Bulk-like Magnetic Moment of Epitaxial Two-dimensional Superlattices

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Over the past four years, the magnetism of 2D magnets has been extensively studied by the full arsenal of probing techniques. 2D magnets can be incorporated to form heterostructures with clean and sharp interfaces, which gives rise to exotic phenomena as a result of the interfacial proximity effect. Here we report a detailed study of the spin (m) and orbital (m) moments of an epitaxial (CrSb/Fe3GeTe2)3 superlattice. The synchrotron-radiation based x-ray magnetic circular dichroism (XMCD) technique was performed to probe the microscopic magnetic properties of the superlattices in an elemental resolved manner. We unambiguously obtained a bulk-like moment of Fe3GeTe2: i.e., m = 1.58 ± 0.2 µμ/Fe and m = 0.22 ± 0.02 µμ/Fe. Future works to explore the tuning of the spin polarized band structure of 2D ferromagnetic superlattices will be of great interest and can have strong implications for both fundamental physics and the emerging spintronics technology.

Index Terms—2D magnets, superlattice, epitaxial thin films, magnetic moment, x-ray magnetic circular dichroism (XMCD), spintronics.

I. INTRODUCTION

The van der Waals (vdWs) crystals or two dimensional (2D) materials, have been widely studied since graphene, the first 2D material, was isolated in 2004 [1], [2]. The research into 2D materials has rapidly covered various fields ranging from semiconductors to highly correlated materials and superconductors [3]. Recent research has focused on the magnetism in 2D materials. The Mermin–Wagner theorem [4] demonstrates that the thermal fluctuation in isotropic 2D systems can destroy long-range magnetic order at any finite temperature (T > 0), which is due to the presence of gapless spin-wave excitations in isotropic systems with continuous symmetry. The magnetocrystalline anisotropy can open the magnon excitation gap in the spin-wave spectrum of 2D system to maintain long-range magnetic order at non-zero temperatures. In 2017, the 2D ferromagnetic order was firstly demonstrated in two vdWs insulators, Cr2Ge2Te6 [5] and CrI3 [6], with the strong perpendicular anisotropy compensating the effect of thermal fluctuation to stabilize magnetic order in 2D systems. One year later, the itinerant 2D ferromagnetism was reported in Fe3GeTe2 monolayers [7]–[9]. The family of 2D magnets has been further expanded, e.g., MnSe2 [10], CrCl3 [11], and CrBr3 [12], and their magnetic properties have been extensively studied using superconducting quantum interference device vibrate sample magnetometer (SQUID-VSM) [10], tunneling magnetoresistance effect (TMR) measurement [11] and scanning tunneling microscope (STM) [12], respectively. The discovered vdWs magnets offer a great platform to study 2D ferromagnetism and have exhibited great potential in developing spintronic devices by manipulating both spin and charge degrees of freedom [13].

Among the discovered 2D magnetic materials, Fe3GeTe2 has become a promising candidate for 2D spintronics because of its relatively high Curie temperature (TC = ~ 220 K) and strong perpendicular anisotropy [14]–[18]. Strong electron correlation effects have been predicated in Fe3GeTe2 single crystals [19]. Fe3GeTe2 has layered hexagonal crystal structure where the covalent bonded metallic Fe3Ge slabs are sandwiched by Te layers to hold the whole structure via vdWs force as shown in Fig. 1a. There are two nonequivalent Fe sites in Fe3Ge slabs, Fe1 and FeII. Two Fe1 atoms are located at the center of each hexagonal plaquettes and separated by the covalent bonded FeII–Ge honeycomb slab that determines the whole crystalline symmetry. The parallel coupled spins of Fe1 and FeII ions have been experimentally confirmed by neutron diffraction [16]. To achieve electric field switchable spintronic devices by Fe3GeTe2, a strong spin-orbital coupling (SOC) or at least an unquenched orbital moment is needed in itinerant magnetic system [20]. Various techniques, including SQUID-VSM [14]–[17], [21]–[25], x-ray magnetic circular dichroism (XMCD) [19], [26], and neutron diffraction [16], [24] have been used to study the atomic-scale magnetic moment of Fe3GeTe2. The calculations of the system have been carried out by local density approximation (LDA) [27], LDA+U [18], and LDA combine with dynamical mean-field theory (LDA+DMFT) [19]. The total magnetic moments (m_total) varies from 1.8 µμ/Fe by Verchenko et al. using SQUID-VSM [24], to 1.63 µμ/Fe by Chen et al. with SQUID-VSM [15] and 1.58 µμ/Fe by Zhu et al. using XMCD [19], and all the way down to approximately 1.2 ± 0.03 µμ/Fe by Deiseroth et al. [14], and Liu et al. [21] using SQUID-VSM. The theoretical result varies from 1.68 µμ/Fe by Zhu et al. [19], to 1.57 µμ/Fe by Lin et al. [27], and down to 1.48 µμ/Fe by Zhuang et al. [18].

