Anisotropic magnetocaloric effect in Fe$_{3-x}$GeTe$_2$

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ABSTRACT

Fe$_{3-x}$GeTe$_2$ is a novel weak-itinerant van der Waals ferromagnet that features gate-tunable room-temperature ferromagnetism in atomically thin crystal and great potential for engineering spintronic devices. The magnetocrystalline anisotropy is established, which could be the origin of long-range ferromagnetism in few-layers of Fe$_{3-x}$GeTe$_2$. The magnetic entropy change $\Delta S_M$ of bulk single crystals is investigated by heat capacity and dc magnetization measurements. The peak value $-\Delta S_M^{\max} \sim 1.20$ J kg$^{-1}$ K$^{-1}$ and the corresponding adiabatic temperature change $\Delta T_{ad} \sim 0.66$ K are obtained from heat capacity analysis with out-of-plane field change of 5 T. Anisotropic $-\Delta S_M$ was further studied by isothermal magnetization. The $-\Delta S_M(T, H)$ can be well scaled into a universal curve. The $-\Delta S_M^{\max}$ follows the power law of $H^n$ with $n = 0.603(6)$, and the relative cooling power RCP depends on $H^m$ with $m = 1.20(1)$.

Introduction

Intrinsic long-range ferromagnetism recently achieved in atomically thin van der Waals (vdW) crystals opens up great possibilities for both studying fundamental two-dimensional (2D) magnetism and engineering novel spintronic vdW heterostructures.$^{1-5}$ Fe$_3$GeTe$_2$ is a promising candidate since its Curie temperature ($T_c$) in bulk is high, ranging from 150 to 230 K depending on Fe occupancy.$^{6,10}$ Intrinsic magnetocrystalline anisotropy in monolayer counteracts thermal fluctuation and preserves the 2D long-range ferromagnetism with a lower $T_c$ of 130 K.$^5$ Most significantly, the $T_c$ can be ionic-gate-tuned to room temperature in few-layers which is of high interest for electrically controlled magnetoelectronic devices.$^{11}$

Fe$_3$GeTe$_2$ has a layered structure which contains Fe$_3$Ge slabs separated by the vdW bonded Te layers crystalized in the $P6_3/mmc$ space group [Fig. 1(a)].$^6$ The Fe atoms occupy two inequivalent Wyckoff positions; Fe1 situated in a hexagonal net in a layer with only Fe atoms and Fe2 covalently bonded with Ge atoms in an adjacent layer. No Fe atoms occupy the interlayer space and Fe vacancies only occur in the Fe2 sites.$^{12}$ Local atomic environment is also studied by Mössbauer and x-ray absorption spectroscopies.$^{13,14}$ Partially filled Fe $d$ orbitals dominate the band structure near the Fermi level, and give rise to itinerant ferromagnetism in Fe$_3$GeTe$_2$,$^{15}$ in line with the critical analysis.$^{16}$ A second-step satellite transition $T''$ is also observed just below $T_c$, and is not fully understood.$^{10,14}$ In addition to a large out-of-plane anisotropy, the strong electron correlation effect and Kondo lattice physics have been discussed.$^{17,18}$

Here we address the anisotropy in Fe$_{3-x}$GeTe$_2$ as well as the magnetocaloric effect investigated by heat capacity and dc magnetization measurements. Isothermal magnetic entropy change $\Delta S_M(T, H)$ can be well scaled into a universal curve independent on temperature and field. Moreover, the $\Delta S_M$ follows the power law of $H^n$ [$n = dln | \Delta S_M | /dln(H)$]. The temperature dependence of $n$ reaches a minimum at $T \sim 154$ K, at $T_c$ of bulk Fe$_{3-x}$GeTe$_2$.

