Anisotropic magnetic entropy change in trigonal Cr$_{0.62}$Te

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(Dated: April 10, 2019)

We report a systematic investigation of dc magnetization and ac susceptibility, as well as anisotropic magnetic entropy change in trigonal Cr$_{0.62}$Te single crystals. A second-stage magnetic transition observed at low field indicates the presence of an additional magnetic phase below the Curie temperature $T_c$. The maximum magnetic entropy change $-\Delta S_M^{\text{max}}$ of 1.36 J kg$^{-1}$ K$^{-1}$ and the corresponding adiabatic temperature change $\Delta T_{\text{ad}}$ of 1.3 K are estimated from the heat capacity analysis with out-of-plane field change of 5 T. This is in agreement with $-\Delta S_M^{\text{max}} \sim 1.39$ (1.73) J kg$^{-1}$ K$^{-1}$ determined by magnetization with in-plane (out-of-plane) field. The rescaled $\Delta S_M(T, H)$ curves collapse onto a universal curve independent of temperature and field. Moreover, the $-\Delta S_M$ follows the power law of $H^n$ with $n = 0.667(2)$, and the relative cooling power RCP depends on $H^m$ with $m = 1.12(2)$.

I. INTRODUCTION

Intrinsic long-range ferromagnetism recently achieved in atomically thin van der Waals (vdW) crystals opens up great possibilities for both investigating fundamental two-dimensional (2D) magnetism and engineering novel spintronic vdW heterostructures. Chromium trihalides CrX$_3$ (X = Cl, Br, I) and trichalcogenides Cr$_2$X$_2$Te$_6$ (X = Si, Ge, Sn) are such promising candidates as a result of intrinsic magnetocrystalline anisotropy. Binary chromium chalcogenides, sulfides and selenides are mostly antiferromagnetic (AFM) however some tellurides are ferromagnetic with $T_c$ of 170 $\sim$ 360 K. Chromium tellurides Cr$_{1-x}$Te with $x < 0.1$ crystallize in the hexagonal NiAs structure, while Cr$_3$Te$_4$ ($x = 0.25$) and Cr$_2$Te$_3$ ($x = 0.33$) form monoclinic and trigonal crystal structures where Cr vacancies are present in every second metal layer. Neutron-diffraction measurement shows that the saturation magnetization in Cr$_{1-x}$Te is small due to possible spin canting and itinerant nature of the electrons. Electron correlation effect in itinerant ferromagnets has also been discussed in the photoemission spectra. There have been only several studies on Cr$_{1-x}$Te with $x = 0.375$ which exhibits a higher $T_c$ in the trigonal, when compared to monoclinic space group. Magnetocaloric effect (MCE) in the FM vdW materials provides important insight into the magnetic properties. Fe$_3$GeTe$_2$ with $T_c = 225$ K shows the maximum value of magnetic entropy change $-\Delta S_M^{\text{max}} \sim 1.1$ J kg$^{-1}$ K$^{-1}$ at 5 T. CrI$_3$ exhibits anisotropic $-\Delta S_M^{\text{max}}$ with values of 4.24 and 2.68 J kg$^{-1}$ K$^{-1}$ at 5 T for $\mathbf{H}///c$ and $\mathbf{H}///ab$, respectively.

In this work we address the anisotropic MCE in the trigonal Cr$_{0.62}$Te by heat capacity and dc magnetization measurements. Ac susceptibility measurements indicate a satellite magnetic transition just below $T_c$. The magnetocrystalline anisotropy constant $K_a$ is confirmed to be temperature-dependent. Isothermal magnetic entropy change $\Delta S_M(T, H)$ can be well scaled onto a universal curve independent on temperature and field. Moreover, the $-\Delta S_M$ follows the power law of $H^n$ with $n$ reaching a minimum at $T_c = 230$ K.

II. EXPERIMENTAL DETAILS

Single crystals of Cr$_{0.62}$Te were fabricated by the self-flux method and characterized as described previously. The x-ray absorption spectroscopy measurement was performed at 8-ID beamline of the National Synchrotron Light Source II (NSLS II) at Brookhaven National Laboratory in the fluorescence mode. The x-ray absorption near edge structure (XANES) and the extended x-ray absorption fine structure (EXAFS) spectra were processed using the Athena software package. The extracted EXAFS signal, $\chi(k)$, was weighed by $k^2$ to emphasize the high-energy oscillation and then Fourier-transformed in a $k$ range from 2 to 12 Å$^{-1}$ to analyze the data in $R$ space. The heat capacity was measured in Quantum Design PPMS-9 system with out-of-plane field up to 5 T. The magnetization data as a function of temperature and field were collected using Quantum Design MPMS-XL5 system in temperature range 200 $\sim$ 280 K with a step of 4 K and field up to 5 T.

