Critical behavior and magnetocaloric effect in \( \text{Mn}_3\text{Si}_2\text{Te}_6 \)
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Critical behavior and magnetocaloric effect in Mn$_3$Si$_2$Te$_6$

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The critical properties and magnetocaloric effect of semiconducting ferrimagnet Mn$_3$Si$_2$Te$_6$ single crystals have been investigated by bulk magnetization and heat capacity around $T_c$. Critical exponents $\beta = 0.41 \pm 0.01$ with a critical temperature $T_c = 74.18 \pm 0.08$ K and $\gamma = 1.21 \pm 0.02$ with $T_c = 74.35 \pm 0.05$ K are deduced by the Kouvel-Fisher plot, whereas $\delta = 4.29 \pm 0.05(3.40 \pm 0.02)$ is obtained by a critical isotherm analysis at $T = 74(75)$ K. The magnetic exchange distance is found to decay as $J(r) \approx r^{-4.79}$, which lies between the mean-field and 3D Heisenberg models. Moreover, the magnetic entropy change $-\Delta S_M$ features a maximum at $T_c$, i.e., $-\Delta S_M^{\text{max}} \approx 2.53(1.67)$ J kg$^{-1}$ K$^{-1}$ with in-plane(out-of-plane) field change of 5 T, confirming large magnetic anisotropy. The heat capacity measurement further gives $-\Delta S_M^{\text{max}} \approx 2.94$ J kg$^{-1}$ K$^{-1}$ and the corresponding adiabatic temperature change $\Delta T_{ad} \approx 1.14$ K with out-of-plane field change of 9 T.

I. INTRODUCTION

Layered intrinsically ferromagnetic (FM) semiconductors hold great promise for both fundamental physics and applications in spintronic devices.\footnote{Yu Liu (刘予) and C. Petrovic.} CrI$_3$ has recently attracted much attention since the long-range magnetism persists in monolayer with $T_c$ of 45 K.\footnote{Yu Liu (刘予) and C. Petrovic.} Intriguingly, the magnetism in CrI$_3$ is layer-dependent, from FM in monolayer, to antiferromagnetic (AFM) in bilayer, and back to FM in trilayer.\footnote{Yu Liu (刘予) and C. Petrovic.} It can further be controlled by electrostatic doping, providing great opportunities for designing magneto-optoelectronic devices.\footnote{Yu Liu (刘予) and C. Petrovic.}

Ternary Cr$_2$X$_2$Te$_6$ (X = Si, Ge) exhibit FM order below $T_c$ of 32 K for Cr$_2$Si$_2$Te$_6$ and 61 K for Cr$_2$Ge$_2$Te$_6$, respectively,\footnote{Yu Liu (刘予) and C. Petrovic.} and also promising candidates for long-range magnetism in nanosheets.\footnote{Yu Liu (刘予) and C. Petrovic.} Many efforts have been devoted to shed light on the nature of FM in this system.\footnote{Yu Liu (刘予) and C. Petrovic.} Multiple domain structure types, self-fitting disks and fine ladder structure within the Y-connected walls, were observed by magnetic force microscopy,\footnote{Yu Liu (刘予) and C. Petrovic.} confirming two-dimensional (2D) long-range magnetism with non-negligible interlayer coupling.\footnote{Yu Liu (刘予) and C. Petrovic.} Mn$_3$Si$_2$Te$_6$ is a little-studied three-dimensional (3D) analog of Cr$_2$Si$_2$Te$_6$.\footnote{Yu Liu (刘予) and C. Petrovic.} The Mn$_3$Si$_2$Te$_6$ layer is composed of MnTe$_6$ octahedra that are edge sharing within the $ab$ plane (Mn1 site) and along with Si-Si dimers [Fig. 1(a)], similar to Cr$_2$Si$_2$Te$_6$. However, the layers are connected by filling one-third of Mn atoms at the Mn2 site within interlayer, yielding a composition of Mn$_3$Si$_2$Te$_6$.\footnote{Yu Liu (刘予) and C. Petrovic.} Recent neutron diffraction experiment gives that Mn$_3$Si$_2$Te$_6$ is a ferrimagnet below $T_c \approx 78$ K and the moments lie within the $ab$ plane.\footnote{Yu Liu (刘予) and C. Petrovic.}

