Magnetic Anisotropy and Low Field Magnetic Phase Diagram of Quasi Two-Dimensional Ferromagnet Cr$_2$Ge$_2$Te$_6$

S. Selter,$^{1,2,*}$ G. Bastien,$^1$ A. U. B. Wolter,$^1$ S. Aswartham,$^{1,†}$ and B. Büchner$^{1,2}$

$^1$Institute for Solid State Research, Leibniz IFW Dresden, Helmholtzstr. 20, 01069 Dresden, Germany
$^2$Institute of Solid State and Materials Physics, Technische Universität Dresden, 01062 Dresden, Germany

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In this work we present a comprehensive investigation on magnetic and thermodynamic properties of the two-dimensional layered honeycomb system Cr$_2$Ge$_2$Te$_6$. Using magnetization and specific heat measurements under magnetic field applied along two crystallographic directions we obtain the magnetic phase diagram for both directions. Cr$_2$Ge$_2$Te$_6$ is a ferromagnet with a Curie temperature $T_C = 65$ K and exhibits an easy magnetization axis perpendicular to the structural layers in the $ab$-plane. Under magnetic fields applied parallel to the hard plane $ab$ below the magnetic saturation, a downturn with an onset temperature $T^*$ is observed in the temperature dependent magnetization curve. $T^*$ shows a monotonous shift towards lower temperatures with increasing field. The nature of this anisotropic and specific behavior for fields in the hard plane is discussed as an interplay among field, temperature and effective magnetic anisotropy. Similarities to structurally related compounds such as CrX$_3$ ($X = Br, I$) hint towards a universality of this behavior in ferromagnetic quasi two-dimensional honeycomb materials.

I. INTRODUCTION

Since the discovery of Graphene in 2004,$^1$ two-dimensional (2D) materials have been in the forefront of research both in fundamental as well as in applied science. This class of materials stands out due to novel electronic properties in combination with unique structural characteristics.$^2–6$. On one hand, when thinned down to the monolayer limit, significant changes in the physical properties have been observed$^2,3,6,7$. On the other hand, some materials conserve their bulk properties down to the monolayer limit, enabling new applications and architectures$^8–10$. Examples are ferromagnetic monolayers, which have a great potential for applications in the field of spintronics and data storage devices. As observed in Cr$_2$Ge$_2$Te$_6$$^{11}$ and in structurally related CrI$_3$$^{12}$, evidence for ferromagnetism at least down to the bilayer could be seen by magneto-optical-Kerr-effect (MOKE) microscopy. The structural relation between Cr$_2$Ge$_2$Te$_6$ and CrI$_3$ is given by a shared honeycomb motif in the $ab$-plane. For the iso-structural compound Cr$_2$Si$_2$Te$_6$ monolayer ferromagnetism is theoretically predicted$^{13}$ but still lacks experimental confirmation. The presence of magnetic anisotropy plays a crucial role in monolayer magnetism. As predicted in the Mermin-Wagner theorem$^{14}$, isotropic Heisenberg interactions in dimensions $\leq 2$ will be disturbed by long range fluctuations. However, taking into account already a weak anisotropy, the proof in the theorem is no longer valid and long range magnetic order may be stabilized in low dimensions. Furthermore, Kitaev interactions were recently discussed to realize the magnetic exchange mechanism in the monolayer of these compounds.$^{15}$ It is also worth mentioning, that VSe$_2$, a diamagnet in bulk, shows ferromagnetic ordering when prepared as a monolayer.$^{16}$ While the discovery of robust ferromagnetism in the monolayer limit itself is without doubt stunning and attracted significant attention in the scientific community due to the potential impact it can have in future applications, the bulk magnetic state in these compounds is not well understood. For example, for all mentioned bulk ferromagnets, an anisotropic magnetic anomaly can be observed applying relatively low fields.$^{17–19}$ Until now the origin and nature of this anomaly remains elusive. However, to entangle the physics behind the intriguing phenomenon of monolayer ferromagnetism, a reliable understanding of the bulk magnetism and anisotropy is a prerequisite in these compounds.

