Critical behavior and magnetocaloric effect in VI\textsubscript{3}

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We investigated critical properties and magnetocaloric effect connected with ferromagnetic transition in VI\textsubscript{3} single crystals. We obtained critical exponents $\beta = 0.244(5)$ with a critical temperature $T_c = 50.10(2)$ K and $\gamma = 1.028(12)$ with $T_c = 49.97(5)$ K from the modified Arrott plot, whereas critical isotherm analysis resulted in $\delta = 5.24(2)$ at $T_c = 50$ K. This suggests that the ferromagnetic phase transition in VI\textsubscript{3} follows the tricritical mean-field model and that it is situated close to a two- to three-dimensional tricritical point. Furthermore, the magnetic entropy change $-\Delta S_M$ features a maximum at $T_c$, i.e., $-\Delta S_M^{max} \sim 2.64$ J kg\textsuperscript{-1} K\textsuperscript{-1} with out-of-plane field change of 5 T. This is consistent with the $-\Delta S_M^{max} \sim 2.80$ J kg\textsuperscript{-1} K\textsuperscript{-1} deduced from the heat capacity and the corresponding adiabatic temperature change $\Delta T_{ad} \sim 0.96$ K with out-of-plane field change of 5 T. The rescaled $\Delta S_M(T, H)$ curves collapse onto a universal curve, indicating a second-order type of the magnetic transition.

I. INTRODUCTION

Layered intrinsically ferromagnetic (FM) semiconductors hold great promise for both fundamental physics and applications in spintronic devices.\cite{1,2} CrI\textsubscript{3} has recently attracted much attention since the long-range magnetism persists in monolayer with $T_c$ of 45 K.\cite{3} Intriguingly, the magnetism in CrI\textsubscript{3} is layer-dependent, from FM in monolayer, to antiferromagnetic (AFM) in bilayer, and back to FM in trilayer.\cite{4} In van der Waals (vdW) heterostructures formed by an ultrathin CrI\textsubscript{3} and a monolayer WSe\textsubscript{2}, the WSe\textsubscript{2} photoluminescence intensity strongly depends on the relative alignment between photoexcited spins in WSe\textsubscript{2} and the CrI\textsubscript{3} magnetization.\cite{5} Furthermore, the magnetism in ultrathin CrI\textsubscript{3} could be controlled by electrostatic doping, providing great opportunities for designing magneto-optoelectronic devices.\cite{6,7} Recently, the two-dimensional (2D) ferromagnetism has also been predicted in VI\textsubscript{3} monolayer with a calculated $T_c$ of 98 K, higher than that in CrI\textsubscript{3}.\cite{8}

Bulk CrI\textsubscript{3} and VI\textsubscript{3} belong to a well-known family of transition metal trihalides MX\textsubscript{3} (X = Cl, Br and I).\cite{9,10} When compared to CrI\textsubscript{3}, in which the chromium has a half filled $t_{2g}$ level yielding $S = 3/2$, the vanadium in VI\textsubscript{3} has two valence electrons that half fill two of the three degenerate $t_{2g}$ states yielding $S = 1$.\cite{11,12} Bulk VI\textsubscript{3} is an insulating 2D ferromagnet with $T_c = 55$ K that crystallizes in a layered structure of BiI\textsubscript{3} with space group R3 below 79 K whereas at higher temperatures VI\textsubscript{3} adopts layered monoclinic $C2/m$ crystal structure with van der Waals bonds along the c-axis.\cite{13,14} Density functional theory (DFT) calculations suggest that the VI\textsubscript{3} not only hosts the long-range ferromagnetism down to a monolayer but also exhibits Dirac half-metallicity, of interest for spintronic applications.\cite{15}

The magnetocaloric effect (MCE) in the FM vdW materials gives additional insight into the magnetic properties. Bulk CrI\textsubscript{3} exhibits anisotropic $-\Delta S_M^{max}$ with values of 4.24 and 2.68 J kg\textsuperscript{-1} K\textsuperscript{-1} at 5 T for H//c and H//ab, respectively.\cite{16} However little is known about VI\textsubscript{3}.

