Two-dimensional (2D) materials have attracted great interest for their fascinating properties such as magnetoelectric effect [1–5], light-matter interaction [6,7], and spin-valley effects [8–11]. Recently discovered intrinsic 2D ferromagnet (FM) in van der Waals ferromagnetic metal Fe₃GeTe₂ (FGT) with the field applied along the easy axis. The paramagnetic-to-ferromagnetic transition occurs at the Curie temperature \( T_c = 180 \text{K} \) at ambient pressure, and \( T_c \) decreases monotonically up to 1.44 GPa, while the magnetization is suppressed by the pressure. By using high-pressure x-ray diffraction techniques, we found that the Fe-Fe bond lengths tend to decrease, and the Fe-Ge(Te)-Fe bond angles deviate away from 90° under hydrostatic pressures, indicating the modification of the exchange interactions. First-principles calculations further confirm the pressure effects. These results suggest that the competition between direct-, super-, and double-exchange interactions plays a crucial role in the pronounced magnetic response under the hydrostatic pressure, i.e., the exchange direct become stronger at a higher pressure and, hence, leading to increased antiferromagnetic components and thus deceased \( T_c \). The highly tunable magnetic properties under hydrostatic pressure in this system provide robust routes for spin manipulation in low-dimensional material systems.

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direct-exchange and super-exchange interaction, which then lead to the changes in saturation magnetization ($M_s$) [29]. Despite these findings, a clear picture of the exchange interaction variation under hydrostatic pressure is still under debate.

In this paper, we conducted extensive studies on the magnetic properties and crystal structure of the high-quality single-crystal FGT samples as a function of hydrostatic pressure at different temperatures. FGT exhibits high magnetocrystalline anisotropy with an easy axis along the $c$ axis, and the coercivity is quite small, showing the soft magnetic nature. The $T_c$ is found to be 180 K at the ambient pressure, which manifests a rapid decrease at a rate of $\sim$10.7 K/GPa. The temperature dependence of the magnetization measurement shows a monotonic decrease of the magnetization as a function of pressure, indicating the destruction of the long-range magnetic order. Powder x-ray diffraction (XRD) measurements under different pressures provide the variations of lattice parameters, yielding the trend for the changes of bond lengths and bond angles. The first-principles calculation further shows similar results that both the $T_c$ and magnetization decrease with applying hydrostatic pressure. This paper indicates the structure of FGT can be suppressed by the pressure, and the changes of the magnetic properties could be explained by the competition between the direct-exchange, super-exchange, and double-exchange interactions from the Fe-Fe, Fe1-Ge(Te)-Fe1, and Fe1-Ge(Te)-Fe2 bonds, as shown in Fig. 1(a).

High-quality single-crystal FGT samples with a nominal composition of Fe$_3$GeTe$_2$ were grown by the self-flux method from a mixture of pure powders Fe (99.99%), Ge (99.99999%), and Te (99.999%). The mixture was heated to 1000 °C in an evacuated quartz ampoule, soaked for 3 h, and then cooled slowly down to 680°C with a rate of 1 °C/h. The ampoule was subsequently quenched in the air, yielding single crystals of $5 \times 5 \times 0.2$ mm with a cleavable layer in the $ab$ plane. The atomic ratio determined via the energy-dispersive spectroscopy was 3:1:2.2 with a slight off-stoichiometry, which may cause the lower $T_c$ compared with the samples grown via chemical vapor transport [38]. The magnetic measurements were performed using the physical property measurement system (Quantum Design-9 T) with a vibrating sample magnetometer (for details, see Supplemental Material S1 [39]).

