of two crystals are shown in Figure 6. The elemental stoichiometry at each numbered site and across the bulk is given in Table 3. The composition analysis reveals that the Fe content in the crystals is consistently lower than the nominal starting compositions for the various growths.

Crystal growths of unsubstituted Fe3GeTe2 were attempted while varying the starting Fe content. For crystal growths starting with a nominal Fe content of 3.25, the resulting estimated Fe content in the crystals is close to 3. This indicates that an excess of Fe in the starting materials is necessary to ensure that a maximum occupancy of the Fe sites is achieved. For crystal growths starting with a particular Fe content, it was found that the Fe content in the resulting crystals varied considerably, providing crystals with a range of compositions. An indication of the typical range of final compositions for a nominal starting Fe content of 3.0 is given in the top half of Table 1. For the Co-substituted crystals obtained by both the flux method and CVT growths, the resulting composition of the crystals differed considerably from the nominal starting compositions. Each growth produced a number of crystals, which, when examined, showed varying Co content. This spread of Co levels estimated for a few typical crystals obtained from crystal growths with two starting Co substitution levels (y = 0.3 and 0.75) are shown in Table 1. These resulting compositions are further affirmed by the correlation with the Tc measured on these crystals through magnetic susceptibility measurements as discussed in the next section.

**Magnetic Susceptibility versus Temperature.** The Curie temperature, Tc, of a polycrystalline sample with a nominal composition Fe3GeTe2 was determined from the temperature-dependent dc magnetic susceptibility χ(T) as shown in Figure 7 and gave Tc = 223(1) K. This transition is not as sharp as that observed in the single crystals; however, the results are in agreement with previously reported magnetization data for polycrystalline Fe3GeTe2.

Field-cooled-cooling dc magnetic susceptibility versus temperature curves for single crystals obtained from CVT with nominal Fe starting compositions of 3 and 3.25 are shown in Figure 8. The compositions given in the legend are estimated from EDX. The magnetic susceptibility confirms a ferromagnetic ordering in Fe3−δGeTe2 indicated by the sharp increase in Tc due to spontaneous magnetization at the transition temperature. Crystals from the various crystal growth experiments carried out have a range of Fe content, which is reflected in the range of Tc’s they exhibit. Fe deficiency in Fe3−δGeTe2 leads to both a disorder and magnetic dilution, and therefore, the highest Tc is obtained when the composition of the resulting crystals is close to Fe3GeTe2. A rather striking linear dependence of the magnetic transition temperature over a range of Fe content in the Fe3GeTe2 crystals obtained is shown in Figure 8c.

---

**Table 2. Crystallographic Parameters Obtained from a Rietveld Refinement of the Powder X-ray Diffraction Pattern Collected at Room Temperature for a Polycrystalline Sample with a Nominal Composition Fe3GeTe2**

| Atom | Wyckoff Position | Position Occupancy | x   | y   | z   |
|------|------------------|--------------------|-----|-----|-----|
| Fe1  | 4e               | 1                  | 0   | 0   | 0.6703(3) |
| Fe2  | 2c               | 0.839(8)           | 2/3 | 1/3 | 3/4 |
| Ge1  | 2d               | 1                  | 1/3 | 2/3 | 3/4 |
| Te1  | 4f               | 1                  | 2/3 | 1/3 | 0.58992(11) |

---

**Figure 4.** (a) Shift of the (013) and (006) diffraction peaks with increasing Co content y in Fe3−yCoGeTe2. The splitting of the peaks is due to the presence of Cu Kα1 and Kα2 radiation in the X-ray source. (b) Variation of the lattice parameters a (left axis, red diamonds) and c (right axis, green circles) with the Co content y in Fe3−yCoGeTe2.
magnetic susceptibility versus temperature behavior in Co-substituted Fe–Ge–Te is shown in Figure 8b. Again the compositions given in the legend are those estimated by EDX. The transition temperatures of the Co-substituted

Figure 6. EDX spectra for single crystals with nominal starting compositions of (a) Fe$_{2.7}$Co$_{0.3}$GeTe$_2$ and (b) Fe$_{3.25}$GeTe$_2$, where the size and relative energies of the peaks indicate the elemental composition of the sample. The bulk stoichiometry was measured to be (a) Fe$_{2.44}$Co$_{0.486}$GeTe$_{2.11}$ and (b) Fe$_{2.97}$GeTe$_{2.22}$. Intensity peaks for each element are labeled. Oxygen peaks are indicated by a red asterisk. On the right is a scanning electron microscope image of the surface of each single crystal studied. EDX spectra were collected over the entire area of each crystal. The elemental stoichiometry at each numbered site and across the bulk is given in Table 3.