Recent attentions have focused on controlling and manipulating the magnetic anisotropy [28] and TC [8], [16], [21] of Fe3GeTe2 using external perturbations, such as doping [16], [21], [28] and gating [8]. By their nature, 2D magnets can be stacked to form vdWs heterostructures with clean and sharp interface, and negligible lattice mismatch. This superiority gives rise to exotic phenomena in 2D magnetic...
longer, i.e., Eq. 1, and graphene/Y \(_3\)GeTe \(_2\) superlattices were carried out under an out-of-plane magnetic field and repeated at the elevated temperatures ranging from 2.5 K to 250 K.

The synchrotron-based XAS and XMCD technique were performed at Fe and Cr \(_{L,2,3}\) at Beamline I10 of the Diamond Light Source to unambiguously determine magnetic moments of the superlattices in an elemental resolved manner. Oppositely circular polarized x-rays with 100% degree of polarization were used successively to resolve XMCD signals from each of the magnetic elements, in which the beam was applied in normal incidence with respect to the film plane and in parallel with external magnetic fields, as shown in Figure 2a. The temperature dependent measurements were performed from 3 K to 150 K under an applied field 5 T (out-of-plane) with total electron yield (TEY) mode. The XMCD was obtained by subtracting the two XAS spectra, \(\sigma - \sigma'\), achieved by switching the XAS helicity at APPLE II undulators [33], [34]. In order to remove the non-magnetic signal due to photoexcitation into continuum states, an arctangent step function was fitted as threshold and subtracted from XAS spectra [35]. The spin and orbital moments, i.e., \(m_s\) and \(m_l\), were calculated by applying sum rules, i.e., Eq. 1, on the integration of total XAS and XMCD spectra at Fe and Cr \(_{L,2,3}\) edges.

\[
m_s = -n_h \frac{\int \sigma_f \sigma dE - \int \sigma_f \sigma' dE}{\int \sigma_f \sigma dE + \int \sigma_f \sigma' dE} \quad \text{<} T_s >
\]

\[
m_l = -n_h \frac{\int \sigma_{f2} \sigma' dE - \int \sigma_{f2} \sigma dE}{\int \sigma_{f2} \sigma' dE + \int \sigma_{f2} \sigma dE}
\]

where \(E\), \(T_s\), and \(n_h\) is the photon energy, the magnetic dipole term, and the 3d band holes, respectively. The \(n_h\) is 4 for Fe [19] and 7 for Cr [36]. The contribution of magnetic dipole term \(< T_s >\) of 3d electrons is typically smaller than 5% and therefore neglected in this work.