Cr$_2$Ge$_2$Te$_6$ crystallizes in the trigonal space group $R3$ (No.148) and belongs to the class of layered van-der-Waals (vdW) transition metal trichalcogenides (TMTC). This class of compounds possesses layers made of the respective transition metal (TM), octahedrally surrounded by the respective chalcogenide (C).$^{20,21}$ Those edge-sharing TM$_6$ octahedra form a honeycomb network. The void of each honeycomb is occupied by a dimer of a IV/V main group element (P, Si, Ge) with the binding axis between the two atoms perpendicular to the honeycomb plane. This dimer is a peculiarity which differentiates this structure from other honeycomb structures, such as CrX$_3$ ($X = Cl, Br, I$). As shown in Fig. 1(b), the honeycomb layers are stacked onto each other, well separated by a van der Waals (vdW) gap, which makes it easy to exfoliate crystals down to a few layers. The stacking of the layers varies in the family of TMTCs. For Cr$_2$Ge$_2$Te$_6$ and Cr$_2$Si$_2$Te$_6$ in the $R3$ space group (No.148), an ABC stacking is found. In contrast, Al$_2$Si$_2$Te$_6$ in the $P3$ (No.147) space group (with a main

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$^*$ s.selter@ifw-dresden.de
$^†$ s.aswartham@ifw-dresden.de
group metal instead of a transition metal) exhibits the highly ordered AAA stacking. For the TM$_2$P$_2$(S,Se)$_6$ family of compounds, the stacking is more difficult to generalize, since the stacking of the layers with respect to a perpendicular direction depends on the monoclinic $\beta$ angle of the space group $C12/m1$ (No. 12)$^{23,24}$. These considerations of the stacking do not explicitly take stacking faults into account.

TMTCs in general possess a non-zero bandgap ranging from 0.5 eV to 3.5 eV mainly depending on the TM and the strong spin-orbit coupling together with electron correlations$^{25}$. Furthermore, these compounds exhibit many different possibilities for long-range magnetic order, mainly depending on the TM ion. Cr$_2$Ge$_2$Te$_6$ in particular has a bandgap of $\sim$0.74 eV (direct) and $\sim$0.2 eV (indirect) and a ferromagnetic ground state with the magnetic easy axis perpendicular to the layers$^{20,26}$. This makes the title compound one of the rare examples of ferromagnetic semiconductors. Owing these properties and the nature of this class of materials to be easy to exfoliate, Cr$_2$Ge$_2$Te$_6$ found use as substrate for ferromagnetic insulator-topological insulator heterostructures$^8$. Furthermore, the magnetic lattice of Cr$_2$Ge$_2$Te$_6$ (and also Cr$_2$Si$_2$Te$_6$) is the same as for CrX$_3$ ($X$ = Br, I), since the Ge dimer in the void of the Cr$_2$Ge$_2$Te$_6$ honeycomb is magnetically inactive. Altogether, the known 2D vdW honeycomb ferromagnets exhibit an excellent platform to compare their magnetic interactions.

Here, we present a comprehensive experimental investigation of the anisotropic bulk magnetic properties of vdW-layered Cr$_2$Ge$_2$Te$_6$ single crystals by means of DC magnetometry and specific heat measurements. We obtain the low-field magnetic phase diagram of this compound for the easy axis and hard plane, with the easy-axis being perpendicular to the honeycomb layers. Under magnetic fields applied parallel to the hard plane $ab$, a downturn with an onset temperature $T^*$ is observed in the temperature dependent magnetization curve. We explain this anisotropic and specific behavior for fields in the hard plane as an interplay among field, temperature and effective magnetic anisotropy in Cr$_2$Ge$_2$Te$_6$.

II. SYNTHESIS, SAMPLE CHARACTERIZATION AND METHODS

Single crystals of Cr$_2$Ge$_2$Te$_6$ with a size up to 6 mm x 5 mm x 0.2 mm (see Fig. 2) were grown by the self flux technique according to X. Zhang et al.$^{17}$. Details regarding the growth procedure and an in-depth characterization of the crystals used in this work are published elsewhere$^{27}$. Both powder X-ray diffraction and energy dispersive X-ray spectroscopy agree well with the published crystal structure in the R3 space group$^{20}$ as well as with the expected stoichiometry of Cr$_2$Ge$_2$Te$_6$. 

FIG. 1. Crystal structure of Cr$_2$Ge$_2$Te$_6$ in the space group R$\bar{3}$ (No. 148). (a) Unit cell of Cr$_2$Ge$_2$Te$_6$. (b) View perpendicular to the $c$-axis showing the structural layers and their stacking. (c) View perpendicular to the $ab$-plane showing the honeycomb network.
DC magnetization was measured as a function of temperature and field using a quantum interference device vibrating sample magnetometer (SQUID-VSM) from Quantum Design. The values obtained for magnetic moments were corrected due to deviation of the measured sample shape and size from a point dipole. This correction follows the procedure described in Ref.\textsuperscript{28}. A detailed description of how this correction is applied can be found in the Appendix of the work of J. Zeisner et al.\textsuperscript{27}. Low-temperature specific heat was determined using a relaxation technique in a Physical Property Measurement System (PPMS) from Quantum Design. The specific heat from the platform and grease used for mounting the sample were subtracted.

