Spin stiffness of chromium-based van der Waals ferromagnets

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Abstract

Low temperature magnetization of CrI₃, CrSiTe₃ and CrGeTe₃ single crystals were systematically studied. Based on the temperature dependence of extrapolated spontaneous magnetization from magnetic isotherms measured at different temperatures, the spin stiffness constant ($D$) and spin excitation gap ($\Delta$) were extracted according to Bloch’s law. For spin stiffness, $D$ is estimated to be $27 \pm 6$ meV Å$^2$, $20 \pm 3$ meV Å$^2$, and $38 \pm 7$ meV Å$^2$ for CrI₃, CrSiTe₃ and CrGeTe₃ respectively. Spin excitation gaps determined via Bloch’s formulation have larger error bars yielding $0.59 \pm 0.34$ meV (CrI₃), $0.37 \pm 0.22$ meV (CrSiTe₃) and $0.28 \pm 0.19$ meV (CrGeTe₃). Among all three studied compounds, larger spin stiffness value leads to higher ferromagnetic transition temperature.

Keywords: ferromagnetism, spin stiffness, van der Waals

(Some figures may appear in colour only in the online journal)

1. Introduction

Magnetic two-dimensional (2D) materials have attracted great attention after long-range magnetic ordering was experimentally discovered in monolayer CrI₃ and CrGeTe₃ [1, 2]. For 2D material research, these discoveries expand the possible tuning parameters from original charge degree of freedom to include magnetic degree of freedom. This additional tuning parameter has enabled further device capabilities and could bring in new opportunities in future microelectronics [3–5]. Recent progress in 2D magnetic materials has been primarily focusing on developing new material candidate with more functional properties [6–8], and on obtaining a better understanding of the mechanism behind such 2D long range magnetic ordering [9–11]. Among the available compounds, chromium-based van der Waals materials were most intensively studied as they were first verified to manifest 2D long range magnetic ordering. CrI₃, CrSiTe₃ and CrGeTe₃ belong to this family. All three compounds share very similar structures. Cr atoms are located at the center of Te or I octahedra. The edge-sharing octahedron are then arranged in a honeycomb lattice within each layer, forming a van der Waals gap between iodine in the case of CrI₃, and tellurium in the cases of CrSiTe₃ and CrGeTe₃. For CrI₃, this honeycomb layers leave an empty site in the center of the honeycomb, whereas double silicon/germanium atoms in CrSiTe₃ and CrGeTe₃ occupy these vacant centers.

Because the Wagner and Mermin theorem [12] requires magnetic anisotropy for any 2D long range magnetic ordering to exist, both magnetic exchange interaction and magnetic anisotropy play key roles in determining the magnetic property of these layered magnets. Measuring and understanding the influence of these fundamental magnetic parameters, therefore, are critical for future material design. Experimentally, bulk sample characterization provides valuable first-hand information, as an important step towards understanding and modeling magnetic behavior at low dimensions. The exchange interaction and anisotropy were previously measured by inelastic neutron scattering, ferromagnetic resonance on bulk CrI₃ [10, 11, 13] and CrSiTe₃ [14]. In this paper, we attempt to extract these parameters for CrI₃, CrSiTe₃, and CrGeTe₃ in the form of spin stiffness and spin excitation gap, via measuring and interpreting low temperature magnetization data based on Bloch’s law [15]. Bulk magnetization measurement, as a more widely available technique, enables this approach to provide a more rapid characterization of future layered ferromagnets.
2. Experimental