III. RESULTS AND DISCUSSIONS

The hysteresis loops of (CrSb/Fe\(_3\)GeTe\(_2\))\(_6\) superlattices at 2.5 – 250 K are shown in Fig. 1b, in which the value of \(R_{xy}\) proportional to the global magnetization. The nearly rectangular loop and the 1.12 T coercive field \((H_c)\) along c-axis (Fig. 1b) prove the strong perpendicular anisotropy of the superlattices, which is consistent with the bulk Fe\(_3\)GeTe\(_2\) [14]–[17], [21]–[25]. The saturation field of the superlattices is nearly 3.5 T at 2.5 K whilst that of bulk Fe\(_3\)GeTe\(_2\) is typically small (< 0.5 T) [15], [22]. The terraced features, double-switching features, were observed near zero field at 2.5 K and persists to 25 K. This double switching feature occurs generally at the interfaces of FM/AFM/FM trilayers due to the FM-AFM interfacial pinning effect [26], [31], [37]. In addition, an enhanced magnetic order is demonstrated by the large \(\mu_0H_c = 1.12\) T of the (CrSb/Fe\(_3\)GeTe\(_2\))\(_6\) superlattices at 2.5 K (Fig. 1c), which is significantly larger than that of bulk Fe\(_3\)GeTe\(_2\) \((\mu_0H_c = 0.02\) T) [16], [18], [19], [23]. As the
temperature increases, the $H_r$ decreases and approaches 3 mT at 230 K (Fig. 1c). The $H_r$ of the superlattices vanishes at 250 K which is close to $T_C$ of the bulk Fe$_3$GeTe$_2$ i.e. 220 K [14]–[18].

**FIG. 1 HERE**

Figure 2b and 2c show typical pairs of XAS and XMCD spectra of the (CrSb/Fe$_3$GeTe$_2$)$_n$ superlattices obtained at 3 K-150 K. The XAS of Fe $L_{2,3}$ edges well resembles that of bulk Fe$_3$GeTe$_2$ [19], and that of Cr show multiple structures for both spin-orbit split core levels. The strongly dichroic spectra of Fe and Cr persist up to 150 K, indicating the ferromagnetic coupling between the Fe$_3$GeTe$_2$ and the CrSb layers in the superlattices. The larger dichroism (thus larger magnetic moments) at Cr $L_{2,3}$ edges was observed at 150 K compared to that of (CrSb/Fe$_3$GeTe$_2$)$_3$ superlattices [26], which is generally obtained with increasing number of periods (n) of magnetic superlattices [31], [38]. The sum rules derived spin and orbital moment of the (CrSb/Fe$_3$GeTe$_2$)$_n$ superlattices are $m_s = 1.58 \pm 0.2 \mu_B$/atom and $m_l = 0.22 \pm 0.02 \mu_B$/atom for the Fe and $m_s = 0.94 \pm 0.09 \mu_B$/atom and $m_l = -0.29 \pm 0.03 \mu_B$/atom for the Cr, respectively (see experimental details). The XMCD derived $m_s$ and $m_l$ of Cr have opposite signs. Figure 2d presents the temperature dependent $m_s$ and $m_l$ for Fe and Cr at 3 K-150 K, respectively, which exhibit the Curie-like trend.

**FIG. 2 HERE**

There has been a big variation in the reported magnetic moments of Fe$_3$GeTe$_2$ systems. With the neutron powder diffraction measurement, Verchenko et al. [24] obtained 1.8 $\mu_B$/Fe of bulk Fe$_3$GeTe$_2$, which is the highest saturation moment of single crystal Fe$_3$GeTe$_2$ reported so far. A slightly reduced moment of 1.63 $\mu_B$/Fe was obtained using VSM in Fe$_3$GeTe$_2$ single crystals by Chen et al. [15]. Zhu et al. [19] performed XMCD measurements of single crystal Fe$_3$GeTe$_2$ and obtained $m_s = 0.1 \mu_B$/Fe and $m_l = 1.48 \mu_B$/Fe at 45 K. This is consistent with our results at 50 K. Further smaller magnetic moment of bulk Fe$_3$GeTe$_2$, i.e. 1.37 $\mu_B$/Fe was reported by Wang et al. [22] using SQUID-VSM, and 1.31 $\mu_B$/Fe and 1.11 $\mu_B$/Fe by May et al. using neutron diffraction [16]. The later has been attributed to the decreased Fe composition during the self-flux growth process of Fe$_3$GeTe$_2$. Similarly Ding et al. [25] reported 1.08 $\mu_B$/Fe of self-flux grown single crystals Fe$_3$GeTe$_2$. The epitaxial grown Fe$_3$GeTe$_2$ thin films were firstly reported by Liu et al. [21] in 2017. The authors obtained 1.23 $\mu_B$/Fe in a wafer-scale 8 nm Fe$_3$GeTe$_2$/Al$_2$O$_3$ (0001) film using SQUID-VSM [21]. In our recent work of the epitaxial (CrSb/Fe$_3$GeTe$_2$)$_n$ superlattices, 1.21 $\mu_B$/Fe was obtained when n=3 [26].

