Tricritical Behavior in Ferromagnetic Semiconductor CrGeTe3

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Abstract

CrGeTe3 exhibits 2D ferromagnetic semiconductor behavior, which holds great promise for applications in spintronic devices. It is known that CrSiTe3 possesses 2D-Ising magnetic characteristics; however, compared to CrSiTe3, CrGeTe3 displays a smaller van der Waals gap and a larger monolayer exfoliation energy, which may induce a transition from 2D to 3D magnetism. To verify this hypothesis, we performed critical behavior analysis on CrGeTe3 near the ferromagnetic phase transition temperature. We found that CrGeTe3 follows the tricritical mean-field model. From this, we conclude that CrGeTe3 exhibits features characteristic of a transition from 2D to 3D magnetism.

Full Text

Tricritical Behavior of Two-Dimensional Intrinsic Ferromagnetic Semiconducting CrGeTe3

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Abstract

CrGeTe has recently emerged as a new two-dimensional ferromagnetic semiconductor that is promising for spintronic device applications. Unlike CrSiTe , whose magnetism can be understood using the 2D-Ising model, CrGeTe exhibits a smaller van der Waals gap and larger cleavage energy, which could lead to a transition of magnetic mechanism from 2D to 3D. To confirm this speculation, we investigate the critical behavior of CrGeTe around the second-order paramagnetic-ferromagnetic phase transition. We obtain critical exponents estimated by several common experimental techniques including the modified Arrott plot, Kouvel-Fisher method, and critical isotherm analysis, which show that the magnetism of CrGeTe follows the tricritical mean-field model with critical exponents β, γ, and δ of 0.240 $\pm$ 0.006, 1.000 $\pm$ 0.005, and 5.070 $\pm$ 0.006, respectively, at the Curie temperature of 67.9 K. We therefore suggest that the magnetic phase transition from 2D to 3D for CrGeTe should be located near a tricritical point. Our experiment provides a direct demonstration of the applicability of the tricritical mean-field model to a 2D ferromagnetic semiconductor.

Since the successful exfoliation of single-layer graphene, 2D materials have attracted significant interest due to their highly tunable physical properties and immense potential in scalable device applications [**?**]. However, pristine graphene exhibits no bandgap and its inherent inversion symmetry suppresses spin-orbit coupling (SOC) [**?**]. The weak SOC and zero bandgap eliminate graphene as a potential candidate for spintronic devices, which requires one to search for alternative 2D materials that extend beyond graphene to other layered materials with van der Waals gaps [**?**]. For example, in single-layer MoS , the large SOC leads to a unique spin-valley coupling which may be useful for spintronic applications [**?**]. Whereas spintronic devices using 2D materials are still in their infancy [**?**], which is due to the lack of long-range ferromagnetic order that is crucial for macroscopic magnetic effects [**?**, **?**]. The emergence of ferromagnetism in 2D materials in combination with their rich electrical and optical properties could open up ample opportunities for 2D magnetic, magnetoelectric, and magneto-optic applications [**?**, **?**, **?**].

Recently, chromium tellurides CrXTe (X = Si, Ge, and Sn) with centrosymmetric structure have attracted significant attention because they belong to a rare category of ferromagnetic semiconductors possessing a 2D layered structure [**?**, **?**]. Extensive theoretical and experimental efforts have been extended towards understanding the properties of these 2D magnets. On the theoretical side, recent studies on CrXTe have focused on their electronic structure and magnetic properties, particularly predictions of single-layer properties [**?**, **?**]. On

the experimental side, CrSiTe and CrGeTe have been prepared and characterized [?, ?, ?, ?, ?]. Compared with CrSiTe , which shows characteristics of 2D-Ising behavior [?, ?, ?], the smaller van der Waals gap and larger in-plane nearest-neighbor Cr-Cr distance in CrGeTe enhance the Curie temperature from 32 K for CrSiTe to 61 K for CrGeTe [?, ?, ?, ?]. In addition, theoretical investigations have suggested that single-layer CrGeTe presents characteristics of 2D-Ising behavior similar to CrSiTe [?, ?]. By contrast, a scanning magneto-optic Kerr microscopy experiment showed that single-layer CrGeTe represents a close-to-ideal 2D Heisenberg ferromagnetic system using rigorous renormalized spin wave theory analysis and calculations [?]. It is known that with the increase of the X atom radius, CrXTe presents a smaller van der Waals gap and larger cleavage energy [?, ?, ?, ?]. We suppose that the CrXTe system may undergo a three-dimensional (3D) magnetic phase transition from 2D with the increase of the X atom radius. Therefore, a method to rapidly characterize the critical behavior of single-crystalline CrGeTe is crucial. For this purpose, we present a detailed investigation of the critical phenomena of CrGeTe using the initial isothermal $M(H)$ curves around the Curie temperature T_C.