### III. RESULTS AND DISCUSSION

#### A. Magnetic Characterization

The zero-field specific heat of Cr\textsubscript{2}Ge\textsubscript{2}Te\textsubscript{6} divided by temperature $C_p/T$, and the temperature dependent normalized magnetization $M/H$ at 1 kOe applied parallel and perpendicular to the crystallographic ab-plane as well as the inverse of the normalized magnetization are represented in Fig. 3(a), Fig. 3(b) and Fig. 3(c), respectively. For the normalized magnetization only the results from field-cooled measurements are shown since no significant difference of zero-field-cooled and field-cooled measurements was observed.

A Λ-shape peak in the temperature dependent specific heat indicates a second-order phase transition at $T_C = 65$ K. In good agreement with this, a similar Curie temperature ($T_C = 66 (\pm 1)$ K) is obtained from the minimum of the first derivative of the temperature dependent normalized magnetization for both crystallographic orientations. While no further phase transition was observed in the specific heat at zero field, the magnetization curves shows an anomalous behavior for $H \parallel ab$ below $T_C$. A downturn towards lower $T$ is observed below $T* = 64$ K for $H \parallel ab$, whereas for $H \perp ab$ a typical ferromagnetic behavior is observed.

![Figure 3](image-url)
A similar anisotropic behavior is also seen for Cr$_2$Si$_2$Te$_6$\textsuperscript{29}, CrI$_3$\textsuperscript{30} and CrBr$_3$\textsuperscript{30}, which are also 2D honeycomb ferromagnets and which show a close relation to Cr$_2$Ge$_2$Te$_6$ regarding their structure. The similarities regarding structure, magnetic ion and magnetic ordering hint towards a main role of these properties for the origin of the observed anisotropy.

At temperatures well above the Curie temperature in the paramagnetic state, a linear dependence between magnetization and field can be assumed. Therefore the magnetic susceptibility can be approximated by the normalized magnetization as shown in Eq. 1.

\[
\chi(T) = \frac{\partial M}{\partial H} \approx \frac{M}{H}.
\]  

Consequently, in the paramagnetic state the normalized magnetization can be used for a Curie-Weiss analysis. From this analysis effective magnetic moments of \(\mu_{eff} = 4.00 \mu_B/\text{Cr} \) for \(H \parallel ab\) and \(\mu_{eff} = 4.06 \mu_B/\text{Cr}\) for \(H \perp ab\) are obtained, which is in good agreement with the theoretically expected spin-only moment of \(\mu_{so} = 3.87 \mu_B\) for Cr$^{3+}$. Furthermore, our Curie-Weiss analysis yields a Curie-Weiss temperature of \(\Theta_{CW} = 95\text{ K}\) for \(H \parallel ab\) and \(\Theta_{CW} = 94\text{ K}\) for \(H \perp ab\) in good agreement with literature\textsuperscript{19,31}.

The positive Curie temperature indicates a dominant ferromagnetic coupling. In three-dimensional ferromagnets \(\Theta_{CW}\) is generally found to be close to \(T_C\). The difference between \(\Theta_{CW}\) and \(T_C\) that is found for Cr$_2$Ge$_2$Te$_6$ is most likely an indication for the suppression of the magnetic order due to the two-dimensional nature of the compound and thus also of the magnetic interactions. This is in line with current results obtained from ferromagnetic resonance (FMR) and electron spin resonance (ESR)\textsuperscript{27}, which demonstrated the intrinsic two-dimensional nature of the magnetic interaction in Cr$_2$Ge$_2$Te$_6$. Also the temperature dependence of \(C_p/T\) in Fig. 3(a) shows characteristic features for the two-dimensional nature of the magnetic interactions in Cr$_2$Ge$_2$Te$_6$: the \(\Lambda\)-shape peak is rather small with an estimated integral of approximately \(\Delta S_{\Lambda} \approx 2\text{ J/mol/K}\) compared to the expected value of the magnetic entropy change at a ferromagnetic ordering of a system with two \(S = 3/2\) magnetic ions per unit cell, the latter being \(S_{mag} = 2R \ln(4) = 23.05\text{ J/mol/K}\). This indicates, that the broad bump in the experimentally determined \(C_p/T\) contains a sizable magnetic contribution in addition to the phononic contribution. Thus magnetic fluctuations give an important contribution to the specific heat even far above and far below the magnetic ordering. This is certainly related to the quasi two-dimensional nature of the magnetism in Cr$_2$Ge$_2$Te$_6$, as previously proposed by G. T. Lin et al.\textsuperscript{31}.