Methods

High quality Fe$_{3-x}$GeTe$_2$ single crystals were grown by the self-flux technique starting from an intimate mixture of pure elements Fe (99.99%, Alfa Aesar) powder, Ge (99.999%, Alfa Aesar) pieces, and Te (99.9999%, Alfa Aesar) pieces with a molar ratio of 2 : 1 : 4. The starting materials were sealed in an evacuated quartz tube, which was heated to 1000 °C over 20 h, held at 1000 °C for 3 h, and then slowly cooled to 680 °C at a rate of 1 °C/h. The element analysis was performed using energy-dispersive x-ray spectroscopy (EDX) in a JEOL LSM-6500 scanning electron microscope (SEM). The selected area electron diffraction pattern was taken via a double aberration-corrected JEOL-ARM200F operated at 200 kV. The dc magnetization and heat capacity were measured in Quantum Design MPMS-XL5 and PPMS-9 systems with the field up to 5 T.

Results and Discussion

The stoichiometry of our flux-grown Fe$_{3-x}$GeTe$_2$ single crystals measured by examination of multiple points using x-ray energy-dispersive spectroscopy is determined to be Fe$_{2.64(6)}$Ge$_{0.87(4)}$Te$_2$ [Fig. 1(b)], and it is referred to as Fe$_{3-x}$GeTe$_2$.
throughout this paper. The as-grown single crystals are mirror-like and metallic platelets with the crystallographic $c$ axis perpendicular to the platelet surface with dimensions up to 10 millimeters [inset in Fig. 1(b)]. In the single-crystal 2θ x-ray diffraction pattern [Fig. 1(c)], only the (00$l$) peaks are detected, confirming the crystal surface is normal to the $c$ axis. The corresponding electron diffraction pattern [inset in Fig. 1(c)] also confirms the high quality of single crystals.

Figure 1(d) presents the low temperature thermal demagnetization analysis for Fe$_{3-x}$GeTe$_2$ with out-of-plane field using both spin-wave (SW) model and single-particle (SP) model. The temperature dependence of zero-field-cooling (ZFC) magnetization of Fe$_{3-x}$GeTe$_2$ measured at $H = 1$ T applied along the $c$ axis is shown in the inset of Fig. 1(d).

Localized-moment spin-wave excitations can be described by a Bloch equation:

$$\frac{\Delta M}{M(0)} = \frac{M(0) - M(T)}{M(0)} = AT^{3/2} + BT^{5/2} + \ldots,$$

where $A$ and $B$ are the coefficients. The $M(0)$ is the magnetization at 0 K, which is usually estimated from the extrapolation of $M(T)$. The $T^{3/2}$ term stems from harmonic contribution and the $T^{5/2}$ term is a high-order contribution in spin-wave dispersion relation. In an itinerant magnetism, it is a result of excitation of electrons from one subband to the other. The single-particle excitation is:

$$\frac{\Delta M}{M(0)} = \frac{M(0) - M(T)}{M(0)} = CT^{3/2} \exp \left( -\frac{\Delta}{k_B T} \right),$$

where $C$, $\Delta$ and $k_B$ are fit coefficient, the energy gap between the Fermi level and the top of the full subband and the Boltzmann constant, respectively. It can be seen that the SW model gives a better fit than the SP model up to 0.9 $T_c$ [Fig. 1(d)], indicating possible localized moment, in agreement with the bad-metallic resistivity of Fe$_{3-x}$GeTe$_2$. It is also understandable that the SP model fails due to strong electron correlation in Fe$_{3-x}$GeTe$_2$. The fitting yields $A = 8.4(7) \times 10^{-5}$ K$^{-3/2}$, $B = 1.24(5) \times 10^{-6}$ K$^{-5/2}$, $C = 3.4(1) \times 10^{-4}$ K$^{-3/2}$ and $\Delta = 3.9(4)$ meV.

Figure 2(a) shows the temperature dependence of heat capacity $C_p$ for Fe$_{3-x}$GeTe$_2$ measured in zero-field and out-of-plane field of 2 and 5 T, respectively. The ferromagnetic order anomaly at $T_c = 153$ K in the absence of magnetic field is gradually suppressed in fields. The entropy $S(T, H)$ can be determined by