In the present work we focus on the nature of the FM transition in bulk VI\textsubscript{3} single crystals. We have investigated the critical behavior by the modified Arrott plot and a critical isotherm analysis, whilst the magnetocaloric effect was studied by the heat capacity and magnetization measurements near $T_c$. Critical exponents $\beta = 0.244(5)$ with $T_c = 50.10(2)$ K, $\gamma = 1.028(12)$ with $T_c = 49.97(5)$ K, and $\delta = 5.24(2)$ at $T_c = 50$ K, suggest that the magnetic transition is second-order and that it is situated near a tricritical point from two- to three-dimensional. This is further confirmed by the scaling analysis of magnetic entropy change $-\Delta S_M(T, H)$, in which the rescaled $-\Delta S_M(T, H)$ collapses onto a universal curve independent on temperature and field.

II. EXPERIMENTAL DETAILS

Bulk VI\textsubscript{3} single crystals were fabricated by chemical vapor transport method starting from an intimate mixture of vanadium powder (99.95 %, Alfa Aesar) and anhydrous iodine beads (99.99 %, Alfa Aesar) with a molar ratio of 1 : 3. The starting materials were sealed in an evacuated quartz tube and then placed inside a multi-zone furnace. Materials were reacted over a period of 7 days with source zone at 650 °C, middle growth zone at 550 °C, and third zone at 600 °C. The x-ray diffraction (XRD) data were taken with Cu K\textsubscript{α} (λ = 0.15418 nm) radiation of Rigaku Miniflex powder diffractometer. The element analysis was performed using an energy-dispersive x-ray spectroscopy in a JEOL LSM-6500 scanning electron microscope, confirming a stoichiometric VI\textsubscript{3} single crystal. The magnetization data as a function of temperature and field were collected using Quantum Design MPMS-XL5 system in temperature range from 10 to 90 K with a temperature step of 1 K around $T_c$ and field up to 5 T. The applied field ($H_a$) has been corrected for the internal field as $H = H_a - NM$, where $M$ is the measured magnetization and $N$ is the demagnetization factor. The corrected $H$ was used for the analysis.
FIG. 1. (Color online) Single crystal x-ray diffraction pattern of VI₃ at room temperature. Inset shows the crystal structure and representative single crystal.

of the critical behavior. The magnetic entropy change $-\Delta S_M$ from the magnetization data was estimated using a Maxwell relation.

III. RESULTS AND DISCUSSIONS

The crystal structure of VI₃ forms in monoclinic AlCl₃ type with space group C2/m at room temperature [inset in Fig. 1], similar to that of CrI₃. The V ions are arranged in a honeycomb network and are located at the centers of distorted edge-sharing octahedra of six I anions. The I-V-I triple layers of composition VI₃ are stacked along the c axis and there are vdW gaps between them. The as-grown single crystals are shiny black platelets with lateral dimensions up to several millimeters, as shown in the inset of Fig. 1. In the single-crystal x-ray diffraction (XRD) scan [Fig. 1], only (00l) peaks are detected, indicating that the crystal surface is normal to the c axis with the plate-shaped surface parallel to the ab plane.

Figures 2(a) and 2(b) present the temperature dependence of dc magnetic susceptibility measured in the fields ranging from 100 Oe to 50 kOe applied in the ab plane and along the c axis, respectively. The magnetic susceptibility is nearly isotropic in 10 and 50 kOe, however, significant magnetic anisotropy is observed in 100 Oe and 1 kOe at low temperature. When $T < T_c$, the divergence of ZFC and FC curves exhibit a characteristic behavior of possible spin-glass or cluster-glass state with the temperature of divergence decreasing with increasing field. An additional weak anomaly at 80 K is also observed for $H//c$, which is field-independent. A structural phase transition accompanies similar feature in the susceptibility of CrI₃, indicating strong spin-lattice coupling. Isothermal magnetization at $T = 2$ K [Fig. 2(c)] shows saturation moments of $M_s \approx 0.72 \mu_B/V$ and $0.95 \mu_B/V$ for $H//ab$ and $H//c$, respectively. The coercive field is about 15 kOe for $H//c$, much larger than that of around 1.5 kOe for $H//ab$. Both are significantly larger than those in
FIG. 3. (Color online) (a) Typical initial isothermal magnetization curves measured in out-of-plane fields from 40 to 60 K with a temperature step of 1 K for VI3. (b) The Arrott plots of $M^2$ vs $H/M$. The $M^{1/3}$ vs $(H/M)^{1/3}$ with parameters of (c) 2D Ising model, (d) 3D Ising model, (e) 3D Heisenberg model, (f) 3D XY model, and (g) tricritical mean-field model. (h) Temperature dependence of the normalized slopes $N_S = S(T)/S(T_c)$ for different models.

