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Enhanced Magnetization in Proton Irradiated $Mn_3Si_2Te_6$ van der Waals Crystals

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Abstract

van der Waals (vdW) engineering of magnetism is a topic of increasing research interest in the community at present. We study the magnetic properties of quasi-two-dimensional layered vdW $Mn_3Si_2Te_6$ (MST) crystals upon proton irradiation as a function of fluence 1×10^{15}, 5×10^{15}, 1×10^{16}, and 1×10^{18} H^+/cm^2. We find that the magnetization is significantly enhanced by 53% and 37% in the ferrimagnetic phase (at 50 K) when the MST was irradiated with the proton fluence of 5×10^{15}, both in *ab* and *c* plane, respectively. From the fluence dependence of magnetization, electron paramagnetic resonance spectral parameters (g-value and signal width), and Raman shifts, we believe that the magnetic exchange interactions (Mn-Te-Mn) are significantly modified at this fluence. This work shows that it is possible to employ proton irradiation in tuning the magnetic properties of vdW crystals, and provide many opportunities to design desired magnetic phases.

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Introduction

The manipulation of the physical properties of materials through irradiation or photo-excitation has been of particular interest for electronic device functionality in space[1–3], and the fundamental understanding of the interaction between light and matter[4–7], respectively. In particular, proton irradiation is known as one of the main sources that hinders the electrical properties of electronics in space-crafts undergoing tasks near earth's orbit[8,9]. However, proton irradiation has the potential to positively impact the magnetic characteristics of materials[10]. Studies have shown that irradiation with protons induces ferromagnetic ordering in some materials such as MoS_2 and graphene, materials that are normally non-magnetic[11–14]. These reports have brought interest towards studying what causes the change in the magnetic characteristic of materials when bombarded with protons[14–17]. For example, MoS_2 has been a popular van der Waals (vdW) material to study due to its similarities to graphene, but with the benefits of having a large direct band gap (1.8 eV), good electrical properties and catalytic activity[18–22]. Using proton irradiation, Mathew *et al.*[11] introduced magnetic ordering in MoS_2, which resulted in a change from diamagnetic to ferrimagnetic behavior above room temperature. This change in magnetism was attributed to vacancies and edge states produced by proton irradiation. Another study by Wang *et al.* shows a change in the bandgap of MoS_2 due to defects that trap excitons after irradiation[1]. In the case of graphite, exposure to irradiation yielded interesting results, as shown by Esquinazi *et al.*[12]. Using proton irradiation, they induced ferromagnetic ordering in highly oriented pyrolytic graphite (HOPG).

vdW materials have recently risen in interest due to the ability of exfoliating the bulk crystals down to a few- or mono-layers and still retain and/or improve their pristine magnetic properties[23–26]. Even though many studies have emerged on these vdW materials, there are various materials, in that family, that have remained less explored in bulk or few-layer form. $Mn_3Si_2Te_6$ (MST), similar to $Cr_2Si_2Te_6$ (CST), which is another vdW magnet, is a part of the vdW family of layered materials that has only recently received some renewed interest[27,28]. May and co-authors[28] appropriately determine the trigonal crystal structure, containing $MnTe_6$ octahedra that share edges within the *ab*-plane (Mn1 site). In MST, one third of the Mn atoms link the layers together by filling the octahedral holes (Mn2 site) within the vdW gap. Later on, Liu and Petrovic performed a study[27] on the critical behavior of MST and confirmed a ferrimagnetic temperature of ~74 K.

To date, various strategies such as electrostatic gating, pressure and iso-valent alloying have been employed to control magnetism in 2D layered magnets. Using proton irradiation, we hope to modify the magnetic properties of MST as a function of proton fluence, which was unreported earlier. However, proton irradiation is uncommon on Earth, but represents the majority of cosmic radiation incident to the Earth's atmosphere. Studying the effects of proton irradiation on vdWs materials can give clues as to their general behavior when irradiated in space environments as exemplified in recent reviews[29,30] and report[31]

In this study, we irradiated MST with protons at an energy of 2 MeV at the different proton fluence of $1x10^{15}$, $5x10^{15}$, $1x10^{16}$ and $1x10^{18}$ H^+/cm^2. A non-linear change in the magnetization (measured from Hysteresis loops) was observed as a function of proton fluence. We noticed no dramatic change in the ferrimagnetic transition temperature upon proton fluence. Electron paramagnetic resonance (EPR) measurements show two signals corresponding to Mn^{2+} paramagnetic centers, assigned due to Mn1 and Mn2 sites. No additional signals were observed indicating the absence of magnetic defects that may have been formed after irradiation. EPR data coupled with the Raman data indicate that the proton irradiation modify the exchange interactions in MST and may have played a key role in the modification of the magnetization.

Experimental methods

MST single crystals (mm in size) were prepared as reported previously by some of us (Y.L and C.P)[27]. A Quantum Design Versalab System with a temperature range of 50 – 400 K and magnetic field range of ±3 T was used for this study. The magnetic field was applied in the *ab* plane as well as in *c* plane. The EPR spectra were recorded on a Bruker EMX Plus X-band (~9.43 GHz) spectrometer, equipped with a high sensitivity probe head. A Cold-Edge™ ER 4112HV In-Cavity Cryo-Free VT system connected with an Oxford temperature measurements was used in combination with the EPR spectrometer. All the samples were carefully handled with nonmagnetic capsules and Teflon tapes to avoid contamination. The 2 MeV proton irradiation was performed by using a 1.7 MV Tandetron accelerator. This energy was chosen to avoid producing unwanted damage in the crystal. The projected range was 30 microns, and the damage profile has a relative flat distribution from the surface up to 30 microns (supplementary information, Fig. S1). The beam current was 100 nA. The beam spot size was 6mm × 6mm and the beam was rastered over an area of 1.2 cm x 1.2 cm to guarantee lateral beam uniformity. The weak beam current and the beam rasterring reduce the beam heating (< 50°C) during the irradiation. The beam was filtered with multiple magnet bending devices to remove carbon contamination[32,33]. The vacuum during the irradiation was $6E^{-8}$ Torr or better. The application of liquid nitrogen trapping during irradiation was performed to improve vacuum. The proton irradiation was carried out on separate crystals for each fluence. Raman spectra were collected using a Renishaw Raman spectrometer using 532 nm laser wavelength excitation and x50 optical microscope objective.

Results and Discussion

To study the variation of magnetization as a function of proton fluence, the isothermal (50 K) magnetization measurements were performed as a function of proton fluence, both in the *ab* and *c* plane in the ferrimagnetic phase, and the data are plotted in Fig 1(a,b). To compare, isothermal magnetization variation for the pristine crystal (shown with the curve in black) in both the directions is also included. As shown in Fig. 1(a) for *ab* plane, square-shaped M-H loops are observed at all the fluences, associated with negligible coercive field, consistent with the previous reports[27,28]. Most interestingly, the *ab* plane magnetization observed at 50 K is enhanced by about 53% when the MST crystal was irradiated with the proton fluence of 5×10^{15} H^+/cm^2, in comparison with that of pristine crystal. A similar trend is observed even when the magnetization was measured in the *c* plane as depicted in Fig. 1(b) as the magnetization in the *c* plane is known[27,28] to have small ferromagnetic contribution. Figure 1 (a,b) shows that the strong magnetic anisotropy is retained even after the proton irradiation. The magnetization in *ab* plane is higher than the *c* plane as ordered moments lie primarily within the *ab* plane in agreement with the previous reports on MST[27,28]. No remanent moment for either orientation confirms the crystal retains its high quality even after the proton irradiation.

The trends in the magnetization as a function of proton fluence are captured in Fig 1(c), both for *ab* and *c* plane magnetization. As it can be immediately evidenced, the highest magnetization value was observed for the isothermal magnetization measurement irradiated with a proton fluence of $5x10^{15}$ H^+/cm^2, with an increase of 53% with respect to its pristine value. In addition, the magnetization experienced a decrease when irradiated with a fluence of $1x10^{16}$ and $1x10^{18}$ H^+/cm^2. Here, the magnetization value is taken for all the samples measured at the temperature of 50 K and at the magnetic field of 3 T from the plots shown in the Fig. 1(a,b).

To study the variation of ferrimagnetic transition temperature as a function of proton fluence, the temperature dependent magnetization measurements were performed, both in the *ab* and *c* plane. Figure 2 (a, b) shows the temperature dependent magnetization measured in *ab* and *c* plane, respectively. In order to verify if a change in the transition temperature of MST occurred after proton irradiation, the dM/dT (shown in Fig. 2 (c, d)) was taken from the *ab* and *c* plane M(T) measurements. The peak in the dM/dT curves provides the value of the ferrimagnetic transition temperature. In the pristine (unirradiated) MST, the ferrimagnetic transition was found at ~74 K, which is in good agreement with previous reports[27,28]. The most noticeable change in the T_C was observed after a proton fluence of $1x10^{18}$ H^+/cm^2 with a small decrease of 1.4 K, shown in Table I. The $1/\chi$ vs. T plots (Supp. Figure 6) were fitted using the Curie-Weiss law, $\chi = C/(T-\theta_W)$, in order to extract the Weiss temperature (θ_W). The fits were done with the temperature range of 200-400 K, and the resulting θ_W values are displayed in Table I. The extracted transition temperature was found to be negative indicating antiferromagnetic correlations[28] and almost three times greater than the T_C estimated from our dM/dT curves. The deviation from the T_C points toward short-range spin correlations and is expected since Ref. [28] shows clear evidence of short-range correlations existing in MST already. Consistent with the MH data, the magnetization in *ab* plane is higher than in the *c* plane as expected[27,28]. For comparison, the temperature dependent magnetization data collected on the pristine crystal is also included as shown in black curve.

To gain insights into the origin of enhancement in the magnetization at the fluence of 5×10^{15}, the temperature dependent EPR measurements were performed across the ferrimagnetic transition on the pristine as well as on all irradiated MST crystals as a function of temperature. EPR is an ideal tool to identify paramagnetic centers that contain unpaired electron spins and their interactions by studying the temperature dependent EPR spectral parameters such as g-value and signal width. We hope to learn the information on magnetic exchange interactions, and whether irradiation produced magnetic defects/secondary phases that can account for the observed increase in the magnetization. The EPR spectra collected on all the compounds in the ferrimagnetic phase at 50 K are plotted in Fig. 3, which includes both the experimental (dotted curve) as well as the computer-generated fits (continuous curve) using the Lorentzian and Dysonian line shapes (supplementary information). From the fits, we identified two overlapped signals. The EPR spectral parameters such as the signal width and g-value were extracted from the fits and are plotted as a function of fluence (Supp. Fig. 2). The g-value and the signal width obtained for the pristine MST are also included in Supp Fig. 2. As it is reflected from these two plots, a clear variation in the EPR spectral parameters is noticed at around the fluence of $5x10^{15}$ H^+/cm^2. At that fluence, the linewidth for both the signals shows minimum due to strong exchange narrowing effect and the g-value is maximum due to the enhanced magnetic corrections.

Now, we will assign the two EPR signals. Previous reports show that this compound has two Mn sites, namely, Mn1 (in *ab* plane) and Mn2 (in *c* plane). It is also known that the multiplicity of Mn1 is twice that of Mn2 and are significantly separated through distance. That means the magnetic moment of Mn1 is expected to be two times higher than Mn2. The first Mn site (Mn1 site) is composed of $MnTe_6$ octahedra that are edge-sharing within the *ab*-plane. The Mn2 site links the layers together by filling one-third of the octahedral holes within the vdW gap[28]. Due to strong exchange interaction among the spins on Mn1 site, the EPR signal width is expected to be smaller. Hence, it is reasonable to assign the sharper signal to Mn1. On the other hand, the broader signal can be assigned to Mn2 site. The different surroundings of these two Mn sites produce EPR signals associated with distinct spectral properties. The main signal is sharper (ΔH_{PP} ~ 176 G), intense, and associated with the g-value of 1.998. The broader (ΔH_{PP} ~ 1300 G) signal is less intense, associated with g ~ 1.85. Besides the Mn^{2+} signals, no additional signals related to (magnetic) defects were observed after proton irradiation. This indicates that the observed changes in magnetization is not due to magnetic defects or vacancies produced after irradiation. Additionally, hydrogen ion implantation can be ruled out as a likely cause to the change in magnetization because of a lack of hyperfine structures[15] in our EPR spectra of the proton irradiated MST crystals.

In order to verify if the proton irradiation induced changes in the lattice vibrations and further influence the magnetization of MST, we performed Raman spectroscopic measurements before and after the irradiation. In Fig. 4 (a), the Raman spectra for pristine MST are shown along with those of irradiated MST crystals. The spectra from pristine MST contain two peaks located at 118.4 and 136.9 cm^{-1}, and the peak position as a function of proton fluence is plotted in Fig. 4 (b). To our knowledge, the Raman spectra for MST has not been reported in the literature. However, the Raman spectra for its analogues compound CST is reported[34,35]. In the CST Raman spectra, the peaks arise from the in-plane and out-of-plane Te vibrational modes, which are sensitive to magnetic interactions. The peak seen in the MST Raman spectra is located at 118.4 cm^{-1} with a shoulder at 136.9 cm^{-1}, and are close to the peaks found for CST for the E^3_g and A^3_g modes[34,35], respectively. The main difference in the spectra of MST and CST arises from the change in mass and lattice parameter effects that cause the peaks to shift. From Fig. 4 (b), the change in the E_g peak as a function of fluence is seen to change in a similar manner as the observed trend in the M_S shown in Fig. 1 (c). Thus, it is very likely the E^3_g and A^3_g modes involve atomic motions of the Te atoms whose bond strength can be very susceptible to the spin interactions, since the Te atoms mediate the super-exchange between the two Cr atoms.

It is more likely that the proton irradiation produced changes in the magnetic interactions within MST. As mentioned before, MST has been shown to contain competing antiferromagnetic interactions that create frustration within the system[28]. In particular, the Mn1-Mn1 interactions were reported to have a rivalry between direct interaction (AFM) and Mn1-Te-Mn1 interactions that can lead to FM or AFM which is determined by whether or not the *p* or *d* orbitals are participating[28]. A recent archived report by Ron *et al.*, studied the ligand-to-metal charge transfer (CT) in $CrSiTe_3$[36]. This was achieved by targeting specific CT transitions in CST using ultrafast laser pulses. They find that by targeting these CT transitions, an enhancement in the nearest-neighbor super-exchange interactions occurs, weakening the AFM direct exchange, and thus resulting in an increase in FM exchange. In respect to proton irradiation upon MST, it is probable that different interactions were affected by the varying fluence of protons, which is why this particular trend in magnetization was observed.

Conclusion

To conclude, the effect of proton irradiation as a function of fluence (1×10^{15}, 5×10^{15}, 1×10^{16}, and 1×10^{18} H^+/cm^2) on the magnetic properties of MST has been studied. A strong enhancement in the magnetization at the fluence of 5×10^{15} is observed. We report that the magnetization is significantly enhanced by 53% and 37% in ferrimagnetic phase when the MST was irradiated with the proton fluence of 5×10^{15}, in the *ab* and *c* plane respectively. From the results obtained from fluence dependent magnetic, EPR and Raman spectroscopic measurements, we believe that the magnetic exchange interactions (Mn-Te-Mn) are significantly modified at this fluence. This work signifies proton irradiation is very effective in tuning the magnetism of vdW crystals.

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