Fig. 4 shows the isothermal magnetization of Cr$_2$Ge$_2$Te$_6$ at 1.8 K for \(H \parallel ab\) and \(H \perp ab\). The hysteresis of the magnetization as function of field is negligible, showing the behavior expected for a soft ferromagnet. From the high-field region, a saturation magnetization of \(M_S \approx 3 \mu_B/\text{Cr}\) is obtained for both orientations. Thus, Cr$^{3+}$ with \(S = 3/2\) leads to an isotropic Landé factor of \(g \approx 2\), which is in excellent agreement with recent results from FMR studies on this compound\textsuperscript{27}. The saturation field is found as the \(x\)-component of the intercept of two linear fits, one being a fit to the saturated regime at high fields and one being a fit of the unsaturated linear regime at low fields. While the saturation magnetization is isotropic, the saturation field is anisotropic and changes from \(H_{sat} = 4.8\text{ kOe}\) for \(H \parallel ab\) to \(H_{sat} = 2.3\text{ kOe}\) for \(H \perp ab\).

This anisotropic behavior in the isothermal magnetization is related to two different contributions: the intrinsic magnetic anisotropy of the material (magnetocrystalline anisotropy) and the shape anisotropy of the measured sample. As Cr$_2$Ge$_2$Te$_6$ grows as thin platelet crystals, the shape anisotropy must be explicitly taken into account. To evaluate the demagnetization factors the sample’s dimensions were measured along its edges from which an equivalent cuboid was constructed. The demagnetization factors of \(N_x = N_y = 0.06\) and \(N_z = 0.88\) were then calculated based on the equivalent-ellipsoid method\textsuperscript{32,33}.

As seen in Fig. 4, this correction strongly reduces the saturation field to 0.1 kOe for the orientation \(H \perp ab\), while only a negligible shift to 4.7 kOe is obtained for \(H \parallel ab\). The remaining anisotropy is purely originating from the magnetocrystalline anisotropy, showing that the magnetocrystalline easy axis is perpendicular to the crystallographic ab-planes (or in turn parallel to the c-direction).

Using the Stoner-Wolfarth model\textsuperscript{34} a value for the magnetocrystalline anisotropy constant \(K_U\) can be estimated from the saturation regime in the isothermal magnetization curve. Within this model the magnetocrys-
talline anisotropy in the single domain state is related to the saturation field $H_{sat}$ and the saturation moment $M_S$ with $\mu_0$ being the vacuum permeability:

$$\frac{2K_U}{M_S} = \mu_0 H_{sat}$$

(2)

For $H \parallel ab$, where the anisotropy becomes maximal, this yields $K_U = 47 \pm 1 \text{kJ/m}^3$ at 1.8K. This value of $K_U$ is in good agreement with $K_U$ obtained previously by FMR on Cr$_2$Ge$_2$Te$_6$\textsuperscript{27}.

In general, it can be expected that the anisotropic anomaly observed in temperature dependent magnetization also manifests in the field dependence for $H \parallel ab$ (via a change of slope). Such a behavior was not resolved in our data at 1.8K. This can be explained by the field dependence of $T^*$, which is investigated in detail in the following subsection.

B. Influence of external fields on the ground state

For $H \perp ab$ (Fig. 5(c) and Fig. 5(d)) the usual field dependence of ferromagnetic materials is observed. In our specific heat studies the $\Lambda$-shape peak at $T_C$ evolves into a broad maximum indicating that the magnetic transition becomes a crossover and this crossover is slightly shifted to higher temperature under magnetic fields. This is in agreement with the change seen in the temperature dependent magnetization curve.

Overall, a different behavior is seen for $H \parallel ab$ (Fig. 5(a) and Fig. 5(b)). While in the magnetization curves the ferromagnetic phase transition at $T_C$ evolves into a broad maximum indicating that the magnetic transition becomes a crossover and this crossover is slightly shifted to higher temperature under magnetic fields. This is in agreement with the change seen in the temperature dependent magnetization curve.

While the crossover resulting from the PM-FM transition shifts towards higher temperatures as seen for $H \perp ab$ for both physical properties $M$ and $C_p$, for $H \parallel ab$ and low fields the dominating $T^*$ shifts towards lower temperatures and is illustrated via an anomaly in $C_p/T(T)$. For fields in the range of 1.7kOe to 5kOe, however, the specific heat measurements clearly show the absence of entropy changes at $T^*$ but seems again to be sensitive to changes at $T_C$. This indicates that $T^*$ is a transition between two states with comparable magnetic entropy. At fields above 5kOe the specific heat behavior is isotropic for fields parallel and perpendicular to ab. This is in good agreement with the fields found for isotropic behavior in the temperature dependent magnetization.