We find that the critical exponents of CrGeTe satisfy the universality class of the tricritical mean-field theory. This indicates that the magnetic phase transition of CrGeTe should be close to a tricritical point from 2D to 3D.

Samples of single-crystalline CrGeTe were prepared by the self-flux technique [?]. The XRD data indicated that the powders are single-phase with rhombohedral structure (see Supporting Information). We measured the heat capacity using the Quantum Design physical properties measurement system (PPMS-9T) and characterized the magnetic properties by the magnetic property measurement system (MPMS-XL5). Density functional theory (DFT) calculations were performed using the Vienna Ab-initio Simulation Package [?]. We used the local density approximation [?, ?] to treat the electron-electron exchange-correlation interactions. The electron-ion interactions are described by potentials based on the projector augmented wave method [?, ?].

Figure 1 [Figure 1: see original paper] (a) and (b) show the inverse of temperature-dependent susceptibility $1/\chi_T$ of CrGeTe under field-cooled cooling with applied magnetic field $H = 100$ Oe, parallel to the ab plane and c axis, respectively. We observe a paramagnetic–ferromagnetic (PM-FM) transition that occurs at a critical temperature of 67.3 K, as determined by the derivative of the susceptibility. This temperature is consistent with the values of 61 K or 70 K reported previously [?]. For a FM system, the $1/\chi_T$ above T_C can be described by the Curie-Weiss law resulting from mean-field theory [?]. The red curves showing the Curie-Weiss law are obeyed only at high temperature. A close observation of Fig. 1(a) and (b) reveals that the $1/\chi_T$ curves deviate from straight lines at around 150 K, which is much higher than T_C, indicating strong short-range FM spin interactions in CrGeTe above T_C. The effective magnetic moment is determined to be $\mu_{\text{eff}} \sim 4.22\mu_B$ (parallel to the ab plane) and $4.35\mu_B$ (parallel to the c axis), which are close to the

theoretical value expected for Cr^{3+} of $3.87\mu_B$ [**?**]. The insets of Fig. 1(a) and (b) show the isothermal magnetization $M(H)$ at 5 K exhibiting typical FM behavior with the saturation field H_S of about 5 kOe (parallel to the ab plane) and 2.5 kOe (parallel to the c axis). In addition, the $M(H)$ curves show almost no coercive force for CrGeTe .

Figure 1 (Color online): (a) and (b) Inverse of temperature-dependent susceptibility $1/\chi_T$ of CrGeTe under field-cooled cooling with an applied magnetic field H of 100 Oe, parallel to the ab plane and c axis, respectively. The red solid lines are the fitted results according to the Curie-Weiss law. The insets show the isothermal magnetization curves $M(H)$ at 5 K. (c) Specific heat C_p as a function of T for CrGeTe and the fitted Debye model; Temperature-dependent magnetic (d) specific heat $C_{\mathrm{mag}}(T)$ and (e) entropy $S_{\mathrm{mag}}(T)$. The blue dashed line refers to $S_{\mathrm{mag}}(T \to \infty)$ calculated with the magnetic moment S of Cr^{3+} being 3/2.

Figure 1(c) shows the variation of the zero-field specific heat $C_p(T)$ with temperature. The sharp anomaly in $C_p(T)$ at 64.8 K corresponds to the Curie temperature T_C^{SH}. Since CrGeTe is a semiconductor [**?**], the electronic contribution to the heat capacity is not considered. The magnetic contribution C_{mag} can be calculated by the following equations [**?**]:

$$C_{\mathrm{mag}} = C_p - C_{\mathrm{Debye}}$$

where C_{Debye} is given by:

$$C_{\mathrm{Debye}} = 9R\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x-1)^2} dx$$