In the present work we investigated the critical behavior of Mn$_3$Si$_2$Te$_6$ single crystal by using modified Arrott plot, Kouvel-Fisher plot and critical isotherm analysis, as well as its magnetocaloric effect. Critical exponents $\beta = 0.41(1)$ with $T_c = 74.18(8)$ K, $\gamma = 1.21(2)$ with $T_c = 74.35(5)$ K, and $\delta = 4.29(5)$ at $T = 74$ K. The magnetic exchange distance is found to decay as $J(r) \approx r^{-4.79}$, which lies between mean-field and 3D Heisenberg models. The resealed $-\Delta S_M(T, H)$ curves can well collapse onto a universal curve, confirming its nature of second-order.

II. METHODS

A. Experimental details

Single crystals of Mn$_3$Si$_2$Te$_6$ were fabricated by melting stoichiometric mixture of Mn (3N, Alfa Aesar) chip, Si (5N, Alfa Aesar) lump and Te (5N, Alfa Aesar) shot. Starting materials were vacuum-sealed in a quartz tube, heated to 1100 °C over 20 h and then cooled to 850 °C at a rate of 1 °C/h. X-ray diffraction (XRD) data were taken with Cu $K_\alpha$ ($\lambda = 0.15418$ nm) radiation of a Rigaku Miniflex powder diffractometer. The magnetization and heat capacity were collected in Quantum Design MPMS-XL5 and PPMS-9 systems. The magnetic entropy change $-\Delta S_M$ from the magnetization data was estimated using a Maxwell relation.

B. Scaling analysis

According to the scaling hypothesis, the second-order phase transition around the Curie point $T_c$ is characterized by a set of interconnected critical exponents $\alpha, \beta, \gamma, \delta, \eta, \nu$ and a magnetic equation of state.\footnote{Yu Liu (刘予) and C. Petrovic.} The exponent $\alpha$ can be obtained from specific heat and $\beta$ and $\gamma$ from spontaneous magnetization $M_s$ and inverse initial susceptibility $\chi^{-1}_0$, below and above $T_c$, respectively, while $\delta$ is the critical isotherm exponent. The mathematical definitions of the exponents from magnetization measurement are given below:

\begin{equation}
M_s(T) = M_0(-\varepsilon)^\beta, \varepsilon < 0, T < T_c,
\end{equation}

\begin{equation}
\chi^{-1}_0(T) = (h_0/m_0)\varepsilon^\gamma, \varepsilon > 0, T > T_c,
\end{equation}
where $\varepsilon = (T - T_c)/T_c$ is the reduced temperature, and $M_0$, $h_0/m_0$ and $D$ are the critical amplitudes.\(^{7}\)

The magnetic equation of state in the critical region is expressed as

$$M(H, \varepsilon) = \varepsilon^\beta f_\pm(H/\varepsilon^{\beta+\gamma}), \quad \text{(4)}$$

where $f_+$ for $T > T_c$ and $f_-$ for $T < T_c$, respectively, are the regular functions. Eq.(4) can be further written in terms of scaled magnetization $m = \varepsilon^{-\beta}M(H, \varepsilon)$ and scaled field $h = \varepsilon^{-(\beta+\gamma)}H$ as

$$m = f_\pm(h). \quad \text{(5)}$$

This suggests that for true scaling relations and the right choice of $\beta$, $\gamma$, and $\delta$ values, scaled $m$ and $h$ will fall on universal curves above $T_c$ and below $T_c$, respectively.

### III. RESULTS AND DISCUSSIONS

The powder XRD pattern of Mn$_3$Si$_2$Te$_6$ confirms high purity of the single crystals, in which the observed peaks can be well fitted with the $P31c$ space group [Fig. 1(c)]. The determined lattice parameters $a = 7.046(2)$ Å and $c = 14.278(2)$ Å are very close to the reported values.\(^?\)\(^?\) In the single-crystal XRD [Fig. 1(d)], only (00l) peaks are detected, indicating that the crystal surface is parallel to the $ab$ plane and perpendicular to the $c$ axis.

