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Magnetic Properties of Proton Irradiated $Fe_{2.7}GeTe_2$ Bulk Crystals

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Abstract

van der Waals (vdW) magnetic materials show promise in being the foundation for future spintronic technology. The magnetic behavior of $Fe_{2.7}GeTe_2$ (FGT), a vdW itinerant ferromagnet, was investigated before and after proton irradiation. Proton irradiation of the sample was carried out at a fluence of 1×10^{18} cm^{-2}. The magnetization measurements revealed a small increase of saturation magnetization (M_s) of about 4% upon proton irradiation of the sample, in which, the magnetic field was applied parallel to the c-axis. X-ray photoelectron spectroscopy for pristine and irradiated FGT revealed a general decrease in intensity after irradiation for Ge and Te and an increase in peak intensity of unavoidable surface iron oxide. Furthermore, no noticeable change in the Curie temperature (T_C =152 K) is observed in temperature dependent magnetization variation. This work signifies the importance of employing protons in tuning the magnetic properties of vdW materials.

INTRODUCTION

Two-dimensional (2D) van der Waals crystals have recently acquired significant attention due to their attractive properties such as ferromagnetism at the monolayer level and one million percent magnetoresistance [1-3]. Furthermore, the

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magnetic properties of vdW crystals are being investigated as these 2D materials bring new prospects to the area of spintronic applications due to the ability to manipulate their magnetic properties depending on the number of layers that are present [3-7]. An example of promising candidates for long-range magnetism in monolayers are CrX_3 (X = Cl, Br, I) and $CrXTe_3$ (X = Si, Ge, Sn) compounds. To expand on the potential that vdW crystals may hold in applications, it has been seen that $CrSiTe_3$ exhibits ferromagnetic ordering at around 32 K in its bulk form and is enhanced to around 80 K in the monolayer form [4]. Although a desirable ferromagnetic behavior is obtained, in order for $CrSiTe_3$ to be implemented into technology, the temperature at which it becomes ferromagnetic is considerably lower than the desired room temperature (300 K). Thus, it would need to be increased in order to be useful in actual applications. For that reason, many researchers are investigating different vdW crystals to understand if a desired ferromagnetic temperature can be reached. Moreover, $Fe_{3-x}GeTe_2$ is of particular interest as it is strongly ferromagnetic at a T_C of approximately 220-230 K [8-10].

$Fe_{3-x}GeTe_2$ is a strongly correlated ferromagnet due to crucial quantum fluctuation effects and significant enhancement in quasiparticle mass, where the ferromagnetism can be tuned by controlling the Fe content of the crystal [6]. Additionally, May *et al.* has observed that T_C tends to decrease by an increasing number of Fe vacancies introduced into the lattice where the in-plane lattice parameter decreases [11]. Proton irradiation is a method previously implemented by Mathew *et al.* in order to induce magnetism in the diamagnetic material MoS_2. The material was irradiated with a 2 MeV beam and was shown to display ferromagnetic behavior at $T_C \approx 895$ K after irradiation [12]. This shows the usefulness in inducing ferromagnetic behavior in vdW materials through proton irradiation by an introduction of lattice distortions, structural disorder and defects [12,13].

In this paper, we report on the magnetic properties of $Fe_{2.7}GeTe_2$ single crystals upon proton irradiation which has not been previously reported. Magnetic measurements were performed on pristine and irradiated single crystals of FGT. A significant splitting between zero-field-cooling (ZFC) and field-cooling (FC) curves in the out-of-plane and in-plane directions is observed in irradiated FGT. Additionally, no significant change in T_C is observed from the temperature dependent magnetization. However, X-ray photoelectron spectroscopy (XPS) reveals a change in intensity for Fe, Ge, and Te components of FGT while confirming their valence state before and after proton irradiation.

EXPERIMENTAL METHODS

FGT single crystals were grown by a self-flux technique described in a previous report [6]. The approximate length of the bulk crystals is 5 mm and belongs to the $P6_3/mmc$ space group. The crystal structure is associated with Fe-Ge slabs separated by van der Waals gapped Te double layers, where the Fe atoms in the unit cell occupy two inequivalent Wyckoff sites. The FGT crystal was irradiated with a 2 MeV proton beam at a fluence of 1×10^{18} cm^{-2} with a proton beam spot size of 6 mm x 6 mm. The beam has a current of ~1 microampere and was filtered with multiple magnet bending devices to remove carbon contamination [15,16]. A vacuum of 6×10^{-8} Torr or better was used during the irradiation process with the application of liquid nitrogen trapping to further improve the vacuum. Quantum Design's Versalab was used in measuring the magnetic properties of the single crystals. The Versalab Vibrating Sample Magnetometer (VSM) was employed to obtain in- and out-of-plane magnetic measurements. The magnetic field (H) was applied parallel with the *c*-axis of the crystal's structure for in-plane (H//c), and applied parallel to the *ab*-axis or, H⊥c, for out-of-plane crystallographic direction. The