where R is the molar gas constant, Θ_D is the Debye temperature, and $N = 5$ is the number of atoms per formula unit. The sum of Debye functions accounts for the lattice contribution to specific heat. We can extract the magnetic contribution $C_{\mathrm{mag}}(T)$ from the measured specific heat of CrGeTe . The fitted $C_p(T)$ for CrGeTe by the equations over the temperature range from about 7 to 250 K is shown by the red curve in Fig. 1(c) using the Debye temperature $\Theta_D = 476.5$ K. We observe a sharp peak at $T_C = 64.8$ K and there are strong dynamic short-range FM spin interactions above T_C (shown in Fig. 1(d)). The magnetic entropy $S_{\mathrm{mag}}(T)$ is calculated by integrating C_{mag}/T. Fig. 1(e) shows the temperature dependence of $S_{\mathrm{mag}}(T)$. The entropy of CrGeTe per mole with completely disordered spins is $S(T \to \infty) = R\ln(2S+1)$. Using $S = 3/2$ for Cr^{3+}, we obtain $S_{\mathrm{mag}}(T \to \infty)$ of 69.2 J/(mol · K). As shown in Fig. 1(e), one observes that the 64.7 J/(mol · K) of $S_{\mathrm{mag}}(T)$ at 150 K is close to the value of $S_{\mathrm{mag}}(T \to \infty)$, which suggests that CrGeTe presents obvious PM behavior above 150 K. However, we observe that S_{mag} is 36.3 J/(mol · K) at T_C, which is only 52.5% of the value for $S_{\mathrm{mag}}(T \to \infty)$ in Fig. 1(e). These results indicate there are strong dynamic short-range FM spin interactions between T_C and 150 K, which is consistent with the above conclusion from fitting the $1/\chi_T$ data to the Curie-Weiss law.

As mentioned above, with increasing X atom radius, the CrXTe compounds present a smaller van der Waals gap and larger cleavage energy [**?**, **?**, **?**, **?**], which may induce a 3D magnetic phase transition. For the purpose of confirmation, we performed a detailed characterization of the critical phenomena using the initial isothermal $M(H)$ curves around T_C for CrGeTe , which are shown in Fig. 2(a).

Figure 2 [Figure 2: see original paper] (Color online): (a) Initial magnetization of CrGeTe around T_C; (b) Arrott plots of M^2 versus H/M (the $M(H)$ curves are measured at temperature intervals of 1 K and 0.5 K approaching T_C); (c) Normalized slopes as a function of temperature; (d) Modified Arrott plot ($M^{1/\beta}$ versus $(H/M)^{1/\gamma}$) of isotherms with $\beta = 0.24$ and $\gamma = 1$ for CrGeTe . The red dashed line is the linear fit of isotherm at 67.9 K; (e) Temperature dependence of M_S and χ_0^{-1}. The T_C and critical exponents are obtained from fitting to Eq. (S1) and (S2); (f) The Kouvel-Fisher plot. The T_C and critical exponents are obtained from the linear fit.

In mean-field theory, the critical exponents and critical temperature can be determined from the Arrott plot with β of 0.5 and γ of 1.0 [**?**, **?**]. According to this method, the M^2 versus H/M (shown in Fig. 2(b)) should be a series of parallel straight lines in the higher field range around T_C and the line at $T = T_C$ should pass through the origin. Note that the lower field data mainly represent the arrangement of magnetic domains, which should be excluded in the fitting process [**?**]. However, all the curves in Fig. 2(b) show nonlinear behaviors with downward curvature even in high field, which indicates non-mean-field-like behavior. Moreover, the positive slope reveals a second-order phase transition according to the criterion proposed by Banerjee [**?**]. As such, a modified Arrott plot should be employed to obtain the critical exponents.

To determine an accurate model, we obtain a modified Arrott plot following Eq. (S9) for single-crystalline CrGeTe at different temperatures. Three groups of possible exponents belonging to the 3D Heisenberg model ($\beta = 0.365$, $\gamma = 1.386$), 3D-Ising model ($\beta = 0.325$, $\gamma = 1.24$) and tricritical mean-field model ($\beta = 0.25$, $\gamma = 1.0$) exhibit nearly straight lines in the high field region [**?**, **?**]. We calculate their normalized slopes (NS) defined as NS $= S(T)/S(67.3\text{ K})$. By comparing NS with the ideal value of unity, one can identify the most suitable model [**?**, **?**]. Figure 2(c) shows the plots of NS versus T employing the three different models, revealing that the tricritical mean-field model is the most appropriate to describe the critical behavior of CrGeTe . By proper selection of β and γ, one can clearly show the isotherms are a set of parallel straight lines in high fields as displayed in Fig. 2(d). The linear extrapolation from the high field region gives the spontaneous magnetization $M_S(T, 0)$ and the inverse of initial susceptibility $\chi_0^{-1}(T, 0)$ (see Fig. 2(e)) corresponding to the intercepts on the $M^{1/\beta}$ and $(H/M)^{1/\gamma}$ axes, respectively. By fitting the data of $M_S(T, 0)$ and $\chi_0^{-1}(T, 0)$ to Eq. (S1) and (S2), one obtains two new values of $\beta = 0.242 \pm 0.006$ with $T_C = 67.95 \pm 0.01$ and $\gamma = 0.985 \pm 0.009$ with $T_C = 67.90 \pm 0.09$. These results are again very close to the critical exponents of the tricritical mean-field

model. In addition, these critical exponents and T_C can be obtained more accurately from the Kouvel-Fisher (KF) method [**?**]. Hence, one can find that the temperature dependence $M_S(dM_S/dT)^{-1}$ and $\chi_0^{-1}(d\chi_0^{-1}/dT)^{-1}$ should be straight lines with slopes $1/\beta$ and $1/\gamma$, respectively. As seen in Fig. 2(f), the linear fit yields β of 0.240 ± 0.006 with T_C of 67.91 ± 0.07 and γ of 1.000 ± 0.005 with T_C of 67.88 ± 0.05, respectively.