$$S(T, H) = \int_0^T \frac{C_p(T, H)}{T} dT.$$
The magnetic entropy change $\Delta S_M(T, H)$ can be approximated as $\Delta S_M(T, H) = S_M(T, H) - S_M(T, 0)$. In addition, the adiabatic temperature change $\Delta T_{ad}$ caused by the field change can be derived by $\Delta T_{ad}(T, H) = T(S, H) - T(S, 0)$ at constant total entropy $S(T, H)$. Figures 2(b) and 2(c) present the temperature dependence of $-\Delta S_M$ and $\Delta T_{ad}$ estimated from heat capacity with out-of-plane field. They are asymmetric and attain a peak around $T_c$. The maxima of $-\Delta S_M$ and $\Delta T_{ad}$ increase with increasing field and reach the values of 1.20 J kg$^{-1}$ and 0.66 K, respectively, with the field change of 5 T. Since a large magnetic anisotropy is observed in Fe$_{3-x}$GeTe$_2$, it is of interest to further calculate its anisotropic magnetic entropy change.

Figures 3(a) and 3(b) present the magnetization isotherms with field up to 5 T applied in the $ab$ plane and along the $c$ axis, respectively, in temperature range from 100 to 200 K with a temperature step of 4 K. The magnetic entropy change can be obtained from dc magnetization measurement as:\textsuperscript{22}

$$\Delta S_M(T, H) = \int_0^H \left[ \frac{\partial S(T, H)}{\partial H} \right]_T dH. \quad (4)$$

With the Maxwell’s relation $\left[ \frac{\partial S(T, H)}{\partial H} \right]_T = \left[ \frac{\partial M(T, H)}{\partial T} \right]_H$, it can be rewritten as:\textsuperscript{23}

$$\Delta S_M(T, H) = \int_0^H \left[ \frac{\partial M(T, H)}{\partial T} \right]_H dH. \quad (5)$$

When the magnetization is measured at small temperature and field steps, $\Delta S_M(T, H)$ is approximated:

$$\Delta S_M(T, H) = \int_0^H \frac{M(T + \Delta T) dH - \int_0^H M(T) dH}{\Delta T}. \quad (6)$$

Figures 3(c) and 3(d) show the calculated $-\Delta S_M(T, H)$ as a function of temperature in various fields up to 5 T applied in the $ab$ plane and along the $c$ axis, respectively. All the $-\Delta S_M(T, H)$ curves feature a pronounced peak around $T_c$, similar to those obtained from heat capacity [Fig. 2(b)], and the peak broadens asymmetrically on both sides with increase in field. Moreover, the value of $-\Delta S_M(T, H)$ increases monotonically with increase in field; the peak $-\Delta S_M$ reaches 1.26 J kg$^{-1}$ K$^{-1}$ with in-plane field change and 1.44 J kg$^{-1}$ K$^{-1}$ with out-of-plane change of 5 T, respectively. We calculated the rotating magnetic entropy change $\Delta S_M^R$ as

$$\Delta S_M^R(T, H) = \Delta S_M(T, H_c) - \Delta S_M(T, H_{ab}). \quad (7)$$

The asymmetry of $-\Delta S_M(T, H)$ is more apparent in the temperature dependence of $-\Delta S_M^R$ [Fig. 3(e)]. Furthermore, there is a slight shift of $-\Delta S_M$ maximum towards higher temperature when the field varies from 1 to 5 T [Figs. 3(c) and 3(d)]. This shift of $T_{peak}$ excludes the mean field model but could be reproduced by the Heisenberg model due to its discrepancy with $T_c$\textsuperscript{24}.

Around the second order phase transition,\textsuperscript{25} the magnetic entropy maximum change is $-\Delta S_M^{max} = aH^n$,\textsuperscript{26} where $a$ is a constant and $n$ is\textsuperscript{27}

$$n(T, H) = d\ln |\Delta S_M| / d\ln(H). \quad (8)$$
Figure 3. (Color online). Initial isothermal magnetization curves from $T = 100$ to $200$ K with temperature step of $T = 4$ K measured with (a) in-plane and (b) out-of-plane fields. Temperature dependence of magnetic entropy change $-\Delta S_M$ obtained with (c) in-plane and (d) out-of-plane field changes, and (e) the difference $-\Delta S_M^R$.