III. RESULTS AND DISCUSSION

The crystal structure of trigonal Cr$_{0.62}$Te was successfully refined in the space group P3m1 with four crystallographically different sites for both Te and Cr. Figure 1 shows the normalized Cr K-edge XANES spectra and Fourier transform magnitudes of EXAFS spectra of trigonal Cr$_{0.62}$Te measured at room temperature. The XANES spectra is close to that of Cr$_2$Te$_3$ with Cr$^{3+}$ state. The prepeak feature is due to a direct quadrupole transition to unoccupied 3d states that are hybridized with Te 4p orbitals. In the single-scattering approximation, the EXAFS could be described by the following
corrected main peak around A, Cr$_2$-Te$_4$: 2.738(16) Å. The structural model includes the Cr$_2$ (site 6) relative displacement of the photoabsorber-backscatter related Debye-Waller factor measuring the mean square amplitude, $\sigma_i^2$ is the correlated Debye-Waller factor measuring the mean square relative displacement of the photoabsorber-backscatter pairs. The structural model includes the Cr$_2$ (site 6i) and Cr$_3$ (site 2c) that occupy the vacancy-free atomic layers; the Cr$_1$ (site 1b) and Cr$_4$ (site 3e) distribute in the metal deficient layers. This arrangement results in a five layer superstructure of the simple CrI$_3$ structure type [22]. The corrected main peak around $R \sim 2.7$ Å in Fig. 1(b) corresponds to the Cr-Te bond distances [Cr$_2$-Te$_1$: 2.698(16) Å, Cr$_2$-Te$_4$: 2.738(16) Å, Cr$_4$-Te$_2$: 2.683(1) Å, Cr$_4$-Te$_3$: 2.751(1) Å] extracted from the model fit in the range 2 to 3 Å, in line with previous study of the average crystal structure [22]. The peaks in high R range are due to the longer Cr-Cr (3.01 $\sim$ 3.05 Å) [Te-Te (3.66 $\sim$ 3.76 Å)] bond distances and multiple scattering effects.

Figure 2(a) shows the low temperature thermal demagnetization for Cr$_{0.62}$Te with out-of-plane field of 10 kOe. For a localized moment, this is generally understood with the spin-wave (SW) excitations which follow Bloch equation, $\Delta M/M(0) = A \tau^{3/2} + B T^{3/2} + \ldots$, where $M(0)$ is the magnetization at 0 K. $A$ and $B$ are the coefficients [30, 32]. In an itinerant or band magnetism such temperature dependence is a result of excitation of electrons from one subband to the other. The single-particle (SP) excitation is generally expressed as $\Delta M/M(0) = C T^{3/2} \exp(\pm \Delta/k_BT)$, where $C$ is the coefficient, $\Delta$ is the energy gap between the top of full subband and the Fermi level, and $k_B$ is the Boltzmann constant. Satisfactory fit obtained only incorporating both SW and SP models indicates the presence of both localized and itinerant type of magnetic moment in Cr$_{0.62}$Te. The fitting yields $A = 1.48(9) \times 10^{-5}$ K$^{-3/2}$, $B = 3.74(7) \times 10^{-7}$ K$^{-5/2}$, $C = 1.3(1) \times 10^{-2}$ K$^{-3/2}$, and $\Delta = 116(3)$ meV. This is in line with the small saturation moment and strong electron correlation in Cr$_{1-x}$Te [17, 21].

Temperature-dependent zero-field cooling (ZFC) and field-cooling (FC) magnetization $M(T)$ for Cr$_{0.62}$Te was measured in $H = 10$ kOe [inset in Fig. 2(a)] and $H = 10$
We observe the divergence of ZFC and FC curves below FM transition. The feature corresponds well to the reported paramagnetic (PM) behavior with small slope at 300 K [Fig. 2(d)]. The magnetization data. Then we can calculate the entropy as $S(T, H) = \int_0^T C_p/T dT$ and the magnetic entropy change as $\Delta S_M(T, H) = S_M(T, H) - S_M(T, 0)$. The adiabatic temperature change caused by the field change during the isentropic process can also be estimated as $\Delta T_{ad}(T, H) = T(S, H) - T(S, 0)$. As shown in Figs. 2(b) and 2(c), the peak $-\Delta S_M$ and $\Delta T_{ad}$ increase with increasing field and reach the values of 1.36 J kg$^{-1}$ K$^{-1}$ and 1.3 K, respectively, with the field change of 5 T. It is slightly larger than the value of Fe$_2$GeTe$_2$ (1.1 J kg$^{-1}$ K$^{-1}$ at 5 T) but smaller than that of Cr$_3$ (3.8 J kg$^{-1}$ K$^{-1}$ and 1.5 K at 5 T). Since there is a large magnetic anisotropy in Cr$_{0.62}$Te, it is of interest to calculate the individual magnetic entropy change for the two directions, respectively.