CrI₃ single crystals were grown using a chemical vapor transport technique [16]. Stoichiometric starting elements (chromium powder, 99.94%, Alfa Aesar; iodine 99.8%, Alfa Aesar) were sealed in an evacuated silica tube. The silica tube was then put in an open-ended tube furnace for 3 days, where the material side was kept at 650 °C and the cooler side was kept at furnace edge, close to room temperature. CrGeTe₃ single crystals were grown using a high temperature solution growth technique. Starting elements in a molar ratio of Cr:Ge:Te = 2:6:36 (germanium, 99.999%, Alfa Aesar; tellurium, 99.999%, Alfa Aesar) [17] were packed in the Canfield Crucible Sets [18] and sealed in a silica tube under vacuum. The silica ampoule was then heated up to 800 °C over 3 h, dwell for 10 h and then slowly cooled to 500 °C over 60 h, at which temperature the remaining liquid was decanted in a centrifuge. CrSiTe₃ single crystals were also grown using a solution method [19]. Starting materials with molar ratio of Cr:Si:Te = 1:2:6 (silicon, 99.999%, Alfa Aesar) were loaded in the same type of crucible-tube set-up as in CrGeTe₃. The sealed tube was then heated up to 1150 °C over 8 h, dwell for 10 h, and then cooled to 700 °C over 120 h for decanting. In all cases, black, layered crystals were obtained with c-axis perpendicular to the layers. CrI₃ crystals were kept and handled in an argon glovebox.

Single crystal x-ray diffraction was measured using a Bruker D8 Discover diffractometer, with a microfocus and Cu Kα radiation. Layered single crystals were placed on sample pucks with facets facing up/down. Sample heights were adjusted for each measurement. Magnetization data were measured using a quantum design physical property measurement system Dynacool equipped with a vibrating sample magnetometer (vsm) (1.8 K–300 K, 0–90 kOe). All samples were measured with applied magnetic field parallel to their c-axis. Sample position drift due to vsm sample rod thermal contraction was addressed by either a periodic re-centering of the sample, or an extended waiting time (≥6 h) at 1.8 K for rod length stabilization.

3. Results and discussion

All samples were first tested by single-crystal x-ray diffraction using a powder diffractometer. Figure 1(a) shows (00L) diffractions for all compounds under study. All observed peaks are consistent with reported structure for CrI₃ [16] CrSiTe₃ [20] and CrGeTe₃ [21]. Sharp diffraction peaks indicate good crystallinity for all samples. Ferromagnetic property was further used to verify the phase purity as well as consistency with existing literatures. In figure 1(b), field cooling, temperature dependent magnetization, measured under 1 kOe, are shown on the left scale. Magnetization curves are normalized to their measured values at 2 K (M₉K) for clarity. Ferromagnetic phase transition temperatures (Tc) were determined from the temperature derivative of magnetization, shown as dashed lines on the right scale. For CrI₃, the Tc was determined to be ~60.1 K, consistent with reported value [16, 22]. CrGeTe₃ and CrSiTe₃ have Tc at 66.4 K and 34.4 K, both consistent with existing literatures [14, 23].

To determine the spontaneous magnetization, or the saturation magnetic moment at each temperature, field-dependent magnetization data were collected. Take CrI₃ as an example. Figure 2 shows a selection of magnetic isotherms at various temperatures between 50 kOe and 90 kOe. Low-field magnetization data show typical ferromagnetic behavior which are in good agreement with previous report [16] and thus not shown here. At higher applied magnetic fields, diamagnetic contribution due to both core diamagnetism [24] and sample holder become visible after magnetic saturation is reached. The diamagnetism is manifested by negative slopes in high field magnetization data, which happens to all samples under current
magnetization will follow the famous Bloch’s law in the form of equation (1):

\[ M(0, 0) - M(T, 0) = (constant) \times T^{1/2}, \]

where: \( M(0, 0) \) is the spontaneous magnetization at zero temperature, zero field; and \( M(T, 0) \) is the spontaneous magnetization at a finite temperature, \( T \). In a more realistic situation, considering the applied magnetic field and spin wave excitation gap, the proportional constant in front of the power law can be expressed as [15, 26–28]:

\[ M(0, H) - M(T, H) = g\mu_B \left( \frac{kT}{4\pi D} \right)^{3/2} f_2(\Delta'/kT), \]  

(2)

where \( f_2(y) = \sum_{n=1}^{\infty} \frac{e^{-ny}}{1+n^2} \) is the Bose–Einstein integral function that can account for the field-dependence of the spin excitation gap, \( \Delta' = \Delta + g\mu_B H \). This method has been widely used to determine the spin stiffness in metallic ferromagnets such as iron, nickel, and their alloys [26, 27, 29–31], as well as other systems such as doped LaMnO\(_3\) [28]. In general, the estimated spin stiffness is consistent with the values obtained from more direct measurements such as inelastic neutron scattering and spin wave resonance [27]. Deviation from the general \( T^{3/2} \) behavior can often be associated to higher order term in the spin wave dispersion approximation [27, 32] or conduction electron’s Stoner contribution [26] which will be discussed later.