Table 3. Composition across Selected Sites of Single Crystals with the Nominal Starting Compositions Fe$_{2.7}$Co$_{0.3}$GeTe$_2$ and Fe$_{3.25}$GeTe$_2$ as Indicated in Figure 6 Determined from Energy-Dispersive X-ray Analysis

| spectrum label | Fe (%) | Co (%) | Ge (%) | Te (%) |
|----------------|--------|--------|--------|--------|
| Fe$_{2.7}$Co$_{0.3}$GeTe$_2$ | 1 | 41.05(1) | 7.76(1) | 16.61(1) | 34.58(1) |
| | 2 | 40.27(1) | 8.16(1) | 16.59(1) | 34.99(1) |
| | 3 | 40.56(1) | 7.93(1) | 16.72(1) | 34.79(1) |
| | 4 | 40.10(1) | 8.31(1) | 16.22(1) | 35.37(1) |
| Fe$_{3.25}$GeTe$_2$ | 5 | 47.90(1) | 0 | 16.16(1) | 35.94(1) |
| | 6 | 47.44(1) | 0 | 16.39(1) | 36.17(1) |
| | 7 | 48.35(1) | 0 | 16.51(1) | 36.04(1) |
| | 8 | 48.13(1) | 0 | 16.38(1) | 35.49(1) |

Figure 7. Zero-field-cooled warming (ZFCW) and field-cooled warming (FCW) dc magnetic susceptibility versus temperature for a polycrystalline sample with a nominal composition Fe$_3$GeTe$_2$ in an applied field of 100 Oe.

Figure 8. (a) Magnetic susceptibility as a function of temperature for several crystals of Fe$_{3-\delta}$GeTe$_2$ with differing levels of Fe content. Data were collected in the field-cooled cooling mode with $H = 100$ Oe applied along the $c$ axis. (b) Magnetic susceptibility as a function of temperature for several crystals of Fe$_{3-\delta}$Co$_{\delta}$GeTe$_2$ with differing levels of Co content. Data were collected in zero-field-cooled warming mode in a field of 100 Oe applied along the $c$ axis. (c) Transition temperature of Fe$_{3-\delta}$GeTe$_2$ as a function of Fe deficiency $\delta$. (d) Transition temperature of Fe$_{3-\delta}$Co$_{\delta}$GeTe$_2$ as a function of Co content $\delta$. The magnetic susceptibility versus temperature behavior in Co-substituted Fe–Ge–Te is shown in Figure 8b. Again the compositions given in the legend are those estimated by EDX. The magnetic susceptibility of Fe$_3$GeTe$_2$ is included for comparison. The transition temperatures of the Co-substituted
Fe₃GeTe₂ are shown in Figure 8d. Ferromagnetism is preserved for all of the Co substitutions attempted here (up to y = 1.27), with an almost linear decrease in Tᵣ with increasing Co levels.