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temperature range at which VSM measurements were performed was from 50 to 350 K with a magnetic field of ± 3 T. XPS is used to verify the valence states of elements before and after irradiation.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependent magnetization for (a) pristine and (b) irradiated FGT measured under a field of 1 kOe in the in-plane and out-of-plane directions of the crystal. An apparent transition from paramagnetic to ferromagnetic behavior is seen at 152 K. These transitions from paramagnetic to ferromagnetic phase indicate clear anisotropic behavior at low temperatures with the *c*-axis as the easy axis. The results observed are similar to those previously reported in literature [6]. ZFC and FC magnetization curves collected at both H//c and H⊥c directions show splitting at low temperatures for pristine and irradiated crystals. A prominent splitting in H//c is also seen, indicating strong magneto-crystalline anisotropy in the *c*-axis [14]. The in-plane splitting had an approximate 49% increase in magnetization from ZFC to FC for both pristine and irradiated samples. Furthermore, field cooled magnetization slightly increases after irradiation from 13.47 emu g^{-1} to 13.7 emu g^{-1} in the H//c direction.

An estimated Curie temperature of approximately 152 K is observed for pristine FGT (Fig. 1(a)) resembling previous reports [6]. Similarly, the T_C for irradiated FGT is approximately the same at 153 K as compared to pristine, showing no significant change upon proton irradiation. At the high temperature region (200 – 300 K), the ZFC curves for both crystal directions were fitted using the Curie-Weiss law (equation (1), see insets of Fig. 1(a,b)),

$$\chi = \frac{C}{T - \theta} \tag{1}$$

where C is the Curie-Weiss constant and θ is the Weiss temperature. The Weiss temperature of the irradiated crystal obtained for H//c and H⊥c are θ_c = 154 K and θ_{ab} = 153 K, respectively. While for pristine, θ_c = 164 K is obtained for in-plane and θ_{ab} = 157 K for out-of-plane in line with Liu *et al.* [6]. The positive values obtained for θ confirm the ferromagnetic interactions among the Fe atoms in the arrangement.

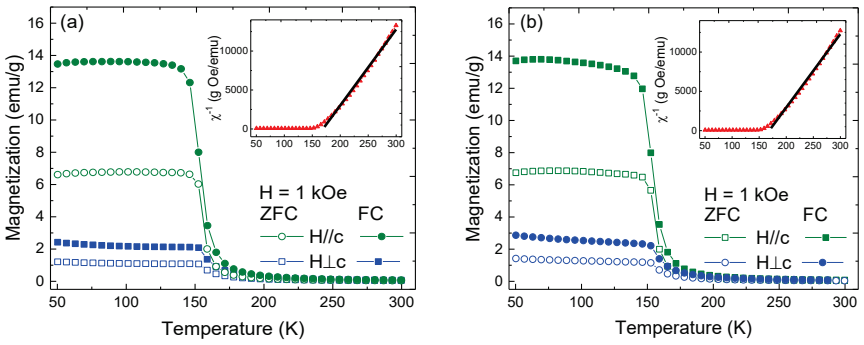

Figure 1. Temperature dependent magnetization ZFC and FC curves for (a) pristine and (b) proton irradiated FGT bulk crystals. Curie-Weiss fit shown in insets (black solid line, 200-300 K).

Figure 2 shows isothermal magnetization of (a) pristine and (b) irradiated FGT performed at H//c and H⊥c directions at 50 K. The saturation magnetization (M_s) at 50 K is 2.82 μ_B/Fe and 2.94 μ_B/Fe for pristine and irradiated crystals in the H//c direction. The saturation field (H_s) observed for both pristine and irradiated samples is H_s = 2.4 kOe and H_s = 14.6 kOe for in-plane and out-of-plane, respectively. Liu *et al.* reported the same trend for a pristine sample with H//c saturation field ($H_s \approx 3$ kOe) being much smaller than H⊥c ($H_s \approx 18$ kOe) and with such trend we confirm the easy axis to be along the *c*-axis for both samples [6]. The saturation magnetization in the H//c direction (T = 50 K) increases from 32.95 emu g^{-1} in pristine, to 34.26 emu g^{-1} in irradiated as seen in Figure 2.