Figures 4(a) and 4(b) present the magnetization isotherms with field up to 5 T in the temperature range from 200 to 280 K for both $H//ab$ and $H//c$. When $H//ab$, the saturation field $H_s$ is associated with the magnetocrystalline anisotropy parameter $K_u$ and the saturation magnetization $M_s$, i.e., $2K_u/M_s = \mu_0 H_s$, where $\mu_0$ is the vacuum permeability. Figure 4(c) shows the temperature dependence of derived $K_u$ for Cr$_{0.62}$Te, which is about 94 kJ cm$^{-3}$ at $T = 160$ K and decreases with increasing temperature. This tendency arises solely from a large number of local spin clusters fluctuating randomly around the macroscopic magnetization vector and activated by a nonzero thermal energy. In a simple classical theory, $(K^{(n)}) \propto M_s^{n(n+1)/2}$, where $(K^{(n)})$ is the anisotropy expectation value for the $n^{th}$ power angular function in the case of uniaxial anisotropy $n = 2$ and of cubic anisotropy $n = 4$, leading to an exponent of 3 and 10, respectively. The temperature-dependent $M_s/M_s(160K)$, $[M_s/M_s(160K)]^4$, and $[M_s/M_s(160K)]^{10}$ are also plotted. The comparison in Fig. 4(c) points to

FIG. 3. (Color online). Temperature dependence of (a) the heat capacity $C_p$, (b) the magnetic entropy change $-\Delta S_M$, and (c) the adiabatic temperature change $\Delta T_{ad}$ for Cr$_{0.62}$Te with out-of-plane field changes of 2 and 5 T.

FIG. 4. (Color online). Typical initial isothermal magnetization curves from $T = 200$ to 280 K with temperature step of 4 K measured (a) in the $ab$ plane and (b) along the $c$ axis, respectively. (c) Temperature-dependent anisotropy constant $K_u$ (left axis) and the ratios of $[M_s/M_s(160K)]^{n(n+1)/2}$ with $n = 1, 2, 4$ (right axis).
the predominant uniaxial anisotropy with some deviation to cubic anisotropy in Cr\textsubscript{0.62}Te.

The magnetic entropy change can be calculated as
\begin{equation}
\Delta S_M(T, H) = \int_0^H \left( \frac{\partial S}{\partial T} \right)_T dH = \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH,
\end{equation}
where \( \frac{\partial S}{\partial T} \) and \( \frac{\partial M}{\partial T} \) are based on Maxwell’s relation.

The inset in Fig. 5(a) shows the field dependence of \( -\Delta S_M \) at low temperature. The rotational magnetic entropy change \( -\Delta S_{M0}^R \) as a function of (c) temperature and (d) field.

with in-plane field is observed. This originates most likely from the competition of temperature dependence of magnetic anisotropy and the magnetization. The magnetic anisotropy decreases with increasing temperature, whereas the magnetization may exhibit opposite behavior. At low fields, the magnetization at higher temperature could be larger than that at lower temperature [Fig. 2(d) and Fig. 4(a)], which gives a negative \( -\Delta S_M \).

The rotational magnetic entropy change \( \Delta S_{M0}^R \) can be calculated as \( \Delta S_{M0}^R(T, H) = \Delta S_M(T, H_c) - \Delta S_M(T, H_{ab}) \).

As shown in Fig. 5(c), the temperature dependence of \( -\Delta S_{M0}^R(T, H) \) also features a peak at \( T_c = 230 \) K with the field change of 0.2 T, however, the temperature of the maximum \( -\Delta S_{M0}^R(T, H) \) moves away from \( T_c \) to lower temperature with increasing field. When \( T \leq T_c \), the field dependence of \( -\Delta S_{M0}^R(T, H) \) increases rapidly at low field and changes slowly at high field [Fig. 5(d)], showing a critical field around \( H = 1 \) T. This possibly reflects the anisotropy field in Cr\textsubscript{0.62}Te, which decreases with increasing temperature and gradually disappears when \( T \geq T_c \).