Remarkably, the obtained values of the critical exponents and T_C using the KF method are in excellent agreement with those using the modified Arrott plot based on the tricritical mean-field model. This suggests that the estimated values are self-consistent and unambiguous.

To further validate the above critical exponents β and γ, we study the relation among these exponents. According to Eq. (S3), δ can be directly estimated from the critical isotherm at T_C. Figure 3 [Figure 3: see original paper] (a) shows the isothermal magnetization $M(H)$ at $T_C = 67.9$ K. The inset of the same plot is demonstrated on a log-log scale. The solid straight line with slope $1/\delta$ is the fitted result using Eq. (S3). From the linear fit we obtained the third critical exponent δ of 5.032 ± 0.005. Moreover, the exponent δ can be calculated by the Widom scaling relation [**?**, **?**]:

$$\delta = 1 + \gamma/\beta$$

Based on the β and γ values calculated in Fig. 2(e) and (f), Eq. (3) yields δ of 5.070 ± 0.006 and 5.167 ± 0.006, respectively. We emphasize that these values are very close to the results from the experimental critical isothermal analysis. Therefore, the critical exponents obtained in this study basically obey the Widom scaling relation, showing that the obtained β, γ and δ are reliable.

Finally, these critical exponents should follow the scaling equation (Eq. (S6)) in the critical region. The scaling equation indicates that m versus h forms two universal curves for $T > T_C$ and $T < T_C$, respectively. Based on Eq. (S7), the isothermal magnetization around the critical temperatures for CrGeTe has been plotted in Fig. 3(b). All experimental data in the higher field region collapse onto two universal curves, in agreement with scaling theory. The inset of Fig. 3(b) shows the corresponding log-log plot. Similarly, all the points also collapse into two different curves in the higher field region. This result shows again that the obtained results of the critical exponents and T_C are valid.

Figure 3 (Color online): (a) Isothermal $M(H)$ at T_C. The inset shows the alternative plot on a log-log scale and the straight line is the linear fit following Eq. (S3); (b) Renormalized magnetization m versus renormalized field h at several typical temperatures around T_C. The inset shows the alternative plot on a log-log scale; (c) Effective exponents β_{eff} below T_C and (d) γ_{eff} above T_C as a function of the reduced temperature ϵ.

To further examine the convergence of the critical exponents, the effective exponents β_{eff} and γ_{eff} can be obtained by Eq. (S8) and (S9) for CrGeTe . As shown in Fig. 3(c) and (d), both β_{eff} and γ_{eff} show non-monotonic variation with ϵ

(see Eq. (S4)). The lowest ϵ (ϵ_{min}) are 5.89×10^{-3} and 1.47×10^{-3} for β_{eff} and γ_{eff}, respectively. We obtain the effective exponents β_{eff} of 0.242 and γ_{eff} of 1.069, indicating that both β_{eff} and γ_{eff} are converged when the temperature approaches T_C.

The experimental critical exponents of CrGeTe , as well as the theoretical values of CrSiTe , MnSi and some other manganites based on various models, are summarized in Table 1 . It is seen that the critical exponents for MnSi and doped manganites are consistent with those of tricritical mean-field theory [**?**, **?**, **?**, **?**]. These compounds have the same characteristics, i.e., a tricritical point separating the first-order from the second-order ferromagnetic phase transitions. This phenomenon shows that element substitution [**?**, **?**], hole or electric doping [**?**], and external magnetic field [**?**] can induce tricritical behavior. However, CrXTe presents second-order ferromagnetic phase transitions [**?**, **?**] and our results indicate that the critical behavior of CrGeTe is close to the theoretical value of the tricritical mean-field model. Compared with CrSiTe , which shows characteristics of the 2D-Ising model [**?**, **?**, **?**], the smaller van der Waals gap and larger planar nearest-neighbor Cr-Cr distance of CrGeTe enhance the Curie temperature from 32 K for CrSiTe to 61 K for CrGeTe [**?**, **?**]. In addition, neutron scattering and isothermal magnetization experiments yield a critical exponent β of around 0.151 or 0.17 for CrSiTe [**?**, **?**, **?**], which is close to the value expected for a 2D transition ($\beta_{\text{Ising2D}} = 0.125$) and well below the values expected for a 3D transition ($\beta_{\text{Ising3D}} = 0.326$). Our results yield a critical exponent β of 0.24 for CrGeTe that is close to the critical exponent of the tricritical mean-field model. Hence, the increase of the X atom radius, facilitating superexchange coupling between the Cr atoms via the Te atom and leading to the smaller van der Waals gap in the CrXTe system [**?**, **?**], could induce a tricritical magnetic phase transition in the CrGeTe single crystal.