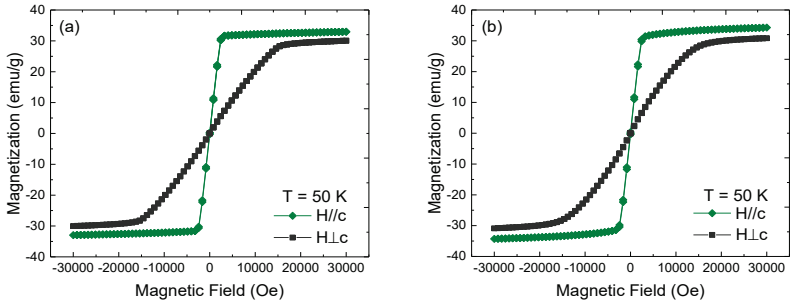

Figure 2. Isothermal magnetization at 50 K for (a) pristine and (b) irradiated FGT performed in H//c and H⊥c directions.

To study the valence states of Fe, Ge and Te, XPS measurements were performed on both crystals with the data plotted in Figure 3 (a,b,c). XPS shows that the valence states of these elements are in line with expected values of binding energy for all three elements [17-19]. In addition, we noticed that the peaks corresponding to Ge and Te reduced in intensity and no additional peaks were observed. Particularly, that it is true in the case of Ge and Te. This trend is different from that of Fe where the unavoidable surface iron oxide content increases after irradiation.

We propose a possible reason for the observed effects as our XPS data provides an evidence to support our argument. The XPS spectra related to ligand atoms such as Te and Ge have been strongly modified. That suggests the bonding and consequently the superexchange interaction between Fe and the ligand atoms is altered upon proton irradiation. This is also in-line with the recent report on ligand induced spin-orbit coupling and magnetic anisotropy [20]. Significant magnetic cluster formation was not observed as the Curie temperature remains the same even after proton irradiation. However, we cannot avoid the formation of iron oxide on the crystal surface. Additional measurements such as electron paramagnetic resonance (EPR) spectroscopy and Raman spectroscopy are being performed to better understand our XPS data and the factors that are responsible for the enhanced magnetization upon proton irradiation.

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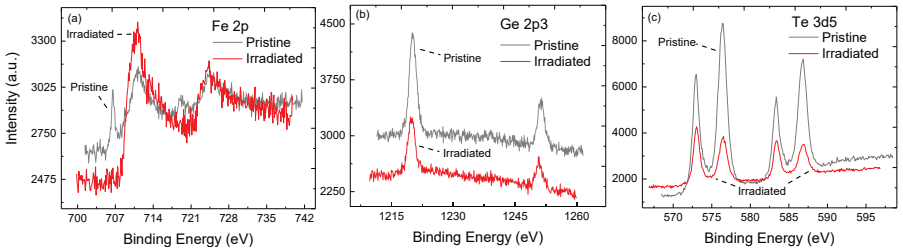

Figure 3. X-ray photoelectron spectroscopy (Intensity vs. Binding energy (eV)) for Fe (a), Ge (b), and Te (c) components of FGT.

CONCLUSION

Magnetic measurements were performed on pristine and proton irradiated $Fe_{2.7}GeTe_2$ bulk crystals. We have observed a splitting between ZFC and FC curves for both H//c and H⊥c orientations with in-plane measurements having the greatest splitting of about 49% increase from ZFC to FC. This splitting is evident in both pristine and irradiated crystals and further indicates that the *c*-axis is the easy axis. Furthermore, an increase in magnetization is observed in out-of-plane direction, possibly indicating that the bulk crystal gains magneto-crystalline anisotropy after proton irradiation due to modification in the bonding between Fe and ligand atoms. Long range ferromagnetic ordering appears at $T_C \approx 152$ K for both crystallographic directions in the irradiated and non-irradiated samples. Saturation magnetization of 2.82 μ_B/Fe and 2.94 μ_B/Fe for in-plane measurements were found, revealing a small but noticeable increase in magnetization upon proton irradiation. XPS revealed a reduction in peak intensity upon proton irradiation of FGT for Ge and Te, however, that trend in reduction is not clearly evident from Fe spectra as the increase in intensity corresponds to the unavoidable surface iron oxide formation. Additional measurements are in progress to better understand the enhancement in saturation magnetization upon proton irradiation. This work can be extended to investigate mono- to few-layer magnetism in FGT upon proton irradiation.

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