Pressure-dependent XRD data were collected on a Bruker D8 VENTURE PHOTON II system equipped with a Microfocus Incoatec Ims 3.0 (Mo Kα, $\lambda = 0.71073$ Å) and a multilayer optic monochromator. The samples were grounded into powders and loaded into a diamond anvil cell fitted with diamonds polished to a culet diameter of $d_{\text{culet}} = 300 \mu$m. Mineral oil (CAS: 8042-47-5) was used as the pressure medium. The pressure was measured by the ruby fluorescence in the experiments [43]. The parameters of the experiments were calibrated with a standard CeO$_2$ sample. The data were collected with a beam size of 110 μm and an exposure time of 600 s. All the preliminary data reduction was performed using the Dioptas program [44]. All of the diffraction data were subsequently analyzed and refined with the Rietveld technique by the FullProf computer code to obtain the lattice constants [45,46]. DFT based on Vienna ab initio calculation was used to study the physical origin of the $M_s$ and $T_c$ under hydrostatic pressure. Details can be found in the Supplemental Material S2 [39].

Figure 1(a) shows the atomic structure of FGT. The three Fe atoms in the unit cell are located at two inequivalent sites referring to Fe$^{1+}$ (Fe$^{3+}$) and Fe$^{2+}$. In each FGT monolayer, the Fe$_3$Ge heterometallic slab is sandwiched between the two Te layers [31]. Theoretical work suggests that the partially filled $d$ orbitals of the Fe atom dominate the energy band structure around the Fermi level, yielding the itinerant ferromagnetism in bulk FGT [19]. The van der Waals gap in adjacent layers is 2.95 Å, and bulk FGT exhibits strong magnetocrystalline anisotropy for the reduced crystal symmetry of the layered structure [17], as shown in Fig. 1(b). The isothermal magnetic hysteresis loops were obtained by applying field along the $c$ axis ($H || c$) and perpendicular to the $c$ axis ($H \perp c$). At 100 K (well below the $T_c$), the magnetization increases with increasing field. It tends to saturate at 0.25 T for $H || c$, whereas for $H \perp c$, the magnetization scales and saturates at a much higher field around 2.5 T. Hence, the $c$ axis is the easy axis for the FGT sample, and such a high anisotropy is believed to be able to stabilize the long-range
magnetic order [19]. The \( M_s \) at 100 K is about 0.88 \( \mu_B/\text{Fe} \) [Fig. 1(b)], which is smaller than the estimated spontaneous magnetization value 1.2–1.6 \( \mu_B/\text{Fe} \) in the literature [20], but it is rational for the measurement temperature of 100 K. The coercive field is around 50 and 110 Oe for \( H \parallel c \) and \( H \perp c \), respectively, indicating a soft FM nature similar to CrI\(_3\) [47] and Cr\(_2\)Ge\(_2\)Te\(_6\) [48].

To understand the evolution of ferromagnetism under the hydrostatic pressure, the temperature dependence of zero-field-cooling magnetization along the \( c \) axis for different applied pressures was performed, and the data are plotted in Fig. 2(a). The paramagnetic (PM)-to-FM transition temperature \( T_c \) decreases monotonically with the increase in the pressure, which shows a similar trend to the study of pressure effect on Cr\(_2\)Ge\(_2\)Te\(_6\) [48]. The simultaneous decrease of magnetization and \( T_c \) is quite reasonable in a simple picture where the smaller magnetization always appears with the lower Curie temperature, indicating a suppression of the ferromagnetism. To systematically determine the pressure dependence of \( T_c \) for FGT, \( T_c \) is estimated from the minimum point of \( dM/dT \) as shown in the inset of Fig. 2(a). For each pressure, \( dM/dT \) curve exhibits a sharp minimum, and the peak continuously shifts to lower temperature with increasing pressure. In the meantime, we notice that the height of the peak gradually decreases for the larger pressure, which indicates that the PM-FM transition is less sharp with applying the pressure. Indeed, the full width of the half-height increases slightly for \( P > 0 \), and we expect that the continuous increase of the pressure would eventually destroy the magnetic order, as has been reported recently [27]. An additional kink was observed in the temperature dependence of magnetization measurement just below the \( T_c \) [Fig. 2(a)], and the peak shifted to the low-temperature region for the larger pressure as well. As reported previously, this additional kink implies the existence of two-step magnetic ordering [49]. This is under further investigation and is not the main point of this paper. Figure 2(b) shows the variation of \( T_c \) under different pressures, and it is noted that \( T_c \) decreases linearly with pressure at a rate of 10.7 K/GPa.