In figure 3, the extrapolated temperature dependent, zero field spontaneous magnetization values for CrI\(_3\) are fitted to both simplified gapless equation (1) and gapped equation (2). It is evident that spin excitation gap should be taken into consideration to properly interpret the low temperature magnetization behavior of CrI\(_3\). Because the fitted magnetization values are zero field, spontaneous magnetization, there is no Zeeman splitting contribution to the excitation gap. Thus, the existence of an intrinsic excitation gap due to magnetic anisotropy in CrI\(_3\) is compatible with the Wagner and Mermin theorem [12] that requires anisotropy to establish 2D long range magnetic ordering in CrI\(_3\) [1].

Similar measurements and fittings were carried out on multiple samples for all compounds under study. Figure 4 shows obtained experimental data on CrSiTe\(_3\), CrGeTe\(_3\) and corresponding fitted curves. In general, fitting according to equation (2) works well for each dataset, whereas different samples reflect slightly different temperature dependence. Such difference may result from the variation in sample quality even within the same batch. The extracted spin stiffness constants and spin excitation gap are listed in table 1. Error bars are calculated according to fitting results on different samples.

Since CrI\(_3\) is of most intense interest recently with more experimental data, we first focus on its physical properties. From our fittings, the estimated \( D \) for CrI\(_3\) is \( 27 \pm 6 \text{ meV Å}^2 \), and \( \Delta \) is \( 0.59 \pm 0.34 \text{ meV} \). The spin stiffness value of CrI\(_3\) is close to the out-of-plane inelastic neutron scattering result [13] at \( D_s \sim 23 \text{ meV Å}^2 \). For semiconducting CrI\(_3\), saturation magnetization should be orientation independent. Therefore, our results reflect an averaged stiffness. Combining the reported anisotropy in magnon spectrum, the current obtained stiffness constant, however, falls short from the averaged spin stiffness [15] based on \( D_{ave} = D_{ab}(1/3'D_{ab}2/3) \), where \( D_{ab} \) was roughly estimated [13] to be 450 meV Å\(^2\). It is unclear at this moment what contribute to this discrepancy. Future high-resolution neutron scattering measurement on in-plane magnon spectrum may help resolve the problem. The obtained spin excitation gap...
value shows a rather large variation among samples, despite relatively smaller difference in fitted spin stiffness values. This likely originates from high sensitivity of the Bose–Einstein integral function to the gap value. Overall, the estimated excitation gap here, $\Delta$, is qualitatively consistent with the inelastic neutron scattering and ferromagnetic resonance results of 0.3–0.4 meV [11, 13]. Going back to the theoretically fitting, it was stated that the Bloch’s law relies on the assumption that magnon spectrum is parabolic in reciprocal space within long wavelength regime. In the case of insulator, such as all the compounds under current study, no additional Stoner’s contribution needs to be considered. Therefore, the Bloch’s law is expected to work at low enough temperature. Typically, low temperature is empirically taken as below $0.2 T_c$ [28]. With a $T_c$ of $\sim 60$ K for CrI$_3$, the fitting temperature range should be smaller than $12$ K, which is what has been used in figure 3. Furthermore, considering recent reported inelastic neutron scattering data [13], within our maximum fitting temperature in terms of energy, $\sim 1$ meV, the magnon spectrum exhibits a good parabolic distribution in reciprocal space. Thus, higher order term corrections are not necessary in our fitting as sometimes needed for other compounds [27, 32].