## SUMMARY AND CONCLUSIONS

The layered magnetic material, Fe₃GeTe₂, has been investigated in both polycrystalline and single-crystal forms. Polycrystalline powders of Fe₃GeTe₂ and Feₓ₋₃CoₙGeTe₂ with several nominal starting compositions and Co substitutions have been synthesized. The effect of varying the nominal starting Fe content on the resulting Fe compositions in the Feₓ₋₃GeTe₂ obtained has been studied. We have also produced high-quality single crystals with varying Co content ranging from y = 0 to 1.5 by both CVT and the flux method. The phase formation, composition analysis, and crystal structures have been investigated using EDX and both powder and single-crystal X-ray diffraction techniques. Our results demonstrate that CVT consistently produces Fe-deficient crystals when starting with the nominal stoichiometry of Fe₃GeTe₂, while starting with an increased Fe content results in crystals with Fe stoichiometry close to the desired Fe₃. With the crystal growth of the Co-substituted crystals by the flux method, starting with a fixed value of y was found to result in crystals exhibiting a range of Co substitutions. The fortuitous range of materials with varying levels of both Fe and Co content produced in this study has allowed us to investigate the dependence of the lattice parameters as well as the magnetic transition temperatures in these systems. The magnetic transition temperatures of all of the crystals synthesized have been measured, and we find a strong correlation of the transition temperature with the estimated Fe content, with compositions close to the optimum of three exhibiting the highest Tᵣ. Similarly, the suppression of the magnetic transition temperature with Co substitution has been found. The systematic study of the structural and magnetic properties of these crystals is of great help in understanding the correlations between the synthesis and the structural and magnetic properties in this interesting magnetic material. Such a study is especially important as materials with Tᵣ’s close to room temperature are seen as being ideal for their applicability to device fabrication. Further studies probing the magnetic properties, especially in relation to their potential to exhibit skyrmions, are currently being explored on these crystals, for which they are ideal. Fe₃GeTe₂ continues to remain as one of the most interesting 2D magnetic materials with great promise for applications.

## AUTHOR INFORMATION

**Corresponding Authors**

Daniel A. Mayoh — Department of Physics, University of Warwick, Coventry CV4 7AL, U.K.; orcid.org/0000-0002-7020-3263; Email: d.mayoh.1@warwick.ac.uk

Geetha Balakrishnan — Department of Physics, University of Warwick, Coventry CV4 7AL, U.K.; Email: g.balakrishnan@warwick.ac.uk

**Authors**

George D. A. Wood — Department of Physics, University of Warwick, Coventry CV4 7AL, U.K.

Samuel J. R. Holt — Department of Physics, University of Warwick, Coventry CV4 7AL, U.K.

**Grady Beckett** — Department of Physics, University of Warwick, Coventry CV4 7AL, U.K.

**Emily J. L. Dekker** — Department of Physics, University of Warwick, Coventry CV4 7AL, U.K.

**Martin R. Lees** — Department of Physics, University of Warwick, Coventry CV4 7AL, U.K.

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.cgd.1c00684

**Notes**

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors acknowledge Tom Orton, Patrick Ruddy, and Daisy Ashworth for their technical support. They also thank David Walker for his assistance with the powder X-ray diffraction and Steve York for his assistance with the energy-dispersive X-ray spectroscopy measurements. This work was financially supported by two Engineering and Physical Sciences Research Council grants: EP/T005963/1 and the UK Skyrmon Programme Grant EP/N032128/1.

## REFERENCES

1. Mak, K. F.; Shan, J.; Ralph, D. C. Probing and controlling magnetic states in 2D layered magnetic materials. Nat. Rev. Phys. 2019, 1, 646–661.

2. Burch, K. S.; Mandrus, D.; Park, J.-G. Magnetism in two-dimensional van der Waals materials. Nature 2018, 563, 47–52.

3. Zhang, Z.; Shang, J.; Jiang, C.; Rasmita, A.; Gao, W.; Yu, T. Direct Photoluminescence Probing of Ferromagnetism in Monolayer Two-dimensional Cr₇Br₆. Nano Lett. 2019, 19, 3138–3142.

4. Li, T.; Jiang, S.; Sivadas, N.; Wang, Z.; Weber, D.; Goldberger, J. E.; Watanabe, K.; Taniguchi, T.; Fenn, C. J.; Mak, K. F.; Shan, J.; et al. Pressure-controlled interlayer magnetism in atomically thin CrI₃. Nat. Mater. 2019, 18, 1303–1308.

5. Liu, Z.; et al. Observation of nonreciprocal magnetophonon effect in nonencapsulated few-layered CrI₃. Sci. Adv. 2020, 6, No. eabc7628.

6. Carteaux, V.; Brunet, D.; Ouvard, G.; Andre, G. Crystallographic, magnetic and electronic structures of a new layered ferromagnetic compound Cr₄Ge₄Te₈. J. Phys.: Condens. Matter 1995, 7, 69–87.