C. Low-Field Magnetic Phase Diagrams

For a better comparison between the peak position in specific heat and the significant temperatures from magnetization, the low-field magnetic phase diagrams for fields along the easy axis and the hard plane were constructed from our data. For fields along the easy axis (6(b)), two phases are seen, i.e., a disordered paramagnetic phase (Phase I) at high temperatures and a ferromagnetic ordered state with $M \parallel H$ (Phase II) at lower temperatures. The transition temperatures from specific heat (peak position) and from magnetization (inflection point) are in good agreement within the range of the measurement uncertainties. In zero field the magnetization direction is supposed to be along the easy axis in the ferromagnetic state. Applying external fields parallel to the magnetic easy axis stabilizes this state for example against thermally activated magnetic fluctuations. Therefore, the observed behavior of Phase II as function of field and temperature is well expected.

However, for $H \parallel ab$ an additional Phase III is ob-
FIG. 5. Left: (a) $C_p/T$ and (b) Magnetization $M$ as a function of temperature under different magnetic fields applied along the easy magnetization axis $c$. Right: (c) $C_p/T$ and (d) Magnetization $M$ as a function of temperature under different magnetic fields applied in the hard magnetization plane $ab$. The maxima in $C_p/T$ are marked with red dots in (a) and (c). The inflection points in $M(T)$ are marked with yellow dots in (b) and (d), while yellow stars in (b) indicate the maxima observed in $M(T)$ with $H || ab$ corresponding to $T^*$. 

served, as shown in Fig. 6(a). While for $H \perp ab$ the iso-magnetization lines are parallel to the T-axis until they deviate towards higher fields very close to $T_C$, for $H \parallel ab$, these lines first show a trend towards lower fields before they finally deviate towards high fields at elevated temperatures. These kinks are the fingerprints of the maximum seen in the temperature dependent magnetization and are well followed by $T^*$. This allows to not just define $T^*(H)$ but also $H^*(T)$ in this low temperature/low field regime. Whereas $T^*(H)$ corresponds to the signature of Phase III in temperature dependent magnetization, $H^*(T)$ corresponds to the same signature in field dependent magnetization. Using the magnetic phase diagram for $H \parallel ab$ to estimate $H^*(1.8 K)$ explains why no anomaly could be resolved in the corresponding isothermal magnetization in Fig. 4, as mentioned before. $H^*(1.8 K)$ is estimated to be in the range of 4.5 – 4.7 kOe which is close to the saturation magnetization at this temperature. Consequently the slope of the $M(H)$ curve significantly changes in this field range and a separate anomaly corresponding to the signature of Phase III is not resolved.

Besides the low temperature/low field regime (Phase III) which is separated from the rest of the phase diagram by $T^*$, both phase diagrams resemble each other. This is best seen by comparing the course of the iso-magnetization lines outside of Phase III. Consequently, the magnetization in Phase I and II is considered as isotropic and the direction of the magnetization is parallel to the field for $T^* < T < T_C$ as seen for $H \perp ab$ (Phase II).

Concluding from this behavior, the most likely scenario for the origin of the downturn in the magnetization curve for $H \parallel ab$ is a continuous reorientation of the magnetization direction as result of an interplay between the magnetocrystalline anisotropy, field and
FIG. 6. Low-field magnetic phase diagram of Cr$_2$Ge$_2$Te$_6$ for (a) $H \parallel ab$ and (b) $H \perp ab$, where Phase I is the paramagnetic state; Phase II is the ferromagnetic state with $M \parallel H$; Phase III only for $H \parallel ab$ is the ferromagnetic state with $M \perp H$ due to the interplay between $K_{U,\text{eff}}$, $H$ and $T$ as schematically shown in Fig. 7. For both phase diagrams iso-magnetization lines at 0.1 $\mu_B$, 0.5 $\mu_B$, 1 $\mu_B$ and 2 $\mu_B$ are shown in white. The legend and the color scale at the bottom are applicable to both phase diagrams. Note that the magnetization shown in the phase diagrams is only the magnetization component parallel to $H$. 
FIG. 7. (a) Schematic representation of the magnetic phase diagram of Cr$_2$Ge$_2$Te$_6$ for $H \parallel ab$ with the three magnetic phases as shown in Fig. 6(a) with three points indicated. These points are arbitrarily chosen, however, fulfill the following conditions: $T_1 < T_2 < T^*(100\text{ Oe})$ and $H_1 > H^*(T_1) > H_2$. (b) shows the parameters $T$ and $H$ for every point together with the expected direction of the magnetization with respect to the $ab$-plane. The black arrows in (a) correspond to the arrows in (b) and indicate which of the parameters $T$ and $H$ is changed. Please note, that the arrow for the magnetization direction is supposed to only show the direction of the magnetization vector and not its absolute value.