The variation also exist in theoretical works. The calculated $m_l = 0.063 \mu_B$/Fe and $m_s = 1.58 \mu_B$/Fe by Zhu et al. using the LDA+DMFT are consistent with the results by them using XMCD measurement [19], which also agree well with our results. A slightly decreased magnetic moment of 1.57 $\mu_B$/Fe was obtained by Lin et al using LDA [27]. Zhuang et al. reported 1.48 $\mu_B$/Fe of bulk Fe$_3$GeTe$_2$ using LDA+U [18]. Table 1 summarizes some of the experimental and theoretical data for the controversy. The magnetic moment in our work (the first line of the table) exhibits a bulk-like magnetic moment of Fe$_3$GeTe$_2$ in the epitaxial (CrSb/Fe$_3$GeTe$_2$)$_n$ superlattices. The large ratio $m_s/m_l = 0.14$ confirms the enhanced $m_s$ of Fe$_3$GeTe$_2$ in the superlattices compared to that of bulk Fe$_3$GeTe$_2$ [19].

**TABLE 1 HERE**

The variation of magnetic moments between single crystals and epitaxial growth films is nearly 30%, which is usually from the less symmetry of Fe$_3$GeTe$_2$ at the surface and interface of epitaxial Fe$_3$GeTe$_2$/Al$_2$O$_3$. Due to the extremely large thickness of Fe$_3$GeTe$_2$ single crystal, the bulk magnetism can be less impacted by the defect at the surfaces. The off stoichiometry also plays a role in reducing saturation magnetization of bulk and the epitaxial grown Fe$_3$GeTe$_2$. By epitaxially growing (CrSb/Fe$_3$GeTe$_2$)$_n$ superlattices, the moment of Fe$_3$GeTe$_2$ has been successfully built up and is comparable to that of Fe$_3$GeTe$_2$ crystals [24]. The enhanced magnetic moment of Fe$_3$GeTe$_2$ originates from the interfacial magnetic proximity effect of CrSb layers. Therefore, our results indicate that the epitaxial (CrSb/Fe$_3$GeTe$_2$)$_n$ superlattices can effectively avoid the drawbacks of epitaxial thin films and obtain bulk-like moment.

IV. CONCLUSION

In conclusion, we have performed magnetotransport and XMCD measurements of the epitaxial (CrSb/Fe$_3$GeTe$_2$)$_n$ superlattices on Al$_2$O$_3$ (0001). High quality of XAS and XMCD spectra were obtained and carefully analyzed with the sum rules. The strongly dichroic spectra of Fe and Cr persist up to 150 K, indicating the ferromagnetic coupling between the Fe$_3$GeTe$_2$ and the CrSb. The sum-rules-derived spin and orbital moment of the (CrSb/Fe$_3$GeTe$_2$)$_n$ superlattices are $m_s = 1.58 \pm 0.2 \mu_B$/atom and $m_l = 0.22 \pm 0.02 \mu_B$/atom for the Fe and $m_s = 0.94 \pm 0.09 \mu_B$/atom and $m_l = -0.29 \pm 0.03 \mu_B$/atom for the Cr, respectively. Regardless the large $H_C$ (1.12 T), a bulk like moment of Fe$_3$GeTe$_2$ was observed in the (CrSb/Fe$_3$GeTe$_2$)$_n$ superlattices. In addition, the unquenched $m_s$ of Fe and Cr suggest sizable spin-orbital coupling in this system. Our work demonstrates the first inch-scale epitaxial 2D magnet thin films showing a bulk-like moment. This makes metallic Fe$_3$GeTe$_2$ a promising candidate for realizing the whole electrical spintronic operations.