For a material displaying a second-order transition, the field dependence of the maximum magnetic entropy change should be \( -\Delta S_{M0}^{max} = a H^n \), where \( a \) is a constant and the exponent \( n \) at \( T_c \) is related to the critical exponents as \( n(T_c) = 1 + (\beta - 1)/2(\beta + \gamma) \), where \( \beta \), \( \gamma \), and \( \delta \) are the critical exponents related to the spontaneous magnetization \( M_s \) below \( T_c \), the inverse initial susceptibility \( H/M \) above \( T_c \), and the isothermal \( M(H) \) at \( T_c \), respectively. Another important parameter is the rel-
Table 1. Critical exponents of Cr$_{0.62}$Te. The MAP, KFP and CI represent the modified Arrott plot, the Kouvel-Fisher plot and the critical isotherm, respectively.

| Technique | $\beta$ | $\gamma$ | $\delta$ | $n$  | $m$  |
|-----------|--------|--------|--------|-----|-----|
| $-\Delta S_{M}^{\text{max}}$ | 0.667(2) | | | | |
| RCP       | 1.12(2) | | | | |
| MAP       | 0.314(7) 1.83(2) | 6.83(7) | 0.680(1) | 1.146(2) | |
| KFP       | 0.315(7) 1.81(2) | 6.75(6) | 0.678(1) | 1.148(1) | |
| CI        | 6.35(4) | | | 1.157(1) | |

...negative cooling power (RCP): $RCP = -\Delta S_{M}^{\text{max}} \times \delta T_{FWHM}$ where $-\Delta S_{M}^{\text{max}}$ is the maximum entropy change near $T_c$ and $\delta T_{FWHM}$ is the full-width at half maximum. The RCP also depends on the magnetic field with $RCP = bH^m$, where $b$ is a constant and $m$ is associated with the critical exponent $\delta$, $m = 1 + 1/\delta$. Figure 6(a) displays the temperature dependence of $n(T)$ in various fields. At low temperatures, well below $T_c$, $n$ has a value which tends to 1. On the other side, well above $T_c$, $n$ approaches 2 as a consequence of the Curie-Weiss law. At $T = T_c$, $n$ reaches a minimum. Figure 6(b) summarized the field dependence of $-\Delta S_{M}^{\text{max}}$ and RCP. The RCP is calculated as 131.2 J kg$^{-1}$ with out-of-plane field change of 5 T for Cr$_{0.62}$Te, which is comparable with that of CrI$_3$ (122.6 J kg$^{-1}$ at 5 T). Fitting of the $-\Delta S_{M}^{\text{max}}$ and RCP gives $n = 0.667(2)$ and $m = 1.12(2)$, which are close to the values estimated from the critical exponents (Table 1).

Scaling analysis of $-\Delta S_{M}$ can be built by normalizing all the $-\Delta S_{M}$ curves against the respective maximum $-\Delta S_{M}^{\text{max}}$, namely, $\Delta S_{M}/-\Delta S_{M}^{\text{max}}$ by rescaling the reduced temperature $\theta_{\pm}$ as defined in the following equations:

$$\theta_{-} = (T_{\text{peak}} - T)/(T_{r1} - T_{\text{peak}}), T < T_{\text{peak}},$$  

$$\theta_{+} = (T - T_{\text{peak}})/(T_{r2} - T_{\text{peak}}), T > T_{\text{peak}},$$

where $T_{r1}$ and $T_{r2}$ are the temperatures of two reference points that corresponds to $\Delta S_{M}(T_{r1}, T_{r2}) = \frac{1}{2} \Delta S_{M}^{\text{max}}$. Following this method, all the $-\Delta S_{M}(T, H)$ curves in various fields collapse into a single curve [Fig. 6(c) and inset].

In summary, we have investigated in detail the magnetocaloric effect of trigonal Cr$_{0.62}$Te with high $T_c$ of 230 K. A second-step transition is observed just below $T_c$. The scaling analysis of magnetic entropy change $-\Delta S_{M}(T, H)$ confirms the accurate estimation of critical exponents for Cr$_{0.62}$Te. The $-\Delta S_{M}(T, H)$ follows the power law of $H^n$ with $n(T, H) = dln |\Delta S_{M}|/dln(H)$ reaching a minimum at $T_c$, as well as the field dependence of RCP. Strong magnetocrystalline anisotropy is also established, calling for further investigation on the thickness-dependent magnetocaloric effect.