In order to follow and describe this effect as function of temperature, a temperature dependent magnetic anisotropy has to be taken into account. The magnetocrystalline anisotropy is caused by the underlying crystallographic lattice which is connected to the electronic spins via the spin-orbit coupling. As such, the magnetocrystalline anisotropy constant $K_U$ is considered as a material constant which itself is independent of temperature and field.

However, if the underlying lattice deforms anisotropically as function of temperature, also $K_U$ changes as a result. In Cr$_2$Ge$_2$Te$_6$ such an anisotropic temperature dependence of the lattice was observed by Carteaux et al.\textsuperscript{20} Down to 100 K the lattice parameters $a$ and $c$ shrink monotonously. However, around 100 K the $a$-axis starts to increase towards lower temperatures while the $c$-axis shrinks further. The increase of the $a$-parameter leads to a value of 6.820 Å at 5 K which is larger than 6.812 Å at 270 K. The temperature-onset of the increase of the $a$-axis with approximately 100 K agrees well with the temperatures which showed first low dimensional magnetic contributions to the linewidth in ESR experiments\textsuperscript{27} and with $\Theta_{CW}$ obtained in Fig. 3(c). Consequently, a connection between the onset of ferromagnetic interactions and the anisotropic behavior of the lattice parameters in form of magnetostriction may be expected. Most probably, however, this behavior is not sufficiently strong to explain the observed anomaly in magnetization.

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C. Zener\textsuperscript{35} described the effect of temperature fluctuations on the anisotropy of the magnetization. According to his work, temperature leads to independent random fluctuations of local magnetization directions. In turn, this leads to an effective reduction of both macroscopic magnetization and anisotropy in the system. However, on a local scale the magnetization and magnetic anisotropy are temperature independent. To differentiate between the local temperature independent and
the global temperature dependent magnetic anisotropy, $K_{U,\text{eff}}$ is introduced as an effective anisotropy constant which includes the effect of thermal fluctuations on a macroscopic scale and its interplay with the temperature independent $K_U$. Based on Eq. 2, the temperature evolution of $K_{U,\text{eff}}$ was extracted from the magnetic phase diagram with fields parallel to the $ab$-plane and is represented in Fig. 8. Details of how $K_{U,\text{eff}}$ was obtained are given in the Appendix A.

As both the macroscopic magnetization and anisotropy are affected by thermal fluctuations, a proportionality between their evolution as function of temperature can be expected. According to the theory by H.B. Callen and E. Callen, this proportionality can be expressed by a power law behavior of

$$
\frac{K_{U,\text{eff}}(T)}{K_U} = \left[ \frac{M_S(T)}{M_S} \right]^{\frac{(l+1)}{2}}.
$$

(3)

Hereinafter, the approximations $K_U \approx K_{U,\text{eff}}(2\text{K})$ and $M_S \approx M_S(2\text{K})$ are used. In the case of uniaxial anisotropy $l = 2$ and an exponent of 3 are expected, while for cubic anisotropy $l = 4$ and an exponent of 10 are found.

Fig. 8 shows the expected evolution of $K_{U,\text{eff}}(T)$ given by the power law dependence of the saturation magnetization in Eq. 3 for exponents 1, 2.6, 3 and 10. The observed temperature dependence of $K_{U,\text{eff}}$ at low temperatures shows a good agreement with the Callen-Callen power law with an exponent of 3, which is expected for purely uniaxial anisotropy. However, at higher temperatures the exponent deviates from 3 towards 2.6. This deviation can most probably be attributed to the change of $K_U$ itself due to lattice deformations as result of magnetostriction as introduced before. For the exponents 1 and 10 the power law behavior does not follow $K_{U,\text{eff}}(T)$ and therefore direct scaling of the saturation magnetization with $K_{U,\text{eff}}$ as well as cubic anisotropy can be ruled out.