We further measured the magnetic hysteresis loop at 100 K along the \( c \) axis with different pressures, as plotted in Fig. 2(c). The magnetization increases rapidly with increasing external field, and the \( M_s \) decreases with the increase in pressure. The magnetization saturates at around 0.25 T at the ambient pressure, while saturation cannot be reached until around 0.5 T for the applied pressure of 1.44 GPa. Meanwhile, we observe a decrease of \( dM/dH \) under higher pressures around zero field. This implies the diminishment of the anisotropy under hydrostatic pressure. The inset of Fig. 2(c) shows the enlarged area for the hysteresis loop in the high field region, where a decrease of the \( M_s \) with increasing pressure is exhibited [details can be found in Fig. 2(d)].

The drastic change in magnetic properties under pressure indicates a substantial modification of the magnetic ground states through exchange interactions. Two types of exchange interactions were considered for the determination of the
magnetic ground state for FGT [27]. The direct exchange arising from the electron hopping between the nearest neighbor Fe sites, formed from the 3d orbitals, is antiferromagnetic (AFM) order in nature; the indirect exchange, depending on Fe electron occupancy of the overlapping orbitals mediated through the nonmagnetic ions (Ge or Te here), can be FM or AFM order depending on the bond angle, which includes super- and double-exchange interactions. Super-exchange interaction mainly describes the exchange interaction between two isovalent ions, while the double-exchange interaction could depict the interaction between the ions, where one ion usually has an extra electron compared with the other one [50]. To further understand the magnetic behavior of FGT under pressure, we performed high-pressure XRD measurement to identify the changes of bond lengths and bond angles at different hydrostatic pressures.

The XRD patterns obtained in situ as a function of the pressure are shown in Fig. 3(a). All the diffraction peaks are well indexed, indicating no structure transition with the variation of the pressure applied, which is consistent with the previous studies [27]. Details for the peak shift can be found in Figs. 3(b) and 3(c), where the (002) and (101) peaks move toward higher scattering angles, indicating shrinkage in the lattice parameters under pressure. The Rietveld refinements of the XRD pattern are used to determine the variation of the lattice parameters, and the evolution of the lattice parameters are shown in Fig. 4(a) (for details, see Supplemental Material S3 [39]). Since the applied pressure is hydrostatic and no structural change is observed in Fig. 3(a), it is reasonable to assume that as the $P6_3/mmc$ space group of FGT remains unchanged with applying pressure; hence, the lattice constant $a$ remains the same with $b$. It is noted from Fig. 4(a) that the values of $a$ and $c$ decrease monotonically from 3.957 ± 0.002 and 16.402 ± 0.008 to 3.921 ± 0.002 and 16.024 ± 0.009 Å when the hydrostatic pressure increases from 0 to 1.7 GPa. The $c/a$ ratio also decreases from 4.145 to 4.086 with the increase in pressure (see Supplemental Material Table S1 [39]), which is consistent with the weak interlayer coupling properties for van der Waals materials. The structural factors in these materials, such as the bond lengths and bond angles, are susceptible to external pressure, leading to tunable magnetic properties. The calculated bond angles and bond lengths between the nearest neighbor atoms are shown in Fig. 4(b) and Table I, which is discussed later.

The magnetic properties are closely related to the anisotropies and exchange interactions, where the various