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Fig. 2. Element-specific magnetic states measured by XAS and XMCD of (1.6 nm CrSb/3.2 nm Fe₃GeTe₂)₆ superlattices. (a) Schematic of experimental setup of XMCD measurement. Inset: the spin configuration of one period (CrSb/Fe₃GeTe₂) superlattices, in which the blue arrows represent the net magnetization of CrSb layers and red arrows represent the magnetization of Fe₃GeTe₂ layers. (b, c) Typical pair of XAS and XMCD spectra at (b) Fe and (c) Cr L₂,3 edge obtained using TEY mode at 3 K and 5 T with their integrals and that at elevated temperature ranging from 3 K to 150 K (XAS and XMCD spectra are offset vertically for clarity). The dash lines indicate the integration of the spectra. (d) Spin (mₛ) (top) and orbital (mₗ) (bottom) moments of the Fe (red) and Cr (blue) versus temperature from 3 K to 150 K.

### TABLE I

The summary of spin, orbital, and total magnetic moments of Fe₃GeTe₂ systems of our samples, and those reported in literatures.

<table>
<thead>
<tr>
<th>System</th>
<th>Method</th>
<th>Fe mₛ (µB/Fe)</th>
<th>Fe mₗ (µB/Fe)</th>
<th>Fe mₗtot (µB/Fe)</th>
<th>mₛ/µB</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1.6 nm CrSb/3.2 nm Fe₃GeTe₂/AlO₃ (0001))</td>
<td>XMCD</td>
<td>1.54 ± 0.2</td>
<td>0.22 ± 0.04</td>
<td>1.8</td>
<td>0.14</td>
<td>[*]</td>
</tr>
<tr>
<td>Bulk Fe₃GeTe₂</td>
<td>Neutron powder diffraction</td>
<td>-</td>
<td>-</td>
<td>1.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bulk Fe₃GeTe₂</td>
<td>SQUID-VSM (in-plane)</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bulk Fe₃GeTe₂</td>
<td>XMCD</td>
<td>1.48</td>
<td>0.1</td>
<td>1.58</td>
<td>0.07</td>
<td>19</td>
</tr>
<tr>
<td>Bulk Fe₃GeTe₂</td>
<td>SQUID-VSM</td>
<td>-</td>
<td>-</td>
<td>1.37</td>
<td>-</td>
<td>22</td>
</tr>
<tr>
<td>Bulk Fe₃GeTe₂</td>
<td>SQUID-VSM</td>
<td>-</td>
<td>-</td>
<td>1.31</td>
<td>-</td>
<td>16</td>
</tr>
<tr>
<td>Bulk Fe₃GeTe₂</td>
<td>Neutron diffraction</td>
<td>-</td>
<td>-</td>
<td>1.31</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bulk Fe₃GeTe₂</td>
<td>SQUID-VSM</td>
<td>-</td>
<td>-</td>
<td>1.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bulk Fe₃GeTe₂</td>
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<td>-</td>
<td>-</td>
<td>1.08</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bulk Fe₃GeTe₂</td>
<td>SQUID-VSM</td>
<td>-</td>
<td>-</td>
<td>1.03</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5 nm Fe₃GeTe₂/AlO₃ (0001)</td>
<td>SQUID-VSM</td>
<td>-</td>
<td>-</td>
<td>1.23</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(1.6 nm CrSb/3.2 nm Fe₃GeTe₂/AlO₃ (0001))</td>
<td>XMCD</td>
<td>1.05 ± 0.1</td>
<td>0.16 ± 0.02</td>
<td>1.21</td>
<td>0.15</td>
<td>26</td>
</tr>
<tr>
<td>Bulk Fe₃GeTe₂ (Theory)</td>
<td>LDA+DMFT</td>
<td>1.58</td>
<td>0.063</td>
<td>1.64</td>
<td>0.04</td>
<td>19</td>
</tr>
<tr>
<td>Bulk Fe₃GeTe₂ (Theory)</td>
<td>LDA</td>
<td>-</td>
<td>-</td>
<td>1.57</td>
<td>-</td>
<td>27</td>
</tr>
<tr>
<td>Bulk Fe₃GeTe₂ (Theory)</td>
<td>LDA+U</td>
<td>-</td>
<td>-</td>
<td>1.48</td>
<td>-</td>
<td>18</td>
</tr>
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[*]: This work