This confirms that the magnetic anisotropy in Cr$_2$Ge$_2$Te$_6$ is uniaxial as expected given the non-cubic crystal structure, and the good agreement of simulations and experimental values of the angular dependence of the resonance field in FMR using an uniaxial model in our previous work

In summary, detailed magnetic and thermodynamic measurements were performed on high-quality Cr$_2$Ge$_2$Te$_6$ single crystals. Analysis of the low field data shows an interesting interplay of $K_U$, applied magnetic field and temperature. Cr$_2$Ge$_2$Te$_6$ is a soft ferromagnet with a Curie temperature $T_C = 65$ K. An effective moment $\mu_{\text{eff}} \approx 4\mu_B$/Cr and an isotropic saturation moment $M_S = 3\mu_B$/Cr were found, both being in

| Compound  | $K_U$ [kJ/m$^3$] | Reference            |
|-----------|------------------|----------------------|
| CrBr$_3$  | 86 (±6)          | N. Richter $et\ al.$$^{30}$ |
| CrI$_3$   | 301 (±50)        | N. Richter $et\ al.$$^{30}$ |
| Cr$_2$Ge$_2$Te$_6$ | 47 (±1) | this work          |

TABLE I. Comparison between $K_U$ for different (quasi-)2D honeycomb ferromagnets. Please note that for CrBr$_3$ and CrI$_3$ $K_U$ was extracted from isothermal magnetization data at $T = 5$ K while for Cr$_2$Ge$_2$Te$_6$ data at $T = 1.8$ K was used.

Assuming a tilted magnetization vector due to the previously discussed interplay between the effective magnetic anisotropy and an external field perpendicular to the easy axis at $T_1$ (Point 2 in Fig. 7), an increase in temperature to $T_2$ leads to a reduction of magnetic anisotropy. Therefore, the alignment along the magnetic easy axis becomes less favorable upon warming, which leads to a stronger tilting of the magnetization vector towards the $ab$-plane and an increased experimentally determined $ab$-component $\| H$ in this case (Point 3 in Fig. 7).

Thus, $T^*$ is the temperature at which the magnetization component along the easy axis becomes finite upon decreasing temperatures at a constant field in the $ab$-plane. Vice versa, $H^*$ is the field in the $ab$-plane below which the easy axis magnetization component becomes finite at a constant temperature. A similar scenario was already proposed to explain a similar downturn of the transverse magnetization upon cooling below the Curie temperature in other ferromagnets: the structurally related quasi two-dimensional ferromagnets Cr$_X$ (X = Br, I)$^{30}$ and the heavy Fermion ferromagnet URhGe$^{39}$.

For Cr$_X$ (X = Br, I) a similar analysis of $K_{U,\text{eff}}(T)$ was performed$^{30}$. While the magnetocrystalline anisotropy constants of the chromium halides are larger than the one found for Cr$_2$Ge$_2$Te$_6$ (shown in Tab. I), their temperature dependence is also well described by exponents according to an uniaxial anisotropy. In the case of URhGe, the tilting of the magnetic moment in between the field direction and the easy magnetization axis was directly observed by neutron diffraction$^{39}$ and NMR$^{40}$. For URhGe a Ginzburg Landau description of the anisotropic ferromagnet proposed by V. Mineev$^{41}$ reproduced the downturn of the magnetization and could possibly also be a promising model for a simple description of the low-field magnetic properties of Cr$_2$Ge$_2$Te$_6$.

### IV. SUMMARY

In summary, detailed magnetic and thermodynamic measurements were performed on high-quality Cr$_2$Ge$_2$Te$_6$ single crystals. Analysis of the low field data shows an interesting interplay of $K_U$, applied magnetic field and temperature. Cr$_2$Ge$_2$Te$_6$ is a soft ferromagnet with a Curie temperature $T_C = 65$ K. An effective moment $\mu_{\text{eff}} \approx 4\mu_B$/Cr and an isotropic saturation moment $M_S = 3\mu_B$/Cr were found, both being in
good agreement with the values expected for Cr$^{3+}$. Furthermore, the isotropic saturation magnetization hints towards an isotropic Landé-factor $g \approx 2$. The difference between $\Theta_{CW} = 95$ K and $T_C$ as well as the shape of the temperature dependent specific heat indicate low-dimensional magnetic fluctuations well above the magnetic ordering temperature. The easy-axis nature of the magnetic properties perpendicular to the structural layers in the $ab$-plane is confirmed and a magnetocrystalline anisotropy constant $K_U = 47 \pm 1$ kJ/m$^3$ is obtained using the Stoner-Wolfarth model.

