Letter

Anomalous temperature dependence of uniaxial magnetocrystalline anisotropy in the van der Waals ferromagnet Fe_3GeTe_2

Jiawei Liu,[1,*] Liang Zhou,[1,*] Shuilin Li,[1] Enyue Zhao,[2] and Nujiang Tang[1,†]

[1]*National Laboratory of Solid State Microstructures, Collaborative Innovation Center of Advanced Microstructures, and Jiangsu Provincial Key Laboratory for Nanotechnology, Nanjing University, Nanjing 210093, China*

[2]*Songshan Lake Materials Laboratory, Dongguan 523808, China*

(Received 23 March 2023; revised 1 November 2023; accepted 23 January 2024; published 12 February 2024)

Uniaxial magnetocrystalline anisotropy (UMA) is vital for fundamental research, such as maintaining two-dimensional ferromagnetic order and realizing topological phases. However, in most cases, UMA rapidly decreases with increasing temperature and finally vanishes approaching the Curie temperature (T_C). The increasing UMA with increasing temperature is very rare in almost all traditional ferromagnetic materials and in emerging van der Waals (vdW) ferromagnets, which generally have relatively low T_C. Here, we experimentally unveil the anomalous temperature dependence of the UMA constant $K_{u1}(T)$ in the vdW ferromagnet Fe_3GeTe_2. Surprisingly, the $K_{u1}(T)$ first anomalously increases and then slowly decreases. We found that the anomalous $K_{u1}(T)$ can be perfectly fitted by Carr's model. Further analysis and temperature-dependent x-ray diffraction measurements suggest that the partial localization of 3*d* electrons and considerable lattice expansion are crucial for anomalous $K_{u1}(T)$. We propose that the complex competition between the two-ion mechanism and the itinerant-electron mechanism leads to the anomalous behavior of $K_{u1}(T)$ in Fe_3GeTe_2. Our findings from this unusual case help deepen the understanding of the temperature dependence of UMA.

DOI: 10.1103/PhysRevB.109.L060404

Introduction. Magnetocrystalline anisotropy (MA) is one of the most vital characteristics inherent to ferromagnets [1]. Phenomenologically, MA makes it easy or hard for ferromagnets to be magnetized along a specific crystallographic axis or plane. On the origin of MA, there exist three interpretations. The first is the single-ion mechanism. This is based on the assumption of independent classical spins, each of which has an anisotropic energy originating from spin-orbit coupling (SOC) and the interaction between a crystalline field and a nonspherical electron cloud [2,3]. Therein, total MA is the sum of anisotropy of independent spins [3]. The second interpretation is the two-ion mechanism, which considers the exchange interaction between two spins or, say, a "spin pair" [4]. The exchange energy between spins is anisotropic because of SOC and the asymmetric overlap of orbits [5]. Therein, total MA results from the sum of anisotropic energy of spin pairs [3]. Different from the above two interpretations, both of which are localized-electron mechanisms, the third one is the itinerant-electron mechanism. Therein, (i) large orbital moments originate from the partial localization nature of itinerant 3*d* electrons, and (ii) SOC contributes to band splitting and thus increases the density of states under the Fermi level, lowering the total energy [6,7]. Due to the band splitting being sensitive to the orientation of spins, MA therefore arises.

As a typical type of MA, uniaxial magnetocrystalline anisotropy (UMA) is especially critical. For example, UMA in a two-dimensional (2D) system opens a spin-wave excitation gap and therefore stabilizes 2D long-range ferromagnetic order at finite temperature [8,9]. Moreover, competitions among UMA, Kitaev, and Heisenberg interactions in magnetic van der Waals (vdW) materials are expected to realize diverse quantum and topological phases [10]. Besides, UMA in ultrathin ferromagnetic films is especially important for spintronic applications such as high-density magnetic storage media [11]. Particularly, temperature dependence of UMA is important, not only for fundamental understanding of magnetism [12–14] but also for various applications such as spintronic memory cell [15], high-frequency devices [16], heat-assisted magnetic recording [17], and so on. In principle, the first UMA constant K_{u1} measures the degree of UMA, and typically K_{u1} rapidly decreases with increasing temperature and finally becomes zero near the Curie temperature (T_C) [18]. The theoretical description of this temperature-dependent UMA is covered by the famous Akulov-Zener-Callen-Callen (AZCC) power law [3,18,19], which is applicable for various localized-electron ferromagnets such as rare-earth compounds [20], ferrites [14], and emerging vdW ferromagnetic insulators $CrBr_3$ and CrI_3 [21]. Nevertheless, the conventional AZCC law is basically derived from the single-ion mechanism [3]. Hence, many experimental results including both localized- and itinerant-electron systems [2,14] still cannot be properly described by the AZCC law. Nonetheless, the rapidly decreasing trend of UMA is universal. As a consequence, a profound question arises naturally: Is there any ferromagnet with unusual temperature-dependent UMA against the rapidly decreasing trend?

Recently, vdW ferromagnetic metal Fe_3GeTe_2 (FGT) has drawn much attention because of its intriguing physical properties such as large anomalous Hall effect induced

*These authors contributed equally to this work.
†tangnujiang@nju.edu.cn

by topological nodal lines [22–25], Kondo lattice physics [26,27], strongly enhanced electron mass [28], electronic correlations [29], and so on [30–32]. Besides, FGT possesses relatively higher T_C than other vdW ferromagnets [33–35], which makes it a promising candidate for real applications [36–40]. Most importantly, density-functional calculations reveal that the large anisotropic energy of 920 μeV per Fe atom originating from SOC leads to significant UMA of single-layer FGT [11], which is also experimentally verified [41–43]. Notably, UMA in nanolayer FGT could be tuned by engineering the electronic structure [44,45], indicating the contribution of itinerant electrons for UMA. Furthermore, topological spin textures, e.g., skyrmions, were experimentally observed in both bulk and nanolayer FGT [46–48], implying complex competition between UMA and magnetic dipole-dipole interaction [49]. Given all the aspects above, UMA of FGT is fascinating. However, more work needs to be done on making deep investigation into temperature-dependent UMA of FGT, which is also crucial for stabilizing topological skyrmions [48] and boosting T_C [10].