Figure 4. (Color online). (a) Temperature dependence of $n$ in various fields. (b) Field dependence of the maximum magnetic entropy change $-\Delta S_M^{max}$ and the relative cooling power RCP with power law fitting in red solid lines. (c) The normalized $\Delta S_M$ as a function of the rescaled temperature $\theta$ with out-of-plane field and in-plane field (inset). (d) Scaling plot based on the critical exponents $\beta = 0.372$ and $\gamma = 1.265$.\textsuperscript{13}
Figure 4(a) shows the temperature dependence of \( n(T) \) in various fields. All the \( n(T) \) curves follow an universal behavior. At low temperatures, \( n \) has a value close to 1. At high temperatures, \( n \) tends to 2 as a consequence of the Curie-Weiss law. At \( T = T_c \), \( n \) has a minimum. Additionally, the exponent \( n \) at \( T_c \) is related to the critical exponents:  

\[
n(T_c) = 1 + \left( \frac{\beta - 1}{\beta + \gamma} \right) = 1 + \frac{1}{\delta} \left( 1 - \frac{1}{\beta} \right),
\]

where \( \beta, \gamma, \) and \( \delta \) are the critical exponents related to the spontaneous magnetization \( M_s \) below \( T_c \), the inverse initial susceptibility \( 1/H/M \) above \( T_c \), and the isotherm \( M(H) \) at \( T_c \), respectively.

Relative cooling power (RCP) could be used to estimate the cooling efficiency:

\[
RCP = -\Delta S_M^{max} \times \delta T_{FWHM},
\]

where \( -\Delta S_M^{max} \) is the entropy change maximum around \( T_c \) and \( \delta T_{FWHM} \) is the width at half maximum. The RCP also depends on the field as \( RCP = bH^m \), where \( b \) is a constant and \( m \) is related to the critical exponent \( \delta \):

\[
m = 1 + \frac{1}{\delta}.
\]

Figure 4(b) presents the field-dependent \( -\Delta S_M^{max} \) and RCP. The RCP is 113.3 J kg\(^{-1}\) within field change of 5 T for Fe\(_{3-x}\)GeTe\(_2\). This is one half of those in manganites and much lower than in ferrites.  

Fitting of the \( -\Delta S_M^{max} \) and RCP gives \( n = 0.603(6) \) and \( m = 1.20(1) \), which are close to the values estimated from the critical exponents (Table I).

| Technique | \( \beta \)      | \( \gamma \)    | \( \delta \)    | \( n \)       | \( m \)       |
|-----------|-----------------|-----------------|-----------------|--------------|--------------|
| \( -\Delta S_M^{max} \) | 0.374(1)        | 1.273(8)        | 4.404(12)       | 0.620(1)     | 1.227(1)     |
| RCP       | 0.372(4)        | 1.265(15)       | 4.401(6)        | 0.616(2)     | 1.227(1)     |
| MAP       | 0.603(6)        |                 |                 |              |              |
| CI        | 4.50(1)         |                 |                 |              |              |

Table 1. Critical exponents of Fe\(_{3-x}\)GeTe\(_2\). The MAP, KFP and CI represent the modified Arrott plot, the Kouvel-Fisher plot and the critical isotherm, respectively.

The scaling of magnetocaloric data is constructed by normalizing all the \( -\Delta S_M \) curves against the maximum \( -\Delta S_M^{max} \), namely, \( \Delta S_M/\Delta S_M^{max} \) by rescaling the temperature \( \theta \) below and above \( T_c \) as defined in:

\[
\theta^- = (T_{peak} - T)/(T_{r1} - T_{peak}), T < T_{peak},
\]

\[
\theta^+ = (T - T_{peak})/(T_{r2} - T_{peak}), T > T_{peak},
\]

where \( T_{r1} \) and \( T_{r2} \) are the temperatures of two reference points corresponding to \( \Delta S_M(T_{r1}, T_{r2}) = \frac{1}{2} \Delta S_M^{max} \). All the \( -\Delta S_M(T, H) \) curves collapse onto a single curve regardless of temperature and field, as shown in Fig. 4(c). In the phase transition region, the scaling analysis of \( -\Delta S_M \) can also be expressed as

\[
-\frac{\Delta S_M}{a_M} = H^n f\left( \frac{\theta}{H^{1/2}} \right),
\]

where \( a_M = T_c^{-1}A^{\delta+1}B \) with \( A \) and \( B \) representing the critical amplitudes as in \( M_s(T) = A(-\theta)^\beta \) and \( H = BM^\delta \), \( \Delta = \beta + \gamma \), and \( f(x) \) is the scaling function.  