The field and temperature dependence of the magnetization was studied in detail for fields parallel and perpendicular to the hard magnetic plane $ab$ up to fields of 30 kOe. Corresponding magnetic phase diagrams were constructed. The field and temperature dependence for fields along the easy axis $|| c$ show the typical behavior of a ferromagnet. However, for fields applied in the hard plane $ab$ below a temperature $T^* < T_C$ a downturn towards lower temperatures is found in magnetization curves below the saturation field $H_{sat,ab} \approx 5$ kOe. The origin of this anisotropic anomaly is discussed in terms of an interplay between the effective magnetic anisotropy $K_{U,eff}$, temperature and the applied magnetic field. In this scenario, the magnetization direction continuously changes between a field-parallel configuration above $T^*$ to a tilted direction with a magnetization component perpendicular to $H$. Thus, the temperature $T^*$ can be understood as the temperature where the magnetization component perpendicular to the $ab$-plane changes from zero to finite.

To investigate the validity of the temperature dependence of the magnetic anisotropy, values for $K_{U,eff}$ were extracted at different temperatures from the magnetic phase diagram for $H \parallel ab$ and compared with a power law scaling of the temperature dependent saturation magnetization according to H.B Callen and E. Callen. The observed power law behavior fits well for uniaxial anisotropy models with a small deviation at higher temperatures, which can most probably be attributed to changes of $K_U$ itself due to temperature dependent anisotropic lattice deformations.

A similar anisotropic anomaly was observed for CrX$_3$ (with X = Br, I) and also discussed in terms of interplay between $K_{U,eff}$ and temperature. All these compounds share the same magnetic ion and easy axis $|| c$ ferromagnetic ordering together with a similar 2D honeycomb lattice. Thus, the magnetocrystalline anisotropies in these systems are similar, although the magnetocrystalline anisotropy constant $K_U$ shows significant differences in its absolute value for the mentioned compounds. This hints towards a universality of this interplay in quasi two-dimensional ferromagnetic materials. Furthermore, the observed anomaly in the temperature dependence of the magnetization can be considered as a fingerprint of this interplay.

Besides all similarities, these compounds also show influential differences in the nature of their magnetism, for example in the type of magnetic coupling. The TMTCs (Cr$_2$Ge$_2$Te$_6$ and Cr$_2$Si$_2$Te$_6$) exhibit 2D Ising like behavior while CrX$_3$ (X = Br, I) display a more 3D Ising-like coupling, according to investigations of the critical behavior of these compounds due to interlayer interactions present at least in the bulk state. Taken the 2D nature and the high Curie temperature of Cr$_2$Ge$_2$Te$_6$, this compound could be a highly promising low-dimensional ferromagnet to gain further insight into low-dimensional ferromagnetism in general and for the use in ferromagnetic heterostructures.

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1 K. S. Novoselov, Science 306, 666 (2004).
2 K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, Physical Review Letters 105, 136805 (2010).
3 A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, and F. Wang, Nano Letters 10, 1271 (2010). https://doi.org/10.1021/nl903868w.
4 X. Xi, L. Zhao, Z. Wang, H. Berger, L. Forró, J. Shan, and K. F. Mak, Nature Nanotechnology 10, 765 (2015), https://doi.org/10.1038/nnano.2015.143.
5 S. Kolekar, M. Bonilla, Y. Ma, H. C. Diaz, and M. Batzill, 2D Materials 5, 015006 (2017).
6 A. W. Tsen, B. Hunt, Y. D. Kim, Z. J. Yuan, S. Jia, R. J. Cava, J. Hone, P. Kim, C. R. Dean, and A. N. Pasupathy, Nature Physics 12, 208 (2015).
7 A.-S. Pawlik, S. Aswartham, I. Morozov, M. Knupfer, B. Büchner, D. V. Efremov, and A. Kozitsch, Physical Review Materials 2 (2018), 10.1103/physrevmaterials.2.104004.
8 L. D. Alegría, H. Ji, N. Yao, J. J. Clarke, R. J. Cava, and J. R. Petta, Applied Physics Letters 105, 053512 (2014).
9 K. S. Novoselov, A. Mishchenko, A. Carvalho, and A. H. C. Neto, Science 353, aac9439 (2016).
Appendix A: Supplementary

1. Extraction of $K_{U\text{, eff}}$ as function of temperature

To obtain the temperature dependence of $K_{U\text{, eff}}$, isothermal magnetization curves were extracted from the magnetic phase diagram for $H \parallel ab$ in the range of 2K to 60K (shown in Fig. 9). The saturation magnetization and the saturation field at each temperature were obtained from the intersection of two linear regressions of the low-field (0kOe to 2kOe) and the high-field region (30kOe to 70kOe), respectively. From these values $K_{U\text{, eff}}$ was obtained for each temperature based on Eq. 2.
FIG. 9. Isothermal magnetization for $H \parallel ab$ in a range from 2 K to 60 K in 2 K steps extracted from the corresponding magnetic phase diagram. The inset shows the evolution of the linear behavior at low fields as function of temperature in more detail.