Acknowledgements

Work at Brookhaven is supported by the Research supported by the U.S. Department of Energy, Office of Basic Energy Sciences as part of the Computation Material Science Program (Y. L. and C. P.) and by the US DOE under Contract No. [de-sc0012704] (C. P.). This research used the 8-ID (ISS) beamline of the National Synchrotron Light Source II, a U.S. DOE Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. [de-sc0012704].

1. M. A. McGuire, H. Dixit, V. R. Cooper, and B. C. Sales, Chem. Mater. 27, 612 (2015).
2. B. Huang, G. Clark, E. Navarro-Moratalla, D. R. Klein, R. Cheng, K. L. Seyler, D. Zhong, E. Schmidgall, M. A. McGuire, D. H. Cobden, W. Yao, D. Xiao, P. Jarillo-Herrero, and X. D. Xu, Nature 546, 270 (2017).
3. K. L. Seyler, D. Zhong, D. R. Klein, S. Guo, X. Zhang, B. Huang, E. Navarro-Moratalla, L. Yang, D. H. Cobden, M. A. McGuire, W. Yao, D. Xiao, P. Jarillo-Herrero, and X. D. Xu, Nature Physics 14, 277 (2018).
4. Z. Fei, B. Huang, P. Malinowski, W. Wang, T. Song, J. Sanchez, W. Yao, D. Xiao, X. Zhu, A. May, W. Wu, D. Cobden, Jian-Haw Chu, and X. D. Xu, arXiv:1803.02509
5. C. Gong, L. Li, Z. L. Li, H. W. Ji, A. Stern, Y. Xia, T. Cao, W. Bao, C. Z. Wang, Y. Wang, Z. Q. Qiu, R. J. Cava, S. G. Louie, J. Xia, and X. Zhang, Nature 546, 265 (2017).
6. M. W. Lin, H. L. Zhuang, J. Q. Yan, T. Z. Ward, A. A. Puretzky, C. M. Rouleau, Z. Gai, L. B. Liang, V. Meunier, B. G. Sumpter, P. Ganesh, P. R. C. Kent, D. B. Geohegan, D. G. Mandrus, and K. Xiao, J. Mater. Chem. C 4, 315 (2016).
7. H. L. Zhuang, Y. Xie, P. R. C. Kent, and P. Ganesh, Phys. Rev. B 92, 035407 (2015).
8. M. Chevreton, M. Murat, and C. Eyraud, J. Phys., 24, 443 (1963).
9 Y. Adachi, M. Yuzuri, T. Kaneko, and S. Abe, J. Magn. Magn. Mater., 104, 887 (1992).
10 Y. B. Li, E. Brück, O. Tegus, Y. Q. Zhang, W. J. Feng, N. K. Sun, D. Li, J. Li, T. J. Gortenmulder, Y. K. Huang, and Z. D. Zhang, J. Alloy Compd., 461, 21 (2008).
11 M. Yuzuri, and Y. Nakamura, J. Phys. Soc. Jpn., 19, 1350 (1964).
12 P. Vaqueiro, A. V. Powell, A. I. Coldea, C. A. Steer, I. M. Marshall, S. J. Blundell, J. Singleton, and T. Ohtani, Phys. Rev. B, 64, 132402 (2001).
13 H. Ipser, K. L. Komarek, and K. O. Klepp, J. Less-Common Met., 92, 265 (1983).
14 G. B. Street, E. Sawatzky, and K. Lee, J. Phys. Chem. Solids, 34, 1453 (1973).
15 T. Hamasaki, and T. Hashimoto, Solid State Commun., 16, 895 (1975).
16 M. Akram, and F. M. Nazar, J. Mater. Sci., 18, 423 (1983).
17 K. Lukoschus, S. Kraschinski, C. Näther, W. Bensch, and R. K. Kremer, J. Solid State Chem., 177, 951 (2004).
18 Z. L. Huang, W. Bensch, S. Mankovsky, S. Polesya, H. Ebert, and R. K. Kremer, J. Solid State Chem., 179, 2067 (2006).
19 Z. L. Huang, W. Kockelmann, M. Telling, and W. Bensch, Solid State Sci., 10, 1099 (2008).
20 A. F. Andresen, Acta Chem. Scand., 24, 3495 (1970).
21 K. Shimada, T. Saitoh, H. Namatame, A. Fujimori, S. Ishida, S. Asano, M. Matoba, and S. Anzai, Phys. Rev. B, 53, 7673 (1996).
22 X. Zhang, T. Yu, Q. Xue, M. Lei, and R. Jiao, J. Alloys Compd. 750, 798 (2018)