7. Han, M.-G.; Garlow, J. A.; Liu, Y.; Zhang, H.; Li, J.; DiMarzio, D. J.; Knight, M. W.; Petrovic, C.; Jariwala, D.; Zhu, Y. Topological Magnetic-Spin Textures in Two-Dimensional van der Waals Cr₄Ge₄Te₈. Nano Lett. 2019, 19, 7859–7865.

8. Carteaux, V.; Ouvard, G.; Grenier, J. C.; Laligant, Y. Magnetic structure of the new layered ferromagnetic chromium hexatellur-olisicate Cr₄Ge₄Te₈. J. Magn. Magn. Mater. 1991, 94, 127–133.

9. Cai, W.; Sun, H.; Xia, W.; Wu, C.; Liu, Y.; Liu, H.; Gong, Y.; Yao, D.-X.; Guo, Y.; Wang, M. Pressure-induced superconductivity and structural transition in ferromagnetic CrSıTe₃. Phys. Rev. B 2020, 102, No. 144525.

10. Deng, Y.; Yu, Y.; Shi, M. Z.; Guo, Z.; Xu, Z.; Wang, J.; Chen, X.; Zhang, Y. Quantum anomalous Hall effect in intrinsic magnetic topological insulator MnBi₂Te₄. Science 2020, 367, 895–900.

11. Susner, M. A.; Chysanavichyus, M.; McGuire, M. A.; Ganesh, P.; Maksymovych, P. Metal Thio- and Selenophosphates as Multifunctional van der Waals Layered Materials. Adv. Mater. 2017, 29, No. 1602852.

12. Kuhlow, B. Magnetic Ordering in CrCl₃ at the Phase Transition. Phys. Status Solidi A 1982, 72, 161–168.

13. Tokunaga, Y.; Okuyama, D.; Kurumaji, T.; Arima, T.; Nakao, H.; Murakami, Y.; Taguchi, Y.; Tokura, Y. Multiferroicity in NiBr₂ with long-wavelength cycloidal spin structure on a triangular lattice. Phys. Rev. B 2011, 84, No. 060406.
(14) Kurumaji, T.; Seki, S.; Ishiwata, S.; Murakawa, H.; Kaneko, Y.; Tokura, Y. Magneto-elastic responses induced by domain rearrangement and spin structural change in triangular-lattice helimagnets Ni2 and CoI, Phys. Rev. B 2013, 87, No. 014429.

(15) Kim, H.-S.; V. V. S.; Catuneanu, A.; Kee, H.-Y. Kitaev magnetism in honeycomb RuCl3 with intermediate spin-orbit coupling. Phys. Rev. B 2015, 91, No. 241110.

(16) Deiseroth, R.-J.; Alexandrov, K.; Reiner, C.; Kienle, L.; Kremer, R. K. Fe8GeTe2 and Ni8GeTe2 – Two New Layered Transition-Metal Compounds: Crystal Structures, HRTEM Investigations, and Magnetic and Electrical Properties. Eur. J. Inorg. Chem. 2006, 2006, 1561–1567.

(17) Chen, B.; Yang, J.; Wang, H.; Imai, M.; Ohta, H.; Michioka, C.; Yoshimura, K.; Fang, M. Magnetic Properties of Layered Itinerant Electron Ferromagnet Fe8GeTe2. J. Phys. Soc. Jpn. 2013, 82, No. 124711.

(18) Li, Q.; et al. Patterning-Induced Ferromagnetism of Fe8GeTe2 van der Waals Materials beyond Room Temperature. Nano Lett. 2018, 18, 5974–5980.

(19) Fei, Z.; Huang, B.; Malinowski, P.; Wang, W.; Song, T.; Sanchez, J.; Yao, W.; Xiao, D.; Zhu, X.; May, A. F.; Wu, W.; Cobden, D. H.; Chu, J.-H.; Xu, X. Two-Dimensional Itinerant Ferromagnetism in Attractively Thin Fe8GeTe2. Nat. Mater. 2018, 17, 778–782.

(20) May, A. F.; Calder, S.; Cantoni, C.; Cao, H.; McGuire, M. A. Magnetic structure and phase stability of the van der Waals bonded ferromagnet Fe8−xSixGeTe2. Phys. Rev. B 2016, 93, No. 014411.