Here, we experimentally investigate the temperature dependence of UMA in single-crystal FGT bulk. Surprisingly, $K_{u1}(T)$ in FGT shows anomalous behavior with first an increasing and then a slowly decreasing trend, completely differing from the AZCC law describing the continuously decreasing MA of most ferromagnets. We found that a modified model which is originally proposed by Carr and based on the two-ion and itinerant-electron mechanisms perfectly fits the anomalous $K_{u1}(T)$. Further analysis together with temperature-dependent x-ray diffraction measurements reveal that (i) partial localization of $3d$ electrons of iron in FGT slows down the decreasing trend of $K_{u1}(T)$, and (ii) considerable lattice thermal expansion leads to the increasing trend of $K_{u1}(T)$. We propose that the anomalous behavior stems from the complex competition between the two-ion mechanism and the itinerant-electron mechanism.

Results. High-quality single-crystal FGT bulks with the easy (hard) axis along the crystallographic c axis (ab plane) were grown and characterized (see Supplemental Material, Notes S1–S3, and Fig. S1 [50]). The law of approach saturation (LAS) was utilized to obtain K_{u1} together with saturated magnetization M_S at different temperatures (see Supplemental Material, Note S4, Fig. S2, and Table S1 [50]). It was found that the LAS-derived $M_S(T)$ monotonically decreases between 2 and 150 K [Fig. 1(a)]. According to either localized molecular field theory [56] or itinerant Stoner's theory [57], the decreasing $M_S(T)$ is definite due to the increasing thermal agitation k_BT, where k_B is the Boltzmann constant. Considering the weak polarization nature of itinerant $3d$ electrons of FGT as reported [11], we then fitted $M_S(T)$ with Stoner's theory for weak itinerant ferromagnetism expressed by Eq. (1) [57]:

$$M_S(T) = M_S(0)\left[1 - \frac{9N^2\mu_B^2\pi^2}{8M_S(0)^2}\left(\frac{k_BT}{E_F}\right)^2\right]. \quad (1)$$

Herein, N is the number of electrons on the conduction band, μ_B is the Bohr magneton, and E_F is Fermi energy. As shown in Fig. 1(a), Eq. (1) perfectly fits $M_S(T)$ with R^2 high up to 0.9988. Hence, Stoner's theory well describes $M_S(T)$,

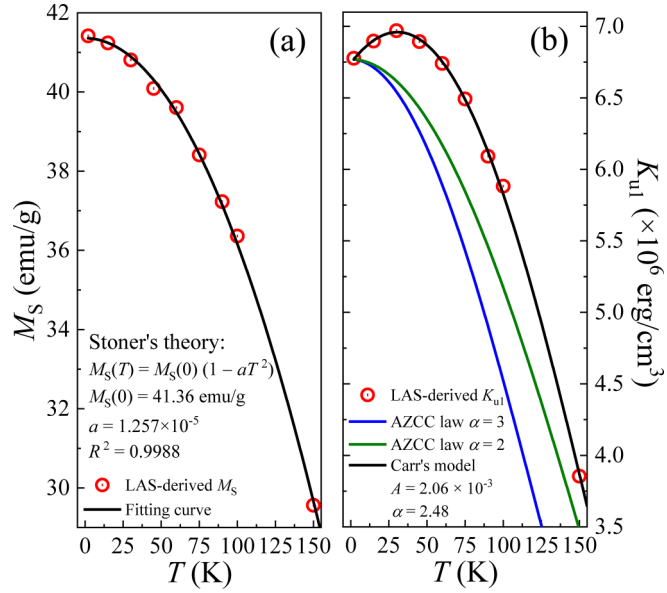

FIG. 1. Temperature-dependent LAS-derived M_S (a) and K_{u1} (b) of FGT, and corresponding fitting curves.

providing evidence that $3d$ electrons of the iron in FGT possess an itinerant nature.

With clear expression of $M_S(T)$, we next examined $K_{u1}(T)$ in FGT. According to the conventional AZCC law [3,18,19], $K_{u1}(T)$ should obey the following relationship with $M_S(T)$:

$$K_{u1}(T) = K_{u1}(0)\left[\frac{M_S(T)}{M_S(0)}\right]^{\alpha}. \quad (2)$$

Herein, the exponent α equals 3. Remarkably, the conventional AZCC law with $\alpha = 3$ is derived from the single-ion mechanism, which is completely based on the localized-electron picture. Recently, Miura and Sakuma considered the itinerant-electron mechanism and proposed that α varies from 2 to 3 depending on the localized degree of $3d$ electrons in a Rashba-type ferromagnet with UMA, such as FGT [2,58]. Namely, α equals 2 or 3 in itinerant- or localized-electron limits, respectively, and ranges from 2 to 3 for ferromagnets with partially localized $3d$ electrons. Hence, the AZCC law with variable α (between 2 and 3) involves itinerant-electron mechanisms. Anyway, regardless of the specific value of α, $K_{u1}(T)$ should have the same monotonicity with monotonic decrease as $M_S(T)$, according to Eq. (2). Unexpectedly, the LAS-derived $K_{u1}(T)$ shows completely different monotonicity compared with $M_S(T)$. It is observed that $K_{u1}(T)$ first increases between 2 and 45 K and then slowly decreases above 60 K [Fig. 1(b)]. Using the expression of $M_S(T)$ obtained above, the fitting curves of Eq. (2) with α equals 2 and 3 both largely deviate from $K_{u1}(T)$ and decrease rapidly [Fig. 1(b)]. Therefore, $K_{u1}(T)$ exhibits anomalous behavior and completely violates the AZCC law. Actually, a similar trend was also measured (but lacks deep discussion) in other works [48,59], confirming the solidity of the anomalous $K_{u1}(T)$ that we observed.