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<tr>
<th>P (GPa)</th>
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<tr>
<td>0</td>
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<td>0.43</td>
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types of the exchange interactions were developed to study the magnetic origin of the magnetic materials, and the key points are the bond length (between the magnetic ions) and bond angle (between the magnetic ions mediated with nonmagnetic ions) [51]. Pressure-induced changes in bond angle or length and magnetic properties have been previously reported in different 2D systems [26–29,47,48]. The study of the pressure effect on Cr$_2$Ge$_2$Te$_6$ shows a monotonic decrease of $\theta$ between the nearest neighbor atoms of Fe ions compared with the other one [50,52]. These two exchange interactions are similar to each other [29]: FM, AFM1, AFM2 [as shown in Fig. 5(a)]. Based on the above results, we would like to conclude that the competition between Fe1-Fe3 and Fe1-Fe2 decrease with the increase of the pressure. The distances of Fe-Ge and Fe-Te also decrease, which indicates the stronger indirect-exchange interaction. As we discussed earlier, the FM coupling gets weaker if the bond angle deviated from 90°, indicating the FM coupling that is favored by indirect-exchange interaction weakens. An abnormal result was found in CrI$_3$ [47], where the $M_t$ decreases monotonically with increasing pressure, whereas the $T_c$ increases. The FM transition is closely related to the strong covalent nature of the Cr-I-Cr bond in the CrI$_3$ system. The Cr-I-Cr bond angle is about 95°, and the author thought that the Cr-I-Cr angle might get closer toward 90° with pressure applied. Thus, the FM super-exchange is strengthened, leading to an increase in $T_c$. We believe here that a similar mechanism could be used to explain the exchange coupling in FGT: the $d$ orbital of the Fe-Fe atom overlaps directly without a mediate atom, which could lead to the AFM coupling. As the pressure increases, the Fe-Fe bond length decreases, and then the AFM coupling is stronger, resulting in a decrease of $T_c$ [29]. The indirect-exchange interaction may include super-exchange and double-exchange interaction, where the super-exchange coupling describes the exchange interaction between two isovalent Fe ions, which mainly contribute to the interaction from Fe1(Fe3)-Ge(Fe)-Fe1(Fe3), whereas for the exchange coupling of the Fe1-Ge(Fe)-Fe2 bond, it could be better depicted by the double-exchange interaction, especially for the itinerant FM, where one atom usually has an extra electron compared with the other one [50,52]. These two exchange interactions are similar to each other. The $d$ orbital of Fe ions overlaps with the $p$ orbital of the Te or Ge ion, and the virtual hopping electrons between the two nearest neighbor Fe ions could reduce the total energy of the system. According to the Goodenough-Kanamori-Anderson rules [50,53,54], the exchange interaction is AFM coupling when the magnetic-ion-magnetic angle is 180°, whereas it is FM coupling if the bond angle approaches 90°.

From Table I and Fig. 4(a), we could conclude that the bond lengths between Fe1-Fe3 and Fe1-Fe2 decrease with the increase of the pressure. The distances of Fe-Ge and Fe-Te also decrease, which indicates the stronger indirect-exchange interaction. Figure 4(b) shows the changes of bond angles $\theta_1$, $\theta_2$ (Fe1-Ge1-Fe1), and $\theta_3$ (Fe1-Te1-Fe1) under pressure. The Fe atoms have a nearly filled $d$ shell, so there should be small spatial hybridization between Fe atoms [29]. In contrast, there is strong covalent interaction between Fe-Ge(Fe), which indicates the predominant contribution of super-exchange and double-exchange interaction compared with the direct-exchange interaction, yielding the FM coupling for FGT. From the experimental result, we can find that all the bond angles, $\theta_1$ (Fe2-Ge-Fe3 related to the double-exchange coupling), $\theta_2$, and $\theta_3$ (Fe1-Ge1-Fe1 and Fe1-Te1 related to super-exchange coupling) diverge away from 90°.

As we discussed earlier, the FM coupling gets weaker if the bond angle diverges away from 90°, leading to a smaller exchange constant and lower $T_c$. Other bond angles like $\theta$ for the Fe1-Te1-Fe2 bond also deviated from 90° with applying pressure, and the detail can be found in the Supplemental Material S3 [39]. Based on the above results, we would like to conclude that the competition between the direct-exchange, super-exchange, and double-exchange interactions could contribute to the pronounced modulation in magnetic properties via the changes of bond lengths and bond angles under the hydrostatic pressure.