Table 1. Critical exponents of CrGeTe with various theoretical models, CrSiTe and other related materials with tricritical mean-field model (SC = single crystal; PC = polycrystalline; cal = Calculated from Eq. (3)).

Composition	Reference	T_C (K)	Technique	β	γ	δ
CrGeTe	This work	67.9	Modified Arrott plot	0.242 ± 0.006	0.985 ± 0.009	5.070 ± 0.006 (cal)
			Kouvel-Fisher method	0.240 ± 0.006	1.000 ± 0.005	5.167 ± 0.006 (cal)
			Critical isotherm	-	-	5.032 ± 0.005

Composition	Reference	T_C (K)	Technique	β	γ	δ
Theory			Tricritical mean-field	0.25	1.0	5.0
			Mean-field	0.5	1.0	3.0
			3D-Heisenberg theory	0.365	1.386	4.8
			3D-Ising	0.325	1.24	4.82
CrSiTe	[43,44]	32	Modified Arrott plot	0.170 ± 0.010	1.532 ± 0.015	4.734 ± 0.047
MnSi (SC)	[46,47]	29.3	Modified Arrott plot	0.242 ± 0.007	0.915 ± 0.012	5.17 ± 0.07
La . Nd . Sr . Mn . O	[51]	249.3	Modified Arrott plot	0.257 ± 0.010	1.12 ± 0.02	7.14 ± 0.14
La . Te . MnO	[52]	239.5	Modified Arrott plot	0.201 ± 0.010	1.27 ± 0.02	5.0 ± 0.1
La . Ca . MnO	[47]	265.5	Modified Arrott plot	0.25 ± 0.01	1.03 ± 0.02	5.0 ± 0.1

Although single-crystalline CrSnTe has not yet been synthesized, we speculate that the magnetism of CrSnTe should be closer to the 3D-Ising model. To support this assumption, we perform DFT calculations with the same calculation parameters that were used in Ref. [**?**]. Figure 4 [Figure 4: see original paper] (a) shows the calculated formation energy E_f, which is defined as the energy cost of extracting a sheet of single-layer CrXTe from their bulk counterparts. As can be seen, E_f increases as the species vary from Si to Ge. This is consistent with the larger theoretical cleavage energy of single-layer CrGeTe than that of CrSiTe , which indicates that the layers are coupled more strongly in CrGeTe [**?**]. The formation energy of CrSnTe is even higher than the other compounds, revealing that it presents the strongest interlayer coupling, which leads to its 3D characteristics. Figure 4(b), (c), and (d) illustrate the charge density of the three compounds. Consistent with the trend of the E_f results, the electron density around the Sn-Sn pair is the least among the three materials. Namely, more electrons in CrSnTe participate in the interlayer coupling.

Figure 4 (Color online): (a) Formation energy of single-layer CrXTe ; The formation energy of single-layer CrSiTe is adopted from Ref. [**?**]. (b), (c), and (d) Charge density of bulk CrXTe with an isosurface value of 0.05 e/r_{Bohr}.

In conclusion, we have performed a comprehensive experimental study on the

critical properties of single-crystalline CrGeTe using isothermal magnetization around the Curie temperature T_C. Based on various experimental techniques including the modified Arrott plot, Kouvel-Fisher method, and critical isotherm analysis, we obtained the critical exponents β, γ, and δ of 0.240 ± 0.006, 1.000 ± 0.005, and 5.070 ± 0.006, respectively, at the Curie temperature of 67.9 K. These numerical results are similar to the theoretical values in the tricritical mean-field model, which is therefore capable of describing the critical magnetic behavior of 2D CrGeTe . DFT calculations show that the formation energy of CrGeTe lies between those of CrSiTe and CrSnTe , which is in line with a crossover of the magnetic phase transition from 2D to 3D. Overall, our findings provide a fundamental understanding of the anomalous PM-FM transition in a novel 2D ferromagnetic semiconductor.

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