Near $T_c$, the second order phase transition is governed by magnetic equation of state and is characterized by critical exponents $\beta$, $\gamma$ and $\delta$ that are mutually related.\(^2\)

Spontaneous magnetization $M_s$ and inverse initial susceptibility $\chi_0^{-1}$, below and above $T_c$ can be used to obtain $\beta$ and $\gamma$ whereas $\delta$ is the critical isotherm exponent. Hence, from magnetization:

$$M_s(T) = M_0(-\varepsilon)^\beta, \varepsilon < 0, T < T_c,$$

$$\chi_0^{-1}(T) = (h_0/m_0)\varepsilon^\gamma, \varepsilon > 0, T > T_c,$$

$$M = DH^{1/\delta}, T = T_c,$$

where $\varepsilon = (T - T_c)/T_c$ is the reduced temperature, and $M_0$, $h_0/m_0$ and $D$ are the critical amplitudes.\(^2\)

Isothermal magnetization in the temperature range from 40 to 60 K with a temperature step of 1 K is shown in Fig. 3(a). The Arrott plot involves mean-field critical exponents $\beta = 0.5$ and $\gamma = 1.0$.\(^2\) Based on this, magnetization isotherms $M^2$ vs $H/M$ should be a set of parallel straight lines and the isotherm at the critical temperature $T_c$ should pass through the origin. As shown in Fig. 3(b), all curves in the Arott plot of VI3 are nonlinear, with a downward curvature, demonstrating that the Landau mean-field model is not applicable to VI3. However, it is possible to estimate the order of the magnetic transition through the slope of the straight line. Inset shows the rescaling of the $M(H)$ curves by $MH^{-1/8}$ vs $\varepsilon H^{1/8}$. Arrot-Noaks equation of state provides modification of
Critical exponents

\[(H/M)^{1/\gamma} = az + bM^{1/\beta},\]  

where \(\varepsilon = (T - T_c)/T_c\) and \(a, b\) are constants. The modified Arrott plots \[^{26}\] Figs. 3(c)-(g)] are obtained by using possible exponents from 2D Ising (\(\beta = 0.125, \gamma = 1.75\)), 3D Ising (\(\beta = 0.325, \gamma = 1.24\)), 3D Heisenberg (\(\beta = 0.365, \gamma = 1.386\)), 3D XY (\(\beta = 0.345, \gamma = 1.316\)), and tricritical mean-field model (\(\beta = 0.25, \gamma = 1.0\)). The modified Arrott plot should be a set of parallel lines in the high field region with the same slope \([S(T) = dM^{1/\beta}/d(H/M)^{1/\gamma}]\) for the correct model. The model which fits the data best is selected by normalized slope \((NS), NS = S(T)/S(T_c)\), that compares with the ideal value of unity. Plot of \(NS\) vs \(T\) for different models is presented in Fig. 3(h). It is clearly seen that the \(NS\) of 2D Ising model shows the largest deviation from unity. The \(NS\) of 3D Ising model is close to \(NS = 1\) mostly above \(T_c\), while that of tricritical mean field model is the best below \(T_c\), suggesting a 3D magnetic behavior in bulk \(\text{VH}_3\).

The final and reliable values of \(M_s\) and \(H/M\) [solid line, Fig. 4(a)] are selected by linear extrapolation from the high field region to \(M^{1/\beta}\) and \((H/M)^{1/\gamma}\) intercepts. \[^{26}\] Critical exponents \(\beta = 0.244(5)\), with \(T_c = 50.10(2)\) K, and \(\gamma = 1.028(12)\), with \(T_c = 49.97(5)\) K, are obtained. According to Eq. (3), the \(M(H)\) at \(T_c\) should be a straight line in log-log scale with the slope of \(1/\delta\). As shown in the inset of Fig. 4(a), such fitting yields \(\delta = 5.24(2)\). The Widom scaling law gives \(\delta = 1 + \gamma/\beta\). From \(\beta\) and \(\gamma\) obtained with the modified Arrott plot, \(\delta = 5.21(4)\), which is very close to that obtained from critical isotherm analysis.