CrSiTe$_3$ was also measured by inelastic neutron scattering [14]. Our results of $D = 20 \pm 3$ meV Å$^2$ is in good agreement with the reported value [14] at $\sim 17$ meV Å$^2$. It worth noting that the spin stiffness anisotropy is lot smaller in CrSiTe$_3$ [14] than in CrI$_3$ [13]. The estimated $\Delta$ from Bloch’s law fitting is $0.37 \pm 0.22$ meV, which is larger than reported 0.075 meV [14]. For CrGeTe$_3$, no magnon information has been reported in literature for comparison. We obtained $D = 38 \pm 7$ meV Å$^2$, $\Delta = 0.28 \pm 0.19$ for CrGeTe$_3$.

Due to the structural similarity in CrI$_3$, CrSiTe$_3$, and CrGeTe$_3$, it is physical to compare the spin stiffness, which is proportional to magnetic exchange interaction [9], to their ferromagnetic transition temperatures. In figure 5, $D$ is plotted against $T_c$ by black squares on the left scale. Given the uncertainty in experimental values, the $T_c$ is roughly proportional to $D$. Since spin stiffness is directly associated with the Heisenberg type isotropic interaction, these data provide a qualitative support to an intuitive picture where the stronger exchange interaction leads to higher $T_c$. It was proposed that the magnetic transition is influenced by both anisotropic and isotropic exchange [9]. However, because the large uncertainty in obtained gap values, a quantitative comparison to theory using $\Delta$ and $D$ values here is not meaningful. Other measurements are needed to provide more accurate excitation gap values [11, 13, 14, 33]. Although no clear correlation can be established between $\Delta$ and $T_c$, future investigation on how $\Delta$ influences the capability of stabilizing long-range magnetic ordering at 2D limit may of great interest.

4. Conclusion

In conclusion, we have synthesized single crystals of CrI$_3$, CrSiTe$_3$ and CrGeTe$_3$, three chromium-based ferromagnetic...
van der Waals compounds, and studied their low temperature magnetic property. Temperature dependent spontaneous magnetization values were accurately determined from magnetic isotherms measured at various temperatures. The temperature dependence of spontaneous magnetization generally follows the Bloch’s law when a finite zero-field spin excitation gap is considered. Spin stiffness and excitation gap values were obtained for all three compounds. The obtained values are in general agreement with inelastic neutron scattering results for CrI3 and CrSiTe3, manifesting the reliability of bulk magnetization measurements in extracting spin stiffness constants. The ferromagnetic transition temperatures of CrI3, CrSiTe3 and CrGeTe3 were observed to positively scale with their spin stiffness.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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References