To describe the anomalous $K_{u1}(T)$, a modified model must be considered. We noted that Carr proposed a model to describe $K_{u1}(T)$ in 1958 [60]. Different from the single-ion mechanism for the AZCC law, the two-ion mechanism

proposed by van Vleck [4] and Kittel *et al.* [5] is considered for Carr's model. Specifically, Carr considered the interactions between charge distributions of atoms, which originate from orbital angular momentum, and expressed them in Coulomb energy [61]. Based on the above considerations, K_{u1} is additionally proportional to a linear term of T expressed by Eq. (3):

$$K_{u1}(T) = K_{u1}(0)(1 + AT)\left[\frac{M_S(T)}{M_S(0)}\right]^{\alpha}. \tag{3}$$

Herein, A is a factor deduced from the consideration of the two-ion mechanism and depends on lattice parameter ratio c/a and its expansion coefficient β [60–62]. In particular, the specific value of α for the $[M_S(T)/M_S(0)]^{\alpha}$ term is independent of the derivation of the $(1 + AT)$ term according to Carr's deduction [60,61]. Therefore, similar to the AZCC law, one can let α vary from 2 to 3 depending on the localized degree of $3d$ electrons. In this way, Carr's model is extended and this extension is based on the itinerant-electron mechanism. Using the expression of $M_S(T)$ obtained above, the fitting curve of Eq. (3) perfectly coincides with $K_{u1}(T)$ as shown in Fig. 1(b) with $A = 2.06\times10^{-3}$, $\alpha = 2.48$, and R^2 high up to 0.9994. In short, $K_{u1}(T)$ exhibits anomalous behavior, which can be well fitted by Carr's model. As reported, few-layer FGT is prone to oxidation and the exact magnetic property of few-layer oxidized FGT (OFGT) remains unclear [63–65]. Nevertheless, the possibility that the observed anomalous $K_{u1}(T)$ in FGT bulk is related to the possible OFGT layer magnetically coupled with the nonoxidized FGT layer can be completely excluded by our x-ray photoelectron energy spectrum results (see Supplemental Material, Note S5 and Fig. S3 [50]).

Discussion. So far, for almost all magnetic materials, the rapidly and monotonically decreasing trend of MA is universal. For instance, rare-earth compounds $CeCo_5$ [20], nickel ferrite $NiFe_2O_4$ [14], and vdW ferromagnetic insulators $CrBr_3$ and CrI_3 [21] follow the conventional AZCC law with $\alpha = 3$ derived from the single-ion mechanism. Moreover, rare-earth-free alloys such as FePt [66], FePd [67], and CoPt and FeCo [68] comply with the modified AZCC law with $\alpha = 2$ based on the itinerant-electron mechanism. Particularly, for $3d$ metals, Fe obeys the AZCC law [3,18], while the magnetocrystalline constants (MCs) of Co and Ni decrease more rapidly than the AZCC law [69,70]. As a result, the temperature-dependent MC of all these ferromagnets would decrease much more quickly than M_S. Hence, the anomalous trend of $K_{u1}(T)$ with first an increase and then a slow decrease observed in FGT is rare.

As mentioned above, α for UMA ferromagnets with partially localized $3d$ electrons would decrease from 3 to 2 according to the itinerant-electron mechanism [2,58], which would lead to a slower decreasing trend than the localized-electron system with $\alpha = 3$ and no doubt favors the anomalous increasing trend of $K_{u1}(T)$ (see Fig. 1(b) and Supplemental Material, Fig. S4 [50]). The fact that our $M_S(T)$ obeys Stoner's theory just implies that the $3d$ electrons of the iron in FGT possess an itinerant nature. Recent angle-resolved photoemission spectroscopy [71] and inelastic neutron scattering results [72] suggest that both localized magnetic moments and itinerant electrons contribute to FGT's ferromagnetism. All these results indicate that these itinerant $3d$ electrons possess a partial localization nature, which consequently leads to the observed $\alpha = 2.48(<3)$. To evaluate the localization degree of $3d$ electrons in FGT, a Rhodes-Wohlfarth plot was obtained by calculating the Rhodes-Wohlfarth ratio p_C/p_S (see Supplemental Material, Note S6 and Fig. S5 [50]). Specifically, p_C/p_S is expected to be inversely proportional to T_C for the itinerant-electron system, while it identically equals 1 regardless of T_C for localized-electron systems [73]. As revealed by the Rhodes-Wohlfarth plot (see Supplemental Material, Fig. S6 [50]), FGT distinctly locates between the line of $p_C/p_S \sim 1$ and the curve of $p_C/p_S \sim T_C^{-1}$, indicating partial localization of its $3d$ electrons. As to the origin of the partial localization of $3d$ electrons in FGT, the $3d$ electrons in $3d$ metals are treated as tight-binding itinerant electrons [74] according to Stoner's theory. Specifically, the $3d$ electrons in FGT are on a narrow band, reflecting a relatively large effective electron mass. This indicates that although $3d$ electrons are itinerant in a lattice, there are considerable chances for them to fall into the potential well of the ion on site and be localized around it. As a result, FGT would exhibit the nature of localized moments to some extent due to the partial localization of its $3d$ electrons. Even if $\alpha = 2$ in some existing itinerant-electron systems, the increasing trend of MC is still absent. Apparently, the non-negligible positive A factor is necessary for anomalous increase of $K_{u1}(T)$ in FGT.

According to Eq. (3), the major discrepancy between Carr's model and the AZCC law is the A factor originating from the two-ion mechanism. With the non-negligible positive A factor, the decreasing trend of the $[M_S(T)/M_S(0)]^{\alpha}$ term would be compensated by the $(1+AT)$ term at low temperature and $K_{u1}(T)$ may even increase if the A factor is sufficiently large. Hence, the non-negligible positive A factor for FGT is key for anomalous $K_{u1}(T)$. To figure out why FGT possesses such A factor, we examined the lattice thermal expansion coefficient β because the A factor is proportional to it (see Supplemental Material, Note S7 [50]). To obtain β, we conducted temperature-dependent x-ray diffraction measurements between 15 and 300 K on a FGT powder sample and the lattice parameters c and a were derived by Rietveld refinement (see Supplemental Material, Note S8, Fig. S7 and Tables S2–S4 [50]). Notably, c slowly increases between 15 and 60 K and rapidly increases above 60 K, while a shows a slight decreasing trend between 15 and 60 K and then suddenly increases above 60 K. The above trend collectively results in a continuously increasing trend of c/a between 15 and 300 K, leading to large β of $3.98\times10^{-6}\,\mathrm{K}^{-1}$ [Fig. 2(c)]. This large β combined with FGT's special lattice symmetry with large c/a and primitive hexagonal structure are enough to result in a non-negligible positive A factor (see Supplemental Material, Note S7 [50]).