Figure 2 presents the temperature dependence of magnetization measured in $H = 1$ and 50 kOe applied in the $ab$ plane and parallel to the $c$ axis, respectively. The magnetization is nearly isotropic in 50 kOe, however, significant magnetic anisotropy is observed in 1 kOe at low temperatures. The ordered moments lie primarily within the $ab$ plane. An additional upturn well above $T_c$ till to 300 K is clearly seen in zero-field-cooling (ZFC) curve for $H//ab$, which may be associated with short-range order or the presence of correlated excitations in the paramagnetic region.\(^?\) Isothermal magnetization at $T = 5$ K [insets in Fig. 2] shows saturation moment of $M_s \approx 1.6 \mu_B$/Mn for $H//ab$ and a small FM component for $H//c$. No remanent moment for either orientation confirms the crystal of high quality. The $T_c$ can be roughly determined by the minimum of $d\chi/dT$ [Figs. 2(c,d)], i.e., $T_c = 75$ K for in-plane field and $T_c = 77$ K for out-of-plane field of 1 kOe, which shifts to $T_c = 80$ K in an increase field of 50 kOe.\(^?\)

From the Landau theory of phase transition, the Gibbs free energy $G$ for FM-paramagnetic(PM) transition can be expressed as

$$G(T, M) = G_0 + aM^2 + bM^4 - MH, \quad \text{(6)}$$

where the equilibrium magnetization $M$ is the order parameter, and the coefficients $a$ and $b$ are the temperature-dependent parameters. At equilibrium $\partial G/\partial M = 0$ (i.e.,
energy minimization) and the magnetic equation of state can be expressed as

\[ H/M = 2a + 4bM^2. \]  

(7)

Thus, the Arrott plot of \( M^2 \) vs \( H/M \) should appear as parallel straight lines for different temperatures above and below \( T_c \) in the high field region.\(^7\) The intercepts of \( M^2 \) on the \( H/M \) axis is negative or positive depending on phenomena below or above \( T_c \) and the line at \( T_c \) passes through the origin. In order to properly determine the \( T_c \) as well as the critical exponents \( \beta \), \( \gamma \), and \( \delta \), the modified Arrott plot with a self-consistent method was used.\(^7\)\(^8\) Figure 3 presents the initial isotherms ranging from 5 to 90 K and the modified Arrott plot of \( M^{1/\beta} \) vs \( (H/M)^{1/\gamma} \) around \( T_c \) for MnSi\(_2\)Te\(_6\). This gives \( \chi_0^{-1}(T) \) and \( M_s(T) \) as the intercepts on the \( H/M \) axis and positive \( M^2 \) axis, respectively.

Figure 4(a) exhibits the final \( M_s(T) \) and \( \chi_0^{-1}(T) \) as a function of temperature. According to Eqs. (1) and (2), the critical exponents \( \beta = 0.41(1) \) with \( T_c = 74.21(1) \) K, and \( \gamma = 1.25(1) \) with \( T_c = 74.25(3) \) K, are obtained. In addition, there is also the Kouvel-Fisher (KF) relation,\(^7\)

\[ M_s(T)[dM_s(T)/dT]^{-1} = (T - T_c)/\beta, \]  

(8)

\[ \chi_0^{-1}(T)[d\chi_0^{-1}(T)/dT]^{-1} = (T - T_c)/\gamma. \]  

(9)

Linear fittings to the plots of \( M_s(T)[dM_s(T)/dT]^{-1} \) and \( \chi_0^{-1}(T)[d\chi_0^{-1}(T)/dT]^{-1} \) vs \( T \) in Fig. 4(b) yield \( \beta = 0.41(1) \) with \( T_c = 74.18(8) \) K, and \( \gamma = 1.21(2) \) with \( T_c = 74.35(5) \) K. The third exponent \( \delta \) can be calculated from the Widom scaling relation \( \delta = 1 + \gamma/\beta \). From \( \beta \) and \( \gamma \) obtained with the modified Arrott plot and the Kouvel-Fisher plot, \( \delta = 4.05(5) \) and 3.95(2) are obtained, respectively, which are close to the direct fits of \( \delta \) taking into account that \( M = DH^{1/3} \) near \( T_c \)\( \delta = 4.29(5) \) at 74 K and 3.40(2) at 75 K, inset in Fig. 4(a).

Scaling analysis can be used to estimate the reliability of the obtained critical exponents and \( T_c \). From Eq. (5), scaled \( m \) vs scaled \( h \), all the data collapse on two separate branches below and above \( T_c \), as depicted in Fig. 5. The

FIG. 3. (Color online) (a) Typical initial isothermal magnetization curves measured in \( H/ab \) from 5 to 90 K for MnSi\(_2\)Te\(_6\). (b) the modified Arrott Plot around \( T_c \) for the optimum fitting with \( \beta = 0.41 \) and \( \gamma = 1.21 \).

FIG. 4. (Color online) (a) Temperature dependence of the spontaneous magnetization \( M_s \) (left) and the inverse initial susceptibility \( \chi_0^{-1} \) (right) with solid fitting curves. Inset shows log\( M \) vs log\( H \) collected at 74 and 75 K with linear fitting curves. (b) Kouvel-Fisher plots of \( M_s(dM_s/dT)^{-1} \) (left) and \( \chi_0^{-1}(d\chi_0^{-1}/dT)^{-1} \) (right) with solid fitting curves.
scaling equation of state takes another form,

\[ \frac{H}{M^\sigma} = k \left( \frac{\varepsilon}{H^{1/\beta}} \right), \tag{10} \]

where \( k(x) \) is the scaling function. From Eq. (10), all the data should also fall into a single curve. This is indeed seen [inset in Fig. 5]; the \( MH^{-1/\beta} \) vs \( \varepsilon H^{-1/(\beta \delta)} \) experimental data for MnSiTe collapse into a single curve and the \( T_c \) locates at the zero point of the horizontal axis. The well-rescaled curves further confirm the reliability of the obtained critical exponents.

Next, it is important to understand the nature as well as the range of interaction in this material. In a homogeneous magnet the universality class of the magnetic phase transition depends on the exchange distance \( J(r) \). In renormalization group theory analysis the interaction decays with distance \( r \) as

\[ J(r) \approx r^{-(3+\sigma)}, \tag{11} \]

where \( \sigma \) is a positive constant.\(^7\) Moreover, the susceptibility exponent \( \gamma \) is predicted as

\[ \gamma = 1 + \frac{4}{d} \left( \frac{n+2}{n+8} \right) \Delta \sigma + \frac{8(n+2)(n-4)}{d^2(n+8)^2} \]

\[ \times \left[ 1 + 2G(\frac{d}{2})(7n+20) \right] \Delta \sigma^2, \tag{12} \]

where \( \Delta \sigma = (\sigma - \frac{d}{2}) \) and \( G(\frac{d}{2}) = 3 - \frac{1}{2}(\frac{d}{2})^2 \). \( n \) is the spin dimensionality.\(^7\) When \( \sigma > 2 \), the Heisenberg model is valid for 3D isotropic magnet, where \( J(r) \) decreases faster than \( r^{-5} \). When \( \sigma \leq 3/2 \), the mean-field model is satisfied, expecting that \( J(r) \) decreases slower than \( r^{-4.5} \). In the present case, \( \sigma = 1.79 \), then the correlation length critical exponent \( \nu = 0.676 \) (\( \nu = \gamma/\sigma \)), and \( \alpha = -0.028 \) (\( \alpha = 2 - \nu d \)). It is found that the magnetic exchange distance decays as \( J(r) \approx r^{-4.79} \), which lies between that of 3D Heisenberg model and mean-field model.

Then we estimate its magnetic entropy change

\[ \Delta S_M(T,H) = \int_0^H \left[ \frac{\partial S(T,H)}{\partial H} \right]_T dH. \tag{13} \]

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 further written as:\(^7\)

\[ \Delta S_M(T,H) = \int_0^H \left[ \frac{\partial M(T,H)}{\partial T} \right]_H dH. \tag{14} \]

In the case of magnetization measured at small discrete magnetic field and temperature intervals [Fig. 3(a)],
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 temperature $\theta$ as defined in the following equations:

\begin{align}
\theta_- &= (T_{\text{peak}} - T)/(T_{\text{r1}} - T_{\text{peak}}), T < T_{\text{peak}}, \\
\theta_+ &= (T - T_{\text{peak}})/(T_{\text{r2}} - T_{\text{peak}}), T > T_{\text{peak}},
\end{align}

where $T_{\text{r1}}$ and $T_{\text{r2}}$ are the temperatures of the two reference points that have been selected as those corresponding to $\Delta S_M(T_{\text{r1}}, T_{\text{r2}}) = \frac{1}{2}\Delta S_M^{\text{max}}$. Following this method, all the $-\Delta S_M(T, H)$ curves in various fields collapse into a single curve in the vicinity of $T_c$ [Fig. 6(b)]. In the framework of the mean-field theory, $-\Delta S_M^{\text{max}} = -1.07q R (g^2 u^2 J H/k_B T_c)^{2/3} H^{2/3}$, where $q$ is the number of magnetic ions, $R$ is the gas constant, and $g$ is the Landé factor. In fact, more universally, it should follow a power law relation, $-\Delta S_M^{\text{max}} = a H^n$, where $n$ depends on the magnetic state of the sample. Fitting of the field dependence of $-\Delta S_M^{\text{max}}$ with $H/ab$ gives $n = 0.665(2)$ [inset in Fig. 6(b)], close to the typical value of 2/3 within mean-field model.

Finally, we also estimate the $-\Delta S_M$ from heat capacity measurement with out-of-plane fields up to 9 T. The $\lambda$ peak observed at $T_c = 74.7$ K in zero field [inset in Fig. 7(a)], corresponding well to the PM-FM transition, is gradually suppressed in fields. Figure 7(a) shows the calculated heat capacity change $\Delta C_p = C_p(T, H) - C_p(T, 0)$ as a function of temperature in various fields. Obviously, $\Delta C_p < 0$ for $T < T_c$ and $\Delta C_p > 0$ for $T > T_c$, whilst, it changes sharply from negative to positive at $T_c$, corresponding to the change from FM to PM. The entropy $S(T, H)$ can be deduced by

$$S(T, H) = \int_0^T \frac{C_p(T, H)}{T} dT.$$  \hspace{1cm} (18)

Assuming the electronic and lattice contributions are not field dependent and in an adiabatic process of changing the field, the magnetic entropy change $-\Delta S_M$ can be straightly obtained $-\Delta S_M(T, H) = S_M(T, H) - S_M(T, 0)$. The adiabatic temperature change $\Delta T_{\text{ad}}$ caused by the field change can be obtained by $\Delta T_{\text{ad}}(T, H) = T(S, H) - T(S, 0)$, where $T(S, H)$ and $T(S, 0)$ are the temperatures in the field $H \neq 0$ and $H = 0$, respectively, at constant total entropy $S(T, H)$. Figures 7(b) and 7(c) exhibit the temperature dependence of $-\Delta S_M$ and $\Delta T_{\text{ad}}$ estimated from heat capacity with out-of-plane field. The maxima of $-\Delta S_M$ and $\Delta T_{\text{ad}}$ increase with increase field and reach the values of 2.94 J kg$^{-1}$ K$^{-1}$ and 1.14 K, respectively, with the field change of 9 T.

**IV. CONCLUSIONS**

In summary, we have studied the critical behavior and magnetocaloric effect around the FM-FM transition in...
Mn$_3$Si$_2$Te$_5$ single crystal. The ferrimagnetic transition in Mn$_3$Si$_2$Te$_5$ is identified to be second order in nature. The critical exponents $\beta$, $\gamma$, and $\delta$ estimated from various techniques match reasonably well and follow the scaling equation, suggesting a long-range magnetic interaction with the exchange distance decaying as $J(r) \approx r^{-4.79}$. Magnetocaloric effect is about one order of magnitude smaller when compared to other magnetorefrigerant candidate materials.

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