[1] Huang B et al 2017 Layer-dependent ferromagnetism in a van Der Waals crystal down to the monolayer limit Nature 546 270–3
[2] Gong C et al 2017 Discovery of intrinsic ferromagnetism in two-dimensional van Der Waals crystals Nature 546 265–9
[3] Klein D R et al 2018 Probing magnetism in 2D van Der Waals crystalline insulators via electron tunneling Science 360 1218–22
[4] Song T et al 2018 Giant tunneling magnetoresistance in spin-filter van Der Waals heterostructures Science 360 1214–8
[5] Wang Z et al 2018 Electric-field control of magnetism in a few-layered van Der Waals ferromagnetic semiconductor Nat. Nanotechnol. 13 554
[6] Fei Z et al 2018 Two-dimensional itinerant ferromagnetism in atomically thin Fe3GeTe2 Nat. Mater. 17 778–82
[7] Kong T, Stolze K, Timmons E I, Tao J, Ni D, Guo S, Yang Z, Prozorov R and Cava R J 2019 VI3—a new layered ferromagnetic semiconductor Adv. Mater. 31 1808074
[8] Mounet N et al 2018 Two-dimensional materials from high-throughput computational exfoliation of experimentally known compounds Nat. Nanotechnol. 13 246–52
[9] Lado J L and Fernández-Rossier J 2017 On the origin of magnetic anisotropy in two dimensional CrI3 2D Mater. 4 035002
[10] Chen L, Chung J-H, Gao B, Chen T, Stone M B, Kolesnikov A I, Huang Q and Dai P 2018 Topological spin excitations in honeycomb ferromagnet CrI3 Phys. Rev. X 8 041028
[11] Lee I, Utermohlen F G, Weber D, Hwang K, Zhang C, Van Tol J, Goldberger J E, Trivedi N and Hammel P C 2020 Fundamental spin interactions underlying the magnetic anisotropy in the Kitaev ferromagnet CrI3 Phys. Rev. Lett. 124 017201
[12] Mermin N D and Wagner H 1966 Absence of ferromagnetism or antiferromagnetism in one- or two-dimensional isotropic Heisenberg models Phys. Rev. Lett. 17 1133–6
[13] Chen L et al 2020 Magnetic anisotropy in ferromagnetic CrI3 Phys. Rev. B 101 134418
[14] Williams T J, Azcel A A, Lumsden M D, Nagler S E, Stone M B, Yan J and Mandrus D 2015 Magnetic correlations in the quasi-two-dimensional semiconducting ferromagnet CrSiTe3 Phys. Rev. B 92 144404
[15] Keffert F 1966 Spin waves Handbuch der Physik vol 18 (Berlin: Springer) pp 1–273
[16] McGuire M A, Dixit H, Cooper V R and Sales B C 2015 Coupling of crystal structure and magnetism in the layered, ferromagnetic insulator CrI3 Chem. Mater. 27 612–20
[17] Ji H et al 2013 A ferromagnetic insulating substrate for the epitaxial growth of topological insulators J. Appl. Phys. 114 114907
[18] Canfield P C, Kong T, Kaluarachchi U S and Jo N H 2016 Use of frit-disc crucibles for routine and exploratory solution growth of single-crystalline samples Phil. Mag. 96 84–92
[19] Casto L D et al 2015 Strong spin-lattice coupling in CrSiTe3 APL Mater. 3 041515
[20] Marsh R E 1988 The crystal structure of Cr2Si2Te6: corrugendum J. Solid State Chem. 77 190–1
[21] Carteaux V, Brunet D, Ouvarov G and Andre G 1995 Crystallographic, magnetic and electronic structures of a new layered ferromagnetic compound Cr2Ge2Te6 J. Phys.: Condens. Mater 7 69–87
[22] Liu Y and Petrovic C 2018 Three-dimensional magnetic critical behavior in CrI3 Phys. Rev. B 97 014420
[23] Selter S, Bastien G, Wolter A U B, Aswartham S and Büchner B 2020 Magnetic anisotropy and low-field magnetic phase diagram of the quasi-two-dimensional ferromagnet Cr2Ge2Te6 Phys. Rev. B 101 014440
[24] Bain G A and Berry J F 2008 Diamagnetic corrections and Pascal’s constants J. Chem. Educ. 85 532–6
[25] Ashcroft N W and Mermin N D 1976 Solid State Physics (Belmont: Cengage Learning)
[26] Riedi P C 1977 The contribution of spin waves and Stoner excitations to the magnetization of nickel and iron Physica B + C 91 43–8
[27] Hüller K 1986 The spin wave excitations and the temperature dependence of the magnetization in iron, cobalt, nickel and their alloys J. Magn. Magn. Mater. 61 347–58
[28] Smolyaninova V N, Hamilton J J, Greene R L, Mukovskii Y M, Karabashev S G and Balbashov A M 1997 Low-temperature field-dependent magnetization of La0.7Sr0.3MnO3 Phys. Rev. B 55 5640
[29] Smith T F, Gardner W E and Budnick J J 1968 Field dependence of the stiffness constant for dilute PdFe alloys Phys. Lett. A 27 326–7
[30] Alfred A T 1976 Ferromagnetism in iron-chromium alloys. I. Bulk magnetization measurements Phys. Rev. B 14 219
[31] Callaway J, Wang C S and Laurent D 1981 Magnetic susceptibility and spin waves in ferromagnetic metals Phys. Rev. B 24 6491
[32] Argyle S B E, Charap S H and Pugh E W 1963 Deviations from T3/2 law for magnetization of ferrometals: Ni, Fe, and Fe + 3% Si Phys. Rev. 132 2051
[33] Tari A 2003 The Specific Heat of Matter at Low Temperatures vol 78 (Singapore: World Scientific)