From the discussions above, the A factor originating from the two-ion mechanism as well as lattice expansion is vital for the anomalous increasing trend of $K_{u1}(T)$ in FGT. Considering that lattice expansion would change the distance between magnetic atoms, the exchange interactions between nearest and next nearest neighbor spins would accordingly change and thus affect UMA. Therefore, having deeper insight into how the two-ion mechanism takes place at the atomic scale is necessary. As shown in the insets of Figs. 3(a) and 3(b),

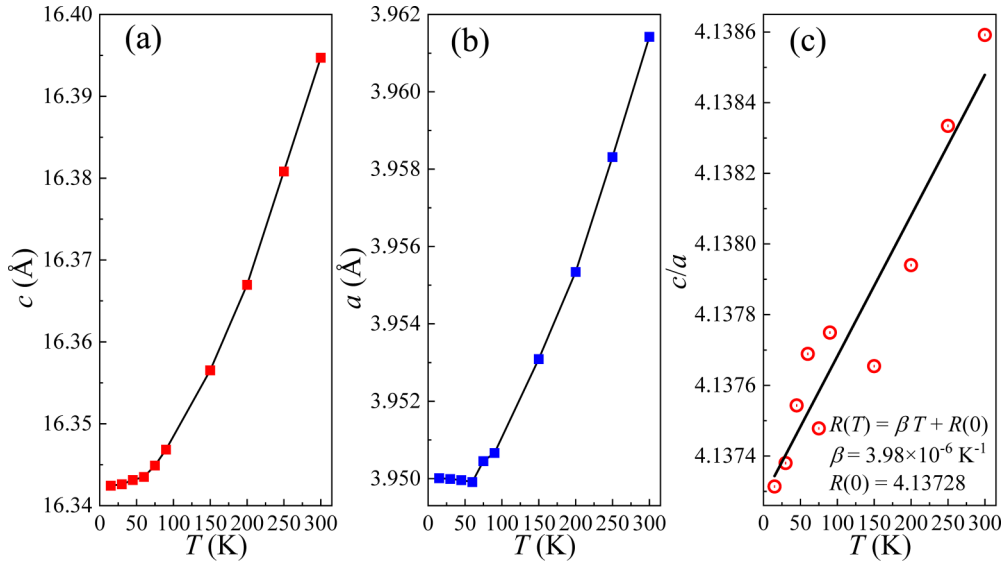

FIG. 2. Temperature-dependent c (a), a (b), and c/a. $R(T)$ in (c) represents the value of c/a at temperature T.

there are two inequivalent Fe atoms, Fe1 and Fe2, in a unit layer of FGT. The distances between two adjacent Fe1's along the c axis, and two neighboring Fe1 and two neighboring Fe2 along the ab plane are denoted as $d_{\mathrm{Fe1-Fe1}}$, and d_{Fe1} and d_{Fe2}, respectively. Notably, the temperature dependence of $d_{\mathrm{Fe1-Fe1}}$, and d_{Fe1} and d_{Fe2} have the same trend as that of lattice parameters c and a (see Supplemental Material, Note S9 [50]). As shown in Fig. 3(a), $d_{\mathrm{Fe1-Fe1}}$, whose temperature dependence is same as that of c, is as low as 2.556 Å at 15 K and monotonically increases to 2.564 Å at 300 K. Given the considerable orbital moment of 0.083 μ_B for Fe1 [75], the short $d_{\mathrm{Fe1-Fe1}}$ would lead to overlap with the $3d$ orbit of Fe1. As illustrated in Fig. 3(c), when magnetization is along the ab plane, the $3d$ orbits overlap along the c axis due to the SOC, and we denote the exchange energy as $(E_{\mathrm{ex}})_{ab} = -J\boldsymbol{S}_{\mathrm{Fe1}} \cdot \boldsymbol{S}_{\mathrm{Fe1}}$, where J represents exchange interaction and $\boldsymbol{S}_{\mathrm{Fe1}}$ is total spin angular momentum of Fe1. With increasing temperature, lattice expansion leads to a longer $d_{\mathrm{Fe1-Fe1}}$, resulting in a lower overlap degree of orbits and smaller J. Therefore, new exchange energy $(E_{\mathrm{ex}})'_{ab}$ is obviously larger than $(E_{\mathrm{ex}})_{ab}$ due to smaller J. Namely, it would be harder for magnetic moments to be magnetized along the ab plane when temperature increases due to the higher energy barrier, resulting in UMA enhancement by suppressing $ab-$plane MA. Notably, temperature dependences of d_{Fe1} and d_{Fe2}, both of which are equal to a, have temperature dependence opposite to that of $d_{\mathrm{Fe1-Fe1}}$ but would contribute similar UMA enhancement. Specifically, when magnetization is along the c axis, $3d$ orbits overlap along the ab plane [denoting exchange energy as $(E_{\mathrm{ex}})_c$] and d_{Fe1}, d_{Fe2} decrease with increasing temperature until 60 K [Fig. 3(b)]. Consequently, the J between neighboring Fe1 and Fe2 along the ab plane would increase, leading to lower exchange energy $(E_{\mathrm{ex}})'_c$ compared to $(E_{\mathrm{ex}})_c$ [Fig. 3(c)]. The lower $(E_{\mathrm{ex}})'_c$ therefore favors magnetization