To capture insight into the magnetic properties of FGT by applying hydrostatic pressure, we performed first-principles calculations to understand the variation of $T_c$ for FGT. The evolution of the $T_c$ can be estimated from the changes in the energy difference between the FM structure and the lower-energy AFM structure. We consider three different magnetic structures [29]: FM, AFM1, AFM2 [as shown in Fig. 5(a)] to calculate the changes of energy with the lattice parameters obtained from the XRD when applying different pressures.
FIG. 5. (a) Three magnetic configurations including the ferromagnetic (FM) structure and two antiferromagnetic (AFM) structures. (b) The calculated evolution of the $T_c$ for Fe$_3$GeTe$_2$ (FGT) under pressure. The energy difference between FM and AFM2, $\Delta E = E(\text{FM}) - E(\text{AFM2})$, is calculated from the changes of the lattice parameters. The decrease in $|\Delta E|$ indicates the weakened FM coupling with applying pressure, thus the $T_c$.

The energy difference between the FM and AFM (the lowest energy) states is $\Delta E = E(\text{FM}) - E(\text{AFM2})$. A negative value of $\Delta E$ implies that the FM configuration is more stable. Neglecting the second and the third nearest neighbors and taking the exchange constant as $J$, we have

$$\Delta E = -2J|S|^2. \quad (1)$$

Here, we could choose $S = 2$ for the bulk FGT [31], and $T_c$ can be roughly estimated via mean-field expression: $T_c = 3J/2K_B$ [14]. Figure 5(b) demonstrates the calculated pressure dependence of the $T_c$. FGT keeps FM states in the range of the hydrostatic pressure applied, and the FM coupling gets weaker for the larger pressure as the value of $|\Delta E|$ decreases. This weakened FM coupling leads to the decrease of the $T_c$, and the calculation is consistent with the experimental results.

We further performed the first-principles calculation of magnetic moment for Fe ions at different pressure, as shown in Fig. 6. The magnetic moments of Fe1(Fe3) and Fe2 are defined as $M_{\text{Fe1}}$ and $M_{\text{Fe2}}$, and the average moment is named as $M_{\text{avg}}$. When the pressure increases, we obtain a decrease in the lattice parameters, as well as the reduction of $M_{\text{Fe1}}$ and $M_{\text{Fe2}}$.

From 0 to 1.7 GPa, the $M_{\text{Fe1}}$ decreases by 9.4% while $M_{\text{Fe2}}$ presents a smaller amount of shrinkage $\sim$4.7%. This might be related to a larger change in the Fe1-Fe3 bond length (2.3%) compared with the change of the Fe1-Fe2 bond length (1.4%) obtained from Table I. The direct exchange favors the AFM coupling, and it could be subtle with applying pressure. The average magnetic moment $M_{\text{avg}}$ decreases monotonically with increasing pressure from 0 to 1.7 GPa, which is consistent with our experimental result. The calculated $M_{\text{avg}}$ is larger than the observed value. This could be caused by the primitive FGT cell (Fe$_3$GeTe$_2$) used in the calculation to carry on the relaxation and self-consistency.

In summary, we studied the magnetic properties of the 2D itinerant FM FGT under hydrostatic pressures. $T_c$ decreases monotonically from 180 to 165 K as the pressure increases from 0 to 1.44 GPa, and the $M_s$ decreases by applying pressure as well. Relying on the high-pressure XRD techniques, we quantitively obtain the changes of bond lengths and bond angles of FGT at various pressures, where the Fe-Fe bond lengths decrease and Fe-Ge(Te)-Fe bond angles deviate away from 90° under the hydrostatic pressure. Our studies shed light on the evolution of the magnetic properties and lattice parameters of FGT under pressure: the variation of the $T_c$ and $M_s$ could be induced by the competition from the direct-exchange and indirect-exchange interactions, which are mainly influenced by changes in the bond lengths and bond angles. This paper also shows that applying hydrostatic pressure on the van der Waals material could efficiently tailor the structures and magnetic properties, which could help to understand the magnetic ordering and might be used for the spin manipulation of low-dimensional materials.

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