(21) Tian, C.-K.; Wang, C.; Ji, W.; Wang, J.-C.; Xia, T.-L.; Wang, L.; Liu, J.-J.; Zhang, H.-X.; Cheng, P. Domain wall pinning and hard magnetic phase in Co-doped bulk single crystalline Fe8GeTe2. Phys. Rev. B 2019, 99, No. 184428.

(22) Hwang, I.; Coak, M. J.; Lee, N.; Ko, D.-S.; Oh, Y.; Jeon, I.; Son, S.; Zhang, K.; Kim, J.; Park, J.-G. Hard ferromagnetic van-der-Waals metal (Fe,Co)xGe3−xTe6: a new platform for the study of low-dimensional magnetic quantum criticality. J. Phys.: Condens. Matter 2019, 31, No. 50LT01.

(23) Kim, K.; et al. Large anomalous Hall current induced by topological nodal lines in a ferromagnetic van der Waals semimetal. Nat. Mater. 2018, 17, 794–799.

(24) You, Y.; Gong, Y.; Li, H.; Li, Z.; Zhu, M.; Tang, J.; Liu, E.; Yao, Y.; Xu, G.; Xu, F.; Wang, W. Angular dependence of the topological Hall effect in the uniaxial van der Waals ferromagnet Fe8GeTe2. Phys. Rev. B 2019, 100, No. 134441.

(25) Zhang, Y.; Lu, H.; Zhu, X.; Tan, S.; Feng, W.; Liu, Q.; Zhang, W.; Chen, Q.; Liu, Y.; Luo, X.; Xie, D.; Luo, L.; Zhang, Z.; Lai, X. Emergence of Kondo lattice behavior in a van der Waals itinerant ferromagnet, Fe8GeTe2. Sci. Adv. 2018, 4, No. eaao6791.

(26) Zhuang, H. L.; Kent, P. R. C.; Hennig, R. G. Strong anisotropy and magnetostriiction in the two-dimensional Stoner ferromagnet Fe8GeTe2. Phys. Rev. B 2016, 93, No. 134407.

(27) Deng, Y.; Xu, Y.; Song, Y.; Zhang, J.; Wang, N. Z.; Sun, Z.; Yi, Y.; Wu, Y. Z.; Wu, S.; Zhu, J.; et al. Gate-tunable room-temperature ferromagnetism in two-dimensional Fe8GeTe2. Nature 2018, 563, 94–99.

(28) Yi, J.; Zhuang, H.; Zou, Q.; Wu, Z.; Cao, G.; Tang, S.; Calder, S. A.; Kent, P. R. C.; Mandrus, D.; Gai, Z. Competing antiferromagnetism in a quasi-2D itinerant ferromagnet: Fe8GeTe2. 2D Mater. 2017, 4, No. 011005.

(29) Kong, X.; Nguyen, G. D.; Lee, J.; Lee, C.; Calder, S.; May, A. F.; Gai, Z.; Li, A.-P.; Liang, L.; Berlijn, T. Interlayer magnetism in Fe8−xGe3−xTe6. Phys. Rev. Mater. 2020, 4, No. 094403.

(30) Jang, S. W.; Yoon, H.; Jeong, M. Y.; Ryeo, S.; Kim, H.-S.; Han, M. J. Origin of ferromagnetism and the effect of doping on Fe8GeTe2. Nanoscale 2020, 12, 13501–13506.

(31) Nguyen, G. D.; Lee, J.; Berlijn, T.; Zou, Q.; Hus, S. M.; Park, J.; Gai, Z.; Lee, C.; Li, A.-P. Visualization and Manipulation of Magnetic Domains in the Quasi-Two-Dimensional Material Fe8GeTe2. Phys. Rev. B 2018, 97, No. 014425.

(32) Ding, B.; Li, Z.; Xu, G.; Li, H.; Hou, Z.; Liu, E.; Xi, X.; Xu, F.; Yao, Y.; Wang, W. Observation of Magnetic Skyrmion Bubbles in a van der Waals Ferromagnet Fe8GeTe2. Nano Lett. 2020, 20, 868–873.