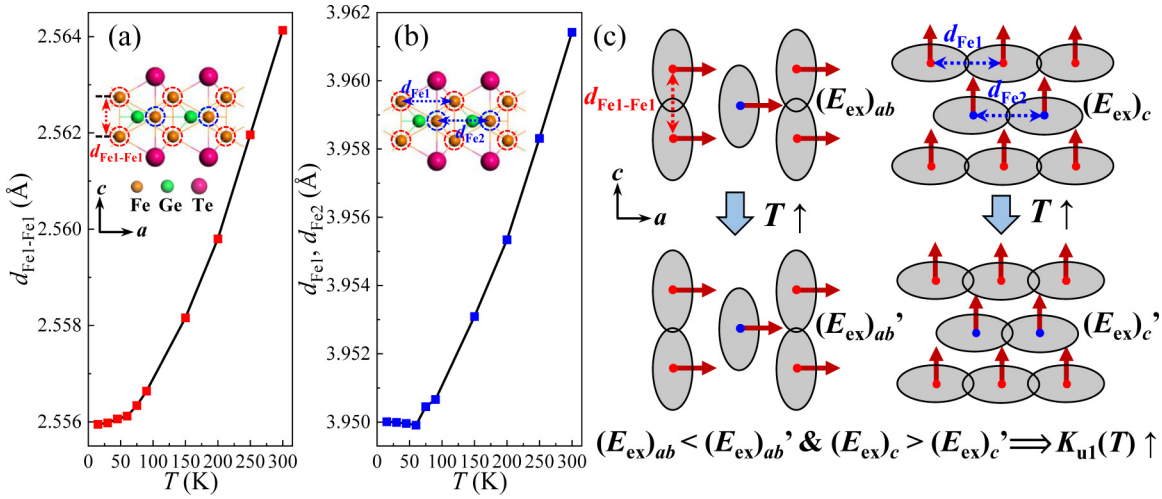

FIG. 3. Temperature-dependent $d_{\mathrm{Fe1-Fe1}}$ (a), and d_{Fe1} and d_{Fe2} (b). Insets of (a,b) are the atomic structure of a unit layer of FGT. Two inequivalent Fe atoms are respectively marked by red (Fe1) and blue (Fe2) circles. (c) Schematic illustrations of the two-ion mechanism in a unit layer of FGT. Red and blue dots represent the positions of Fe1 and Fe2. Gray ellipses represent orbits. Dark red arrows represent magnetic moments magnetized along the c axis or ab plane.

along the c axis further and thus enhances UMA. Overall, both increase on $d_{Fe1-Fe1}$ and decrease on d_{Fe1} and d_{Fe2} below 60 K contribute to the anomalous increasing of $K_{u1}(T)$. Nevertheless, with temperature further increases to higher temperature above 60 K, the $[M_S(T)/M_S(0)]^{\alpha}$ term would be considerable and thus lead to decreasing $K_{u1}(T)$ as observed despite $\alpha = 2.48$ being below 3. In short, we propose that the complex competition between the two-ion mechanism and the itinerant-electron mechanism is responsible for the anomalous temperature-dependent UMA of FGT.

Anyway, it is clear that (i) $\alpha = 2.48$ arising from partial localization of $3d$ electrons slows down the decreasing trend of $K_{u1}(T)$; while (ii) the non-negligible positive A factor arising from large β monotonically increases $K_{u1}(T)$, both of which stimulate emerging anomalous $K_{u1}(T)$ in FGT. Namely, during the increase of T, the complex competition between the enhancement term of $(1+AT)$ and the decay term $[M_S(T)/M_S(0)]^{\alpha}$ leads to this anomalous behavior. Subsequently, giving a brief analysis on why this anomalous behavior is absent in most ferromagnets is meaningful. For vdW ferromagnets CrI_3 and $Cr_2Ge_2Te_6$ [21,76], both of them are a localized-electron system with $p_C/p_S = 1$ (see Supplemental Material, Fig. S6 [50]) and would have a maximum $\alpha = 3$, which no doubt results in a large decay term $[M_S(T)/M_S(0)]^{\alpha}$ and thus sufficiently inhibits the appearance of anomalous $K_{u1}(T)$. For $3d$ metals with partially localized $3d$ electrons such as Co, rapidly decreasing temperature-dependent MC is still universal and follows the localized-electron mechanism with a maximum $\alpha = 3$ [60], which may be attributed to the strong localization nature of $3d$ electrons for their p_C/p_S close to the localized limit 1.

In addition, it should be noted that with increasing temperature, UMA typically vanishes approaching T_C [18]. Apparently, a combination of high T_C and large $K_{u1}(T)$ is significant to FGT's UMA application [18]. The anomalous decrease of lattice parameter a below 60 K [Fig. 2(b)] is interesting and is favorable to its high β, which substantively favors a non-negligible positive A factor. The decreasing lattice parameter a with increasing T just implies the shortening of d_{Fe1} and d_{Fe2} with increasing T. Inevitably, this shortening would improve exchange energy and thus contribute to high T_C of FGT because T_C is proportional to total exchange energy. Therefore, the anomalous $K_{u1}(T)$ may be considered as one of the key factors for the relatively high T_C of FGT (∼220 K) compared with other vdW ferromagnets such as $CrCl_3$ (∼16 K), $CrBr_3$ (∼31 K) [77], CrI_3 (∼68 K) [34], and $Cr_2Ge_2Te_6$ (∼66 K) [35], whose $K_{u1}(T)$ decrease rapidly. In this way, further decreasing lattice parameter a by applying mechanical or chemical strains would simultaneously improve $K_{u1}(T)$ and T_C. Furthermore, decreasing exponent α may also be effective in improving $K_{u1}(T)$ and T_C, which can be realized by gating or heteroatom doping that increase the bandwidth and thus increase the itinerant nature of the $3d$ electrons. For practical application, anomalous $K_{u1}(T)$ offers FGT high thermal stability of K_{u1}. Typically, in high-density magnetic data storage, large K_{u1} at relatively high temperature saves energy when cooling during the writing process [67]. Also, this anomalous $K_{u1}(T)$ would stimulate manipulation and understanding of the complex phase diagrams of skyrmions in FGT [48]. Besides, the good description of this anomalous behavior by the Carr's model also suggests the directions to design or search new structures with superior high-temperature UMA for high-temperature applications. Additionally, for 2D FGT with a few-layer number, the $K_{u1}(T)$ would be much more complex than that in bulk FGT due to the complex alteration on anisotropic exchange energy. This complex alteration would arise from the decreased interlayer ferromagnetic coupling range compared to the intralayer one and the different temperature dependences of c/a and β compared to bulk FGT. More importantly, 2D FGT is prone to oxidation [40], and antiferromagnetic coupling is expected for OFGT [65]. In this antiferromagnetic system, the UMA undoubtedly would vanish. Hence, detailed studies on $K_{u1}(T)$ in pristine 2D FGT are meaningful.

Conclusion. In summary, we experimentally demonstrate a rare instance of anomalous temperature-dependent UMA with first an increasing and then a slowly decreasing trend in FGT. Carr's model well fits the anomalous $K_{u1}(T)$. Further analyses indicate that (i) partial localization of $3d$ electrons of iron slows down the decreasing trend of $K_{u1}(T)$, and (ii) considerable lattice thermal expansion together with special lattice symmetry with large lattice parameter ratio c/a and primitive hexagonal structure contribute to a non-negligible positive A factor and thus to an increasing trend of $K_{u1}(T)$. We propose that the anomalous behavior stems from the complex competition between the two-ion mechanism and the itinerant-electron mechanism. The anomalous $K_{u1}(T)$ in FGT is a significant example for deeply understanding the temperature dependence of UMA.

Acknowledgments. This work was financially supported by the State Key Program for Basic Research (Grant No. 2017YFA0206304) and National Natural Science Foundation of China (Grant No. 51972166). A portion of this work was performed on the Steady High Magnetic Field Facilities, High Magnetic Field Laboratory, CAS, and Songshan Lake Materials Laboratory.

[1] R. Skomski and D. J. Sellmyer, in *Handbook of Advanced Magnetic Materials*, edited by Y. I. Liu, D. J. Sellmyer, and D. Shindo (Springer, New York, 2006), Vol. 1, pp. 1–57.
[2] D. Miura and A. Sakuma, J. Phys. Soc. Jpn. **91**, 023706 (2022).
[3] H. B. Callen and E. Callen, J. Phys. Chem. Solids **27**, 1271 (1966).
[4] J. H. van Vleck, Phys. Rev. **52**, 1178 (1937).
[5] C. Kittel, P. McEuen, and P. McEuen, *Introduction to Solid State Physics* (Wiley, New York, 1996).
[6] N. Mori, Y. Fukuda, and T. Ukai, J. Phys. Soc. Jpn. **37**, 1263 (1974).
[7] N. Mori, T. Ukai, and H. Yoshida, J. Phys. Soc. Jpn. **37**, 1272 (1974).
[8] C. Gong, L. Li, Z. Li, H. Ji, A. Stern, Y. Xia, T. Cao, W. Bao, C. Wang, Y. Wang, Z. Q. Qiu, R. J. Cava, S. G. Louie, J. Xia, and X. Zhang, Nature (London) **546**, 265 (2017).
[9] C. Gong and X. Zhang, Science **363**, eaav4450 (2019).
[10] K. S. Burch, D. Mandrus, and J. G. Park, Nature (London) **563**, 47 (2018).

[11] H. L. Zhuang, P. R. C. Kent, and R. G. Hennig, Phys. Rev. B **93**, 134407 (2016).

[12] J. B. Staunton, S. Ostanin, S. S. A. Razee, B. L. Gyorffy, L. Szunyogh, B. Ginatempo, and E. Bruno, Phys. Rev. Lett. **93**, 257204 (2004).

[13] S. D. Pappas, V. Kapaklis, A. Delimitis, P. E. Jönsson, E. Th. Papaioannou, P. Poulopoulos, P. Fumagalli, D. Trachylis, M. J. Velgakis, and C. Politis, J. Appl. Phys. **112**, 053918 (2012).

[14] B. K. Chatterjee, C. K. Ghosh, and K. K. Chattopadhyay, J. Appl. Phys. **116**, 153904 (2014).

[15] S. Ikeda, K. Miura, H. Yamamoto, K. Mizunuma, H. D. Gan, M. Endo, S. Kanai, J. Hayakawa, F. Matsukura, and H. Ohno, Nat. Mater. **9**, 721 (2010).

[16] S. X. Wang, N. X. Sun, M. Yamaguchi, and S. Yabukami, Nature (London) **407**, 150 (2000).

[17] W. A. Challener, C. B. Peng, A. V. Itagi, D. Karns, W. Peng, Y. G. Peng, X. M. Yang, X. B. Zhu, N. J. Gokemeijer, Y.-T. Hsia, G. Ju, R. E. Rottmayer, M. A. Seigler, and E. C. Gage, Nat. Photon. **3**, 220 (2009).

[18] C. Zener, Phys. Rev. **96**, 1335 (1954).

[19] N. Akulov, Z. Phys. **100**, 197 (1936).

[20] H. P. Klein, A. Menth, and R. S. Perkins, Physica B+C (Amsterdam) **80**, 153 (1975).

[21] N. Richter, D. Weber, F. Martin, N. Singh, U. Schwingenschlögl, B. V. Lotsch, and M. Kläui, Phys. Rev. Mater. **2**, 024004 (2018).

[22] Y. R. You, Y. Y. Gong, H. Li, Z. F. Li, M. M. Zhu, J. X. Tang, E. K. Liu, Y. Yao, G. Z. Xu, F. Xu, and W. H. Wang, Phys. Rev. B **100**, 134441 (2019).

[23] Y. H. Wang, C. Xian, J. Wang, B. J. Liu, L. S. Ling, L. Zhang, L. Cao, Z. Qu, and Y. M. Xiong, Phys. Rev. B **96**, 134428 (2017).

[24] K. Kim, J. Seo, E. Lee, K. T. Ko, B. S. Kim, B. G. Jang, J. M. Ok, J. Lee, Y. J. Jo, W. Kang, J. H. Shim, C. Kim, H. W. Yeom, B. Il Min, B. J. Yang, and J. S. Kim, Nat. Mater. **17**, 794 (2018).

[25] Y. Liu, E. Stavitski, K. Attenkofer, and C. Petrovic, Phys. Rev. B **97**, 165415 (2018).

[26] Y. Zhang, H. Y. Lu, X. G. Zhu, S. Y. Tan, W. Feng, Q. Liu, W. Zhang, Q. Y. Chen, Y. Liu, X. B. Luo, D. H. Xie, L. Z. Luo, Z. J. Zhang, and X. C. Lai, Sci. Adv. **4**, eaao6791 (2018).

[27] M. Zhao, B. B. Chen, Y. Xi, Y. Zhao, H. Xu, H. Zhang, N. Cheng, H. Feng, J. Zhuang, F. Pan, X. Xu, W. Hao, W. Li, S. Zhou, S. X. Dou, and Y. Du, Nano Lett. **21**, 6117 (2021).

[28] J.-X. Zhu, M. Janoschek, D. S. Chaves, J. C. Cezar, T. Durakiewicz, F. Ronning, Y. Sassa, M. Mansson, B. L. Scott, N. Wakeham, E. D. Bauer, and J. D. Thompson, Phys. Rev. B **93**, 144404 (2016).

[29] M. Corasaniti, R. Yang, K. Sen, K. Willa, M. Merz, A. A. Haghighirad, M. Le Tacon, and L. Degiorgi, Phys. Rev. B **102**, 161109(R) (2020).

[30] N.-T. Dang, D. P. Kozlenko, O. N. Lis, S. E. Kichanov, Y. V. Lukin, N. O. Golosova, B. N. Savenko, D.-L. Duong, T.-L. Phan, T.-A. Tran, and M.-H. Phan, Adv. Sci. **10**, 2206842 (2023).

[31] D. Rana, A. R, B. G, C. Patra, S. Howlader, R. R. Chowdhury, M. Kabir, R. P. Singh, and G. Sheet, Phys. Rev. B **106**, 085120 (2022).

[32] Y. Sun, J. Zhang, T. Yao, X. F. Sun, S.-H. Ke, J. Zhang, and S. M. Zhou, Phys. Rev. B **107**, 094416 (2023).

[33] H.-J. Deiseroth, K. Aleksandrov, C. Reiner, L. Kienle, and R. K. Kremer, Eur. J. Inorg. Chem. **2006**, 1561 (2006).

[34] M. A. McGuire, H. Dixit, V. R. Cooper, and B. C. Sales, Chem. Mater. **27**, 612 (2015).

[35] Y. Liu and C. Petrovic, Phys. Rev. B **96**, 054406 (2017).

[36] Y. Wang, C. Wang, S. J. Liang, Z. Ma, K. Xu, X. Liu, L. Zhang, A. S. Admasu, S. W. Cheong, L. Wang, M. Chen, Z. Liu, B. Cheng, W. Ji, and F. Miao, Adv. Mater. **32**, 2004533 (2020).

[37] K. Zhang, S. Han, Y. Lee, M. J. Coak, J. Kim, I. Hwang, S. Son, J. Shin, M. Lim, D. Jo, K. Kim, D. Kim, H. W. Lee, and J. G. Park, Adv. Mater. **33**, 2004110 (2021).

[38] X. Wang, J. Tang, X. X. Xia, C. L. He, J. W. Zhang, Y. Z. Liu, C. H. Wan, C. Fang, C. Y. Guo, W. L. Yang, Y. Guang, X. M. Zhang, H. J. Xu, J. W. Wei, M. Z. Liao, X. B. Lu, J. F. Feng, X. X. Li, Y. Peng, H. X. Wei *et al.*, Sci. Adv. **5**, eaaw8904 (2019).

[39] Ø. Johansen, V. Risinggard, A. Sudbo, J. Linder, and A. Brataas, Phys. Rev. Lett. **122**, 217203 (2019).

[40] F. Martin, K. Lee, M. Schmitt, A. Liedtke, A. Shahee, H. T. Simensen, T. Scholz, T. G. Saunderson, D. Go, M. Gradhand, Y. Mokrousov, T. Denneulin, A. Kovács, B. Lotsch, A. Brataas, and M. Kläui, Mater. Res. Lett. **11**, 84 (2022).

[41] C. Tan, J. Lee, S. G. Jung, T. Park, S. Albarakati, J. Partridge, M. R. Field, D. G. McCulloch, L. Wang, and C. Lee, Nat. Commun. **9**, 1554 (2018).

[42] Z. Y. Fei, B. Huang, P. Malinowski, W. B. Wang, T. C. Song, J. Sanchez, W. Yao, D. Xiao, X. Y. Zhu, A. F. May, W. D. Wu, D. H. Cobden, J.-H. Chu, and X. D. Xu, Nat. Mater. **17**, 778 (2018).

[43] Y. Deng, Y. Yu, Y. Song, J. Zhang, N. Z. Wang, Z. Sun, Y. Yi, Y. Z. Wu, S. Wu, J. Zhu, J. Wang, X. H. Chen, and Y. Zhang, Nature (London) **563**, 94 (2018).

[44] S. Y. Park, D. S. Kim, Y. Liu, J. Hwang, Y. Kim, W. Kim, J. Y. Kim, C. Petrovic, C. Hwang, S. K. Mo, H. J. Kim, B. C. Min, H. C. Koo, J. Chang, C. Jang, J. W. Choi, and H. Ryu, Nano Lett. **20**, 95 (2020).

[45] B. Liu, S. S. Liu, L. Yang, Z. D. Chen, E. Z. Zhang, Z. H. Li, J. Wu, X. Z. Ruan, F. X. Xiu, W. Q. Liu, L. He, R. Zhang, and Y. B. Xu, Phys. Rev. Lett. **125**, 267205 (2020).

[46] M. J. Meijer, J. Lucassen, R. A. Duine, H. J. M. Swagten, B. Koopmans, R. Lavrijsen, and M. H. D. Guimaraes, Nano Lett. **20**, 8563 (2020).

[47] B. Ding, Z. F. Li, G. Z. Xu, H. Li, Z. P. Hou, E. K. Liu, X. K. Xi, F. Xu, Y. Yao, and W. H. Wang, Nano Lett. **20**, 868 (2020).

[48] M. T. Birch, L. Powalla, S. Wintz, O. Hovorka, K. Litzius, J. C. Loudon, L. A. Turnbull, V. Nehruji, K. Son, C. Bubeck, T. G. Rauch, M. Weigand, E. Goering, M. Burghard, and G. Schutz, Nat. Commun. **13**, 3035 (2022).

[49] Q. Li, M. Yang, C. Gong, R. V. Chopdekar, A. T. N'Diaye, J. Turner, G. Chen, A. Scholl, P. Shafer, E. Arenholz, A. K. Schmid, S. Wang, K. Liu, N. Gao, A. S. Admasu, S. W. Cheong, C. Hwang, J. Li, F. Wang, X. Zhang *et al.*, Nano Lett. **18**, 5974 (2018).

[50] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.109.L060404 for details of preparation and characterizations of single-crystal FGT, details of characterization, LAS measurements, XPS measurements, calculation of Rhodes-Wohlfarth ratio, a brief description of Carr's model, and the temperature-dependent x-ray diffraction measurements. The Supplemental Material also contains Refs. [51–55].

[51] L. M. Zhang, X. Y. Huang, H. W. Dai, M. S. Wang, H. Cheng, L. Tong, Z. Li, X. T. Han, X. Wang, L. Ye, and J. B. Han, Adv. Mater. **32**, 2002032 (2020).

[52] A. F. May, S. Calder, C. Cantoni, H. Cao, and M. A. McGuire, Phys. Rev. B **93**, 014411 (2016).
[53] J. J. Liu, W. J. Ren, Z. D. Zhang, D. Li, J. Li, X. G. Zhao, W. Liu, and S. W. Or, J. Appl. Phys. **100**, 023904 (2006).
[54] J. F. Herbst and F. E. Pinkerton, Phys. Rev. B **57**, 10733 (1998).
[55] E. P. Wohlfarth, J. Magn. Magn. Mater. **7**, 113 (1978).
[56] J. S. Smart, *Effective Field Theories of Magnetism* (Saunders, Philadelphia, PA, 1966).
[57] E. C. Stoner, Proc. R. Soc. London **165**, 372 (1938).
[58] D. Miura and A. Sakuma, J. Phys. Soc. Jpn. **90**, 113601 (2021).
[59] Y. Liu, J. Li, J. Tao, Y. Zhu, and C. Petrovic, Sci. Rep. **9**, 13233 (2019).
[60] W. J. Carr, Phys. Rev. **109**, 1971 (1958).
[61] W. J. Carr, Phys. Rev. **108**, 1158 (1957).
[62] L. W. McKeehan, Phys. Rev. **52**, 18 (1937).
[63] D. S. Kim, J. Y. Kee, J.-E. Lee, Y. Liu, Y. Kim, N. Kim, C. Hwang, W. Kim, C. Petrovic, D. R. Lee, C. Jang, H. Ryu, and J. W. Choi, Curr. Appl. Phys. **30**, 40 (2021).
[64] Y. Wu, W. Wang, L. Pan, and K. L. Wang, Adv. Mater. **34**, 2105266 (2022).
[65] M.-H. Phan, V. Kalappattil, V. O. Jimenez, Y. Thi Hai Pham, N. W. Y. A. Y. Mudiyanselage, D. Detellem, C.-M. Hung, A. Chanda, and T. Eggers, J. Alloys Compd. **937**, 168375 (2023).
[66] S. Okamoto, N. Kikuchi, O. Kitakami, T. Miyazaki, Y. Shimada, and K. Fukamichi, Phys. Rev. B **66**, 024413 (2002).
[67] J. B. Staunton, L. Szunyogh, A. Buruzs, B. L. Gyorffy, S. Ostanin, and L. Udvardi, Phys. Rev. B **74**, 144411 (2006).
[68] N. Kobayashi, K. Hyodo, and A. Sakuma, Jpn. J. Appl. Phys. **55**, 100306 (2016).
[69] F. Ono, J. Phys. Soc. Jpn. **43**, 1194 (1977).
[70] F. Ono and O. Yamada, J. Phys. Soc. Jpn. **46**, 462 (1979).
[71] X. Xu, Y. W. Li, S. R. Duan, S. L. Zhang, Y. J. Chen, L. Kang, A. J. Liang, C. Chen, W. Xia, Y. Xu, P. Malinowski, X. D. Xu, J. H. Chu, G. Li, Y. F. Guo, Z. K. Liu, L. X. Yang, and Y. L. Chen, Phys. Rev. B **101**, 201104(R) (2020).
[72] S. Bao, W. Wang, Y. Y. Shangguan, Z. W. Cai, Z. Dong, Z. T. Huang, W. D. Si, Z. Ma, R. Kajimoto, K. Ikeuchi, S. Yano, S. Yu, X. G. Wan, J.-X. Li, and J. S. Wen, Phys. Rev. X **12**, 011022 (2022).
[73] P. Rhodes and E. P. Wohlfarth, Proc. R. Soc. London **273**, 247 (1963).
[74] J. Hubbard, Proc. R. Soc. A **296**, 82 (1967).
[75] S. Laref, K.-W. Kim, and A. Manchon, Phys. Rev. B **102**, 060402(R) (2020).
[76] X. Zhang, Y. L. Zhao, Q. Song, S. Jia, J. Shi, and W. Han, Jpn. J. Appl. Phys. **55**, 033001 (2016).
[77] M. Abramchuk, S. Jaszewski, K. R. Metz, G. B. Osterhoudt, Y. Wang, K. S. Burch, and F. Tafti, Adv. Mater. **30**, 1801325 (2018).