Enhanced Magnetization from Proton Irradiated Bulk van der Waals Magnet CrSiTe$_3$

L. M. Martinez$^1$, Y. Liu$^2$, C. Petrovic$^2$, L. Shao$^3$, Q. Wang$^4$, S. R. Singamaneni$^1$

$^1$Department of Physics, The University of Texas at El Paso, El Paso, Texas 79968, USA
$^2$Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, New York 11973, USA
$^3$Department of Nuclear Engineering, Texas A&M University, College Station, TX 77845, USA
$^4$Department of Physics and Astronomy, West Virginia University, Morgantown, WV 26506, USA

Abstract

Van der Waals (vdWs) crystals have attracted a great deal of scientific attention due to their interesting physical properties and widespread practical applications. Among all, CrSiTe$_3$ (CST) is a ferromagnetic semiconductor with the Curie temperature ($T_C$) of ~32 K. In this letter, we study the magnetic properties of bulk CST single crystal upon proton irradiation with the fluence of $1 \times 10^{18}$ protons/cm$^2$. Most significantly, we observed an enhancement (23%) in the saturation magnetization from 3.9 µ$_B$ to 4.8 µ$_B$, and is accompanied by an increase in coercive field (465-542 Oe) upon proton irradiation. Temperature dependent X-band electron paramagnetic resonance measurements show no additional magnetically active defects/vacancies that are generated upon proton irradiation. The findings from X-ray photoelectron spectroscopy and Raman measurements lead us to believe that modification in the spin-lattice coupling and introduction of disorder could cause enhancement in saturation magnetization. This work demonstrates that proton irradiation is a feasible method in modifying the magnetic properties of vdWs crystals, which represents a significant step forward in designing future spintronic and magneto-electronic applications.

*immartinez12@miners.utep.edu

$srao@utep.edu
Irradiation with protons, neutrons, electrons, and swift heavy ions has been shown to be an effective method in inducing and manipulating the magnetic and electronic properties of several advanced materials including graphite, MoS$_2$ single crystals, 4H-SiC, LaMnO$_3$, La$_{0.9}$Ca$_{0.1}$CoO$_3$, carbon nanotubes, fullerenes, GaAs: Cr, MgO, and other materials$^{1-21}$. For instance, it has been shown that it is possible to introduce ferromagnetism in non-magnetic materials such as proton and electron irradiated MoS$_2$ single crystals$^{1,14}$, proton irradiated graphite, fullerenes, TiO$_2$, and 4H-SiC; and neutron irradiated MgO single crystals$^{2,3,12,13,16,18}$. The radiation induced defects and vacancies were believed to generate ferromagnetism in the above materials. Interestingly, it is also shown that neutron and electron irradiation can be employed in manipulating the magnetic properties of magnetically active materials such as LaMnO$_3$ (antiferromagnetism to ferromagnetism) and La$_{0.9}$Ca$_{0.1}$CoO$_3$ (increase in magnetization)$^{7,21}$. These changes were attributed to ion displacements and lattice expansion. In addition, proton irradiation has been shown to drastically modify the electrical properties of GaAs: Cr, carbon nanotubes, WSe$_2$ and MoS$_2$ field effect transistors$^{10,11,15,20}$ due to proton induced traps and hydrogen attachment. Using first principles calculations, Komsa and co-authors have studied the response of two-dimensional inorganic materials to electron irradiation$^{22}$.

The effect of proton and other sources of radiation on functional materials and devices is a subject of current intensive interest because vdWs materials-based nanoelectronics and data storage devices, if successful, will be used in future Earth orbit and solar system explorations. 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$^{23,24}$ and report$^{25}$.

Tuning the magnetic properties of vdWs crystals is a central topic of recent studies because of its fundamental significance for next generation low power spintronics and magnetoelectronic applications at the monolayer level$^{26-31}$. Therefore, vdW materials have piqued many research groups due to the exciting physical properties these materials exhibit. Layer dependence, electric field, electrostatic doping, and mixed halide chemistry have been shown to control the magnetic properties (saturation magnetization, coercive field, and magnetic order) of these materials$^{5,26-31}$. For instance, CrI$_3$ is a ferromagnetic material at $\sim 61$ K in bulk form. By exfoliating this material to a few layers, its magnetic ordering (Curie) temperature ($T_C$) decreases to 45 K$^{28}$. Another example is an itinerant ferromagnetic compound known as Fe$_{3-x}$GeTe$_2$ (FGT)$^{27}$, which has recently garnered a great deal of attention. FGT has a $T_C$ at $\sim 220$ K. Most interestingly, the authors demonstrated$^{27}$ the robust ferromagnetic nature of FGT when reduced to a monolayer and by applying an external electric field, the group was able to tune FGT’s magnetic properties. Among the possible sources, the effect of proton irradiation on the magnetic properties of vdWs magnetic crystals received no attention to date. That forms the motivation for this work.

A worthy vdW material to study is CrSiTe$_3$ (CST), a semiconductor with a bandgap of 0.7 eV and ferromagnetic ordering at $\sim 32$ K$^{32-35}$. CST is made up of three unit cells stacked in an ABC sequence and its magnetic ion (Cr$^{3+}$) is located in the center of a slightly warped octahedral of Te atoms. In this structure, the Cr ions form a honeycomb sub-lattice that has Si pairs in the center of the hexagons. CST crystallizes in the rhombohedral crystal structure, described by R3. The super-exchange interactions via the chalcogenide atoms for CST are ferromagnetic, and the ferromagnetic interactions are also favored when (i) the Cr-Cr distances increases and (ii) by the covalent character of the Cr-X ($X = S, Se, Te$) bonds. Strong spin—lattice coupling is also reported
on CST. Most importantly, prior research has shown that this material can be exfoliable to stable monolayer, for possible device applications. In this letter, we report that the saturation magnetization of CST increases by 23% (from 3.9 \( \mu_B \) to 4.8 \( \mu_B \)) upon the proton irradiation with the fluence of \( 1 \times 10^{15}/\text{cm}^2 \). EPR studies show signatures associated with \( \text{Cr}^{3+} \) centers, and we observed no trace of magnetically active vacancies introduced after proton irradiation. Most likely, as reflected from XPS and Raman measurements, the modification of spin-lattice coupling and introduction of disorder upon proton irradiation could lead to enhancement in saturation magnetization.

CST (mm in size) single crystals were prepared as reported previously. A Quantum Design Physical Properties Measurements System with a temperature range of 2 – 300 K and magnetic field range of \( \pm 7 \) T was used for this study. The electron paramagnetic resonance (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 using a 1.7 MV Tandetron accelerator. This energy was chosen not to produce unwanted damage in the crystal. The projected range is 35 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 6 mm \( \times \) 6 mm and the beam was rastered over an area of 1.2 cm \( \times \) 1.2 cm to guarantee lateral beam uniformity. The weak beam current and the beam rastering reduce (< 50°C) the beam heating during the irradiation. The beam was filtered with multiple magnet bending devices to remove carbon contamination. The vacuum during the irradiation was 6E-8 Torr or better. The application of liquid nitrogen trapping during irradiation was performed to improve vacuum. X-ray Photoelectron Spectroscopy (XPS) measurement was performed using a commercial Physical Electronics PHI 5000 VersaProbe system. The system is equipped with a monochromatic Al K-alpha X-ray source at 1486.6 eV with 100 um beam size. Compositional survey scans were obtained using a pass energy of 117.4 eV and an energy step of 0.5 eV. High-resolution detailed scans of each element were acquired using a pass energy of 23.5 eV and an energy step of 0.1 eV. Raman spectra were collected using a Renishaw Raman spectrometer using 532 nm laser wavelength excitation and a 50x optical microscope objective.

Figure 1 shows the comparison of isothermal magnetization curves recorded at 2 K measured on both pristine (shown in blue) and irradiated (shown in red) CST crystal, in which the magnetic field was applied parallel to the c-axis of this crystal. Most strikingly, up on proton irradiation, there is a significant enhancement (23%) in saturation magnetization (\( M_S \)) observed. The pristine CST crystals exhibited a \( M_S \) of 3.9 \( \mu_B \). After exposure to protons, the \( M_S \) of CST increases to 4.8 \( \mu_B \). This change is also accompanied by a noticeable increase in the coercive field (\( H_C \)) from \( \sim 465 \) Oe for pristine CST to \( \sim 542 \) Oe after irradiation. Such enhancement in magnetization has been reported previously from laser irradiated Nd\(_{0.7}\)Sr\(_{0.3}\)CoO\(_3\), Cr\(_2\)O\(_3\), La\(_{0.5}\)Pr\(_{0.5}\)CrO\(_3\), Pr\(_{0.5}\)Ca\(_{0.5}\)Mn\(_{0.99}\)Cr\(_{0.01}\)O\(_3\) compounds, argued to be due to the increasing population of high spin states and formation of microscopic phase separation. We see no indication of exchange bias (shift in the hysteresis loop along the field axis), and that infers the absence of magnetic phase separation due to proton irradiation. This is consistent with the findings collected from the temperature dependent magnetization and EPR (see below) measurements.
Figure 2 presents the temperature-dependent magnetization performed in the H//c plane by employing both zero-field cooled (ZFC) and field (1kOe) cooled (FC) conditions. The T_c is observed at around ~ 35 K for both pristine and irradiated CST crystal, which is in good agreement with previous reports published on pristine CST crystal. This observation confirms that proton irradiation has no/minimal effect on T_c. The T_c remains unchanged even when the proton fluence was reduced to 5×10^{16}/cm^2 (data not shown). Notably, consistent with isothermal magnetization measurements (see, Fig. 1), temperature dependent magnetization measurements (see, Fig. 2) also show that there is a significant increase in the magnetization measured in the ferromagnetic phase (<35 K) of irradiated CST crystal. Furthermore, interestingly, as reflected in Fig. 2, we observed a larger bifurcation at 30 K between ZFC and FC arms of irradiated CST crystal compared to pristine CST crystal. This is an indication of stronger magnetic anisotropy present in the irradiated CST. Curie-Weiss (CW) fits were performed (supplementary information, Fig. S2) on the inverse susceptibility vs. temperature (200-400 K) [1/\chi (T)] curves, which gave an effective moment for pristine CST of 3.9 \mu_B, consistent with the theoretical and experimental (spin-only) value of 3.87 \mu_B. After proton irradiation, CW fits present an effective moment of \mu_{eff} = 4.8 \mu_B. Similar observations were made when the measurements were performed with the magnetic field applied perpendicular to the c-axis of the crystal. These observations point out that there are no secondary magnetic impurities (such as Cr\_2Te\_3, T_c = 240 K) that would have been resulted upon proton exposure.

EPR measurements are particularly useful to detect local minute magnetic phases, and better understand the microscopic mechanisms that lead to enhanced magnetization upon irradiation. We have performed temperature dependent X-band (9.43 GHz) EPR measurements on both pristine and irradiated CST crystals. Figure 3 depicts the EPR signals measured (0-6000 G) at 10 K (ferromagnetic phase) for both the pristine (shown in black) and irradiated (shown in blue) crystals. We detected a single Dysonian-like EPR signal, originating from conduction carriers, from each crystal and see no additional EPR signals upon proton irradiation. A similar line shape was reported previously in the case of proton-irradiated graphite due to the conduction carriers. This signal shape is consistent at all the temperatures from 10-50 K that we measured across T_c on both of these crystals. In addition, both crystals show g-value of 1.95 and peak to peak EPR signal width of 600-650 G, which are the benchmark signatures of Cr^{3+} (S = 3/2). That suggests the expected valence state of Cr is retained, and there are no additional vacancies produced that are magnetically active during the proton irradiation, consistent with the SRM damage profile (supplementary information). Most notably, a decrease in EPR signal intensity (proportional to number of paramagnetic centers) is observed up on proton irradiation, possibly, due to the defects in which the hydrogen atoms compensate for unpaired electrons are nonparamagnetic, and cannot be observed by EPR. We did not detect EPR signal originating from localized paramagnetic spins, radiation-induced paramagnetic defects, and uncoordinated atoms such as vacancies that might have generated from proton irradiation. In contrast to the present work, Nakayama and co-authors have reported EPR signal intensity increased upon infrared photoexcitation on La_{0.5}Pr_{0.5}CrO_3 and Cr_2O_3 compounds, possibly due to the irradiated photons excite the t_{2g} electrons to the e_g state. While various forms of hydrogen-adsorbed defects were suggested as origins of the localized magnetic moment, no hyperfine structure was apparent in our EPR spectra, which can be taken as a negative evidence for the hydrogen-adsorbed defects as an origin of the magnetic moment. Even if we consider that the enhanced magnetism is due to H-related defect, the expected magnetization would be 3 orders of magnitude smaller, which is clearly not the case here.
To gain addition details, we performed XPS measurements (supplementary information, Fig. S3) on both the crystals. Our findings confirm the expected composition of the elements on both the crystals, though we detected unavoidable adventitious carbon\textsuperscript{49} and surface oxidation\textsuperscript{50}. High-resolution XPS data were also collected (see Fig. 4 (a,b)) on both samples. Despite the strong overlap between Te 3d peak and Cr 2p peak, the much higher atomic concentration together with the larger sensitive factor of Tellurium\textsuperscript{51} make the spectra between 570 eV – 590 eV dominated by the Te 3d signal. This allows us to assign the major peak to be Te\textsuperscript{4+} (oxide phase) and Te\textsuperscript{2-} (intrinsic phase) unambiguously (see, Fig. 4(a)). As it can be clearly seen, the intrinsic phase of Te is significantly increased in the irradiated sample compared to its pristine counterpart, as suggested in both 3d peak (Fig. 4(a)) and 3p3/2 peak (Fig. 4(b)) that will change the Cr-Te-Cr super exchange pathway. In addition, we noticed a strong suppression in the intensity of Raman peaks (supplementary information, Fig. S4) and significant shift in A\textsuperscript{3}g mode from 139.4 to 136.8 cm\textsuperscript{-1} (out-of-plane vibrations of Te atoms), and E\textsuperscript{3}g mode remains practically constant at 118.4 cm\textsuperscript{-1} upon proton irradiation. Noticeable shift in A\textsuperscript{3}g phonon mode indicates spin-lattice coupling\textsuperscript{33} is modified upon proton irradiation due to the introduction of disorder. No additional peaks were detected from the proton irradiated CST.

As discussed in the previous paragraphs, the observed increase in M\textsubscript{S} up on proton irradiation is 4.8 µB that corresponds to the Cr\textsuperscript{2+}, which is in high-spin (S = 2, 3d\textsuperscript{4} configuration) state\textsuperscript{52}. Such change in the spin state is commonly observed in many spin-cross over compounds upon illumination\textsuperscript{53,54}. In the present context, one would expect\textsuperscript{55} to see much sharper (~ 31 G) EPR signal related to Cr\textsuperscript{2+}, and its super hyperfine structure. However, we did not see an explicit evidence of change in valence state from XPS and EPR measurements. That may infer that the charge transfer is transient (faster than nanoseconds), could not be captured in XPS and EPR measurements. Alternatively, due to its large zero-field splitting (D = -2.48 cm\textsuperscript{-1})\textsuperscript{56}, it could not be detected at X-band (9.43 GHz) frequency employed in the present work, often higher frequencies (>20 GHz) need to be employed. The presence of Cr\textsuperscript{4+} (S = 1)\textsuperscript{57} is ruled out from the absence of doublet with the separation about 1900 G. The increase in magnetization is too large to be explained solely by the adsorption of protons implanted. In that context, regarding the origin of enhanced magnetization, among others, the modification in the spin-lattice coupling and introduction of disorder appear to be the most general one. Though proton irradiated CST retains the pristine crystal structure, our initial laboratory room temperature X-ray diffraction measurements could not yield conclusive evidence on the changes in the lattice parameters, bond angles, and bond lengths, which certainly requires additional work. In addition, we will perform temperature dependent synchrotron X-ray magnetism circular dichroism and coherent x-ray scattering measurements to probe the local electronic and magnetic structure at the atomic scale on both the crystals that might provide the exact mechanism underlying the increase in saturation magnetization upon proton irradiation.

In summary, proton irradiation (1x10\textsuperscript{15}/cm\textsuperscript{2}) on CST single crystal caused a significant increase (23\%) in the saturation magnetization, and accompanied by increase in the coercive field and no change in Tc. EPR measurements show no additional paramagnetic signals demonstrating that proton irradiation did not generate new magnetically active defects or vacancies in this material. XPS and Raman measurements infer that spin-lattice coupling is modified and disorder is introduced upon proton irradiation and that could enhance the saturation magnetization. While the exact mechanism needs additional work, these findings may help in tuning the magnetic properties of vdWs materials.
L.M.M acknowledges the useful discussions with H. S. Nair. L.M.M and S.R.S acknowledge support from a UTEP start-up grant. L.M.M acknowledges the Wiemer Family for awarding Student Endowment for Excellence, and NSF-LSAMP Ph.D. Fellowship. This publication was prepared by S. R. Singamaneni and co-authors under the award number 31310018M0019 from The University of Texas at El Paso (UTEP), Nuclear Regulatory Commission. The Statements, findings, conclusions, and recommendations are those of the author(s) and do not necessarily reflect the view of the (UTEP) or The US Nuclear Regulatory Commission. Work at Brookhaven was supported by the US Department of Energy, Office of Basic Energy Sciences as part of the Computation Material Science Program (material synthesis and characterization). Authors thank S. R. J. Hennadige for his help in EPR measurements, and Alex Price for XRD measurements.
Figures

**Figure 1:** The magnetization vs. magnetic field curves for both pristine and irradiated CST crystals. M(H) measurements were performed when the magnetic field was applied parallel to the c-axis of the crystal.
**Figure 2:** Temperature dependent magnetization ZFC and FC curves collected in H//c plane. The FC curves were measured after the sample was cooled down with a 1 KOe field and measured with a 500 Oe field.
Figure 3: X-band (9.43 GHz) EPR spectra for pristine (in black) and irradiated (in blue) CST, collected at 10 K.
Fig. 4: High-resolution detailed XPS scans for (a) Te 3d peak and (b) Te 3p3/2 peak
References

1. S. Mathew, K. Gopinadhan, T.K. Chan, X.J. Yu, D. Zhan, L. Cao, A. Rusydi, M.B.H. Breese, S. Dhar, Z.X. Shen, T. Venkatesan, and J.T.L. Thong, Appl. Phys. Lett. 101, 102103 (2012).
2. P. Esquinazi, D. Spemann, R. Höhne, A. Setzer, K.-H. Han, and T. Butz, Phys. Rev. Lett. 91, 227201 (2003).
3. R.-W. Zhou, X.-C. Liu, H.-J. Wang, W.-B. Chen, F. Li, S.-Y. Zhuo, and E.-W. Shi, AIP Advances 5, 047146 (2015).
4. U. Abdurakhmanov, A.B. Granovskii, A.A. Radkovskvii, M.K. Usmanov, S.M. Sharipov, and V.P. Yugai, Phys. Solid State 44, 312 (2002).
5. M. Matsushita, H. Wada, and Y. Matsushima, Journal of Magnetism and Magnetic Materials 394, 491 (2015).
6. T.L. Makarova, A.L. Shelankov, I.T. Serenkov, V.I. Sakharov, and D.W. Boukhvalov, Phys. Rev. B 83, 085417 (2011).
7. Y. Chukalkin, A. Teplykh, and B. Goshchitskii, Physica Status Solidi (B) 242, R70 (2005).
8. S.W. Han, Y.H. Hwang, S.-H. Kim, W.S. Yun, J.D. Lee, M.G. Park, S. Ryu, J.S. Park, D.-H. Yoo, S.-P. Yoon, S.C. Hong, K.S. Kim, and Y.S. Park, Phys. Rev. Lett. 110, 247201 (2013).
9. L. Madaü, O. Ochedowski, H. Lebius, B. Ban-d’Esat, C.H. Naylor, A.T.C. Johnson, J. Kotakoski, and M. Schleberger, 2D Materials 4, 015034 (2017).
10. T. Shi, R.C. Walker, I. Jovanovic, and J.A. Robinson, Scientific Reports 7, 4151 (2017).
11. V.N. Brudnyi and A.I. Potapov, Semiconductors 35, 1361 (2001).
12. K.W. Lee and C.E. Lee, Phys. Rev. Lett. 97, 137206 (2006).
13. K.W. Lee, H. Kweon, and C.E. Lee, Adv. Mater. Weinheim 25, 5663 (2013).
14. S.W. Han, Y. Park, Y.H. Hwang, W.G. Lee, and S.C. Hong, Appl. Phys. Lett. 109, 252403 (2016).
15. T.-Y. Kim, K. Cho, W. Park, J. Park, Y. Song, S. Hong, W.-K. Hong, and T. Lee, ACS Nano 8, 2774 (2014).
16. H. Thakur, P. Thakur, R. Kumar, N.B. Brookes, K.K. Sharma, A.P. Singh, Y. Kumar, S. Gautam, and K.H. Chae, Appl. Phys. Lett. 98, 192512 (2011).
17. P. Esquinazi, R. Höhne, K.-H. Han, A. Setzer, D. Spemann, and T. Butz, Carbon 42, 1213 (2004).
18. M. Cao, Y. Ma, X. Wang, C. Ma, W. Zhou, X. Wang, W. Tan, and J. Du, AIP Advances 7, 056413 (2017).
19. B. Khare, M. Meyyappan, M.H. Moore, P. Wilhite, H. Imanaka, and B. Chen, Nano Lett. 3, 643 (2003).
20. B. Wang, S. Yang, J. Chen, C. Mann, A. Bushmaker, and S.B. Cronin, Appl. Phys. Lett. 111, 131101 (2017).
21. Q.Q. Lan, X.J. Zhang, X. Shen, H.W. Yang, H.R. Zhang, X.X. Guan, W. Wang, Y. Yao, Y.G. Wang, Y. Peng, B.G. Liu, J.R. Sun, and R.C. Yu, Phys. Rev. Mater. 1, 024403 (2017).
22. H.-P. Komsa, J. Kotakoski, S. Kurasch, O. Lehtinen, U. Kaiser, and A.V. Krasheninnikov, Phys. Rev. Lett. 109, 035503 (2012).
23. R.C. Walker, T. Shi, E.C. Silva, I. Jovanovic, and J.A. Robinson, Physica Status Solidi (A) 213, 3065 (2016).
24. A.V. Krasheninnikov and K. Nordlund, Journal of Applied Physics 107, 071301 (2010).
25. A. Geremew, F. Kargar, E.X. Zhang, S.E. Zhao, E. Aytan, M.A. Bloodgood, T.T. Salguero, S. Rumyantsev, A. Fedoseyev, D.M. Fleetwood, and A.A. Balandin, ArXiv:1901.00551 [Cond-Mat, Physics:Physics] (2019).
26. D.L. Duong, S.J. Yun, and Y.H. Lee, ACS Nano 11, 11803 (2017).
27. Z. Fei, B. Huang, P. Malinowski, W. Wang, T. Song, J. Sanchez, W. Yao, D. Xiao, X. Zhu, A.F. May, W. Wu, D.H. Cobden, J.-H. Chu, and X. Xu, Nature Materials 17, 778 (2018).
28. B. Huang, G. Clark, E. Navarro-Moratalla, D.R. Klein, R. Cheng, K.L. Seyler, D. Zhong, E. Schmidgall, M.A. McGuire, D.H. Cobden, W. Yao, D. Xiao, P. Jarillo-Herrero, and X. Xu, Nature 546, 270 (2017).
29. M. Bonilla, S. Kolekar, Y. Ma, H.C. Diaz, V. Kalappattil, R. Das, T. Eggers, H.R. Gutierrez, M.-H. Phan, and M. Batzill, Nature Nanotechnology 13, 289 (2018).
30. M. Abramchuk, S. Jaszewski, K.R. Metz, G.B. Osterhoudt, Y. Wang, K.S. Burch, and F. Tafti, Advanced Materials 30, 1801325 (2018).
31. K.S. Burch, Nature Nanotechnology 13, 532 (2018).
32. Y. Liu and C. Petrovic, Phys. Rev. Materials 3, 014001 (2019).
33. L.D. Casto, A.J. Clune, M.O. Yokosuk, J.L. Musfeldt, T.J. Williams, H.L. Zhuang, M.-W. Lin, K. Xiao, R.G. Hennig, B.C. Sales, J.-Q. Yan, and D. Mandrus, APL Materials 3, 041515 (2015).
34. V. Carteaux, G. Ouvrard, J.C. Grenier, and Y. Laligant, Journal of Magnetism and Magnetic Materials 94, 127 (1991).
35. B. Siberchicot, S. Jobic, V. Carteaux, P. Gressier, and G. Ouvrard, J. Phys. Chem. 100, 5863 (1996).
36. X. Li and J. Yang, J. Mater. Chem. C 2, 7071 (2014).
33 M.-W. Lin, H.L. Zhuang, J. Yan, T.Z. Ward, A.A. Puretzky, C.M. Rouleau, Z. Gai, L. Liang, V. Meunier, B.G. Sumpter, P. Ganesh, P.R.C. Kent, D.B. Geohegan, D.G. Mandrus, and K. Xiao, J. Mater. Chem. C 4, 315 (2015).
34 L. Shao, J. Gigax, D. Chen, H. Kim, F.A. Garner, J. Wang, and M.B. Toloczko, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 409, 251 (2017).
35 J.G. Gigax, H. Kim, E. Aydogan, F.A. Garner, S. Maloy, and L. Shao, Materials Research Letters 5, 478 (2017).
36 Y. Okimoto, Y. Ogimoto, M. Matsubara, Y. Tomioka, T. Kageyama, T. Hasegawa, H. Koinuma, M. Kawasaki, and Y. Tokura, Appl. Phys. Lett. 80, 1031 (2002).
37 D. Bahadur, S. Asthana, C. Carbonera, C. Desplanches, and J.-F. Létard, Solid State Communications 142, 132 (2007).
38 S. Sasaki, Y.F. Zhang, O. Yanagisawa, and M. Izumi, Journal of Magnetism and Magnetic Materials 310, 1008 (2007).
39 T. Nakayama, O. Yanagisawa, M. Arai, and M. Izumi, Physica B: Condensed Matter 329–333, 747 (2003).
40 J.F. Dillon and C.E. Olson, Journal of Applied Physics 36, 1259 (1965).
41 J.F. Dillon, Journal of Applied Physics 33, 1191 (1962).
42 S. Chehab, J. Amiel, P. Dienan, and S. Flandrios, Physica B: Condensed Matter 173, 211 (1991).
43 L.S. Vlasenko, M.P. Vlasenko, V.A. Kozlov, and V.V. Kozlovskii, Semiconductors 33, 1059 (1999).
44 S. Mathew, B. Satpati, B. Joseph, B.N. Dev, R. Nirmala, S.K. Malik, and R. Kesavamoorthy, Phys. Rev. B 75, 075426 (2007).
45 T.L. Barr and S. Seal, Journal of Vacuum Science & Technology A 13, 1239 (1995).
46 L.V. Yashina, S.P. Kobleva, T.B. Shatalova, V.P. Zlomanov, and V.I. Shtanov, Solid State Ionics 141–142, 513 (2001).
47 J.F. Moulder, Handbook of X-Ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data (Physical Electronics Division, Perkin-Elmer Corporation, 1992).
48 M. Saes, N.P. Raju, and