If the critical exponents are appropriately chosen, the \( -\Delta S_M(T) \) curves should be rescaled into a single curve, consistent with normalizing all the \( -\Delta S_M \) curves with two reference temperatures. By using the values of \( \beta = 0.372 \) and \( \gamma = 1.265 \) obtained by the Kouvel-Fisher plot, we have replotted the scaled \( -\Delta S_M \) for Fe\(_{3-x}\)GeTe\(_2\) [Fig. 4(d)]. The good overlap of the experimental data points clearly indicates that the obtained critical exponents for Fe\(_{3-x}\)GeTe\(_2\) are not only in agreement with the scaling hypothesis but also intrinsic.

Then we estimated the magnetocrystalline anisotropy of Fe\(_{3-x}\)GeTe\(_2\). The saturation magnetic field \( H_s \) is a direct measurement of the magnetocrystalline anisotropy, which contributes to the total micromagnetic energy density with a term \( E_A = K_u sin^2(\theta - \varphi) \). The \( K_u \) denotes the uniaxial anisotropy constant, \( \theta \) is the direction of the preferred magnetization,
and $\varphi$ is the direction in which the magnetization points, and when $\theta - \varphi = 90^\circ$ ($H//ab$) the effect of the magnetocrystalline anisotropy reaches maximal. Based on the Stoner-Wohlfarth model, the anisotropy constant can be derived via

$$\frac{2K_u}{M_s} = \mu_0 H_{sat},$$

(15)

where $\mu_0$ is the vacuum permeability. We estimated the saturation magnetization $M_s$ by using a linear fit of $M(H)$ above a magnetic field of 2.5 T with in-plane field [Fig. 5(b)], which monotonically decreases with increasing temperature. Then we determined $dM/dH$ in low-field regime and the intersection point of these two lines yields the values of $H_s$ [Fig. 5(c)]. The value of $H_s$ increases at low temperature, which is possibly related to a spin reorientation transition, and then decreases with increasing temperature. Figure 5(d) presents the temperature dependence of $K_u$ for Fe$_{3-x}$GeTe$_2$, which can not be described by the $l(l + 1)/2$ power law. The value of $K_u$ for Fe$_{3-x}$GeTe$_2$ is about 69 kJ cm$^{-3}$ at 10 K, slightly increases to 78 kJ cm$^{-3}$ at 50 K, and then decrease with increasing temperature, which are comparable to those for CrBr$_3$, but smaller than those for CrI$_3$. In the theory developed by Zener and Carr, the decrease of $K_u$ with increasing temperature arises solely from a large number of local spin clusters. Clusters fluctuate randomly around the macroscopic magnetization vector, activated by nonzero thermal energy, while the anisotropy constants themselves are explicitly independent of temperature. These insights into the nature of the magnetocrystalline anisotropy are key for the understanding of ferromagnetism in few-layers sample. While in pure two-dimensional systems no magnetic order is expected, mechanical corrugations and magnetic anisotropy are possible pathways to establish magnetism in quasi-two-dimensional few-layers of Fe$_{3-x}$GeTe$_2$.

**Conclusion**

In summary, we have investigated in detail the magnetocaloric effect of bulk Fe$_{3-x}$GeTe$_2$ single crystals. The $-\Delta S_M$ follows the power law of $H^n$, as well as the field dependence of RCP. The uniaxial magnetocrystalline anisotropy is identified to be the likely origin of the long-range ferromagnetism in few-layers Fe$_{3-x}$GeTe$_2$. Considering its tunable room-temperature ferromagnetism and hard magnetic properties in nanoflakes, further investigation on the size dependence of magnetocaloric effect is of interest.
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**Author contributions statement**

Y.L. and C.P. designed this study and synthesized crystals; Y.L. performed magnetization and heat capacity measurements. J.L., J.T. and Y.Z. contributed TEM measurement. Y.L. and C.P. organized and wrote the paper with input from all collaborators. This manuscript reflects the contribution and ideas of all authors.

**Additional information**

Competing interests: The authors declare no competing interests.