Scaling analysis can be used to estimate the reliability of the obtained critical exponents and \(T_c\). Near phase transition the magnetic equation of state is:

\[M(H, \varepsilon) = \varepsilon^{\beta} f_{\pm}(H/\varepsilon^{\beta+\gamma}),\]

where \(f_+\) for \(T > T_c\) and \(f_-\) for \(T < T_c\), respectively, are the regular functions. Eq. (5) can be expressed via rescaled magnetization \(m = \varepsilon^{-\beta} M(H, \varepsilon)\) and rescaled field \(h = \varepsilon^{-(\beta+\gamma)} H\) as:

\[m = f_{\pm}(h).\]  

For the correct scaling relations and correct choice of \(\beta, \gamma,\) and \(\delta\), scaled \(m\) and \(h\) fall on universal curves above \(T_c\) and below \(T_c\), respectively. Figure 4(b) presents the scaled \(m^2\) vs \(h/m\) that collapse on two separate branches below and above \(T_c\), respectively, confirming proper treatment of the critical regime. The scaling equation of state also takes another form

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

where \(k(x)\) is the scaling function. From Eq. (7), all the experimental data should fall into a single curve. This

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

This can be expressed using Maxwell’s relation \([\partial S(T, H)/\partial H]_T = [\partial M(T, H)/\partial T]_H\), as:

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

For magnetization measured at small \((H, T)\) intervals, \(\Delta S_M(T, H)\) is becomes:

\[\Delta S_M(T_i, H) = \int_0^{H_i} M(T_i, H) dH - \int_0^{H_{i+1}} M(T_{i+1}, H) dH / T_i - T_{i+1}.\]
change of 5 T. The maximum value of $\Delta S_M(T,H)$ in different magnetic fields fall on a single line near $T_c$ [inset in Fig. 5(b)].

At a second-order transition, the magnetic entropy change can be expressed as $-\Delta S_M^{\text{max}} = aH^n$. The relative cooling power (RCP) is defined: $RCP = -\Delta S_M^{\text{max}} \times \delta T_{FWHM}$. Here $-\Delta S_M^{\text{max}}$ is the maximum entropy change around $T_c$ whereas $\delta T_{FWHM}$ is the full-width at half maximum. The RCP changes in magnetic field as with $RCP = bH^m$. Figure 5(b) presents the summary of the out-of-plane field dependence of $-\Delta S_M^{\text{max}}$ and RCP. The calculated value of RCP is about 42 J kg$^{-1}$ for VI$_3$ with out-of-plane field change of 5 T. Fitting of the $-\Delta S_M^{\text{max}}$ and RCP give that $n = 0.60(2)$ and $m = 1.03(1)$ for VI$_3$.

The $-\Delta S_M$ can also be obtained from the heat capacity measurement with out-of-plane fields up to 5 T. The signature of magnetic order at $T_c = 50$ K in $H = 0$ [Fig. 6(a)] is suppressed in fields. Heat capacity change $\Delta C_p = C_p(T,H) - C_p(T,0)$ [Fig. 6(a)] is $\Delta C_p < 0$ for $T < T_c$ and $\Delta C_p > 0$ for $T > T_c$. At $T_c$ there is a sharp change from negative to positive. In contrast, the sharp peak at higher temperature ($\sim 80$ K) is insensitive to external field and there is almost no shift when the field is up to 5 T. This heat capacity anomaly corresponds to the structural transition, in line with the magnetic susceptibility anomaly, indicating strong spin-lattice coupling in VI$_3$. The entropy $S(T,H)$ can be deduced by

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

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 $\Delta T_{ad}$ caused by the field change can be obtained by $\Delta T_{ad}(T,H) = T(S,H) - T(S,0)$, 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 6(b) and 6(c) show the temperature dependence of $-\Delta S_M$ and $\Delta T_{ad}$ estimated from heat capacity with out-of-plane field. The maxima of $-\Delta S_M$ and $\Delta T_{ad}$ increase with increase field and reach the values of $2.80$ J kg$^{-1}$ K$^{-1}$ and $0.96$ K, respectively, with the field change of 5 T.
IV. CONCLUSIONS

In summary, we have studied the critical behavior and magnetocaloric effect around the FM-PM transition in bulk VI$_3$ single crystal. The PM-FM transition in VI$_3$ is identified to be of the second order. The critical exponents $\beta$, $\gamma$, and $\delta$ estimated from the modified Arrott plot follow the tricritical mean-field model. Considering its ferromagnetism can be maintained upon exfoliating bulk crystals down to a single layer, further investigation on the size-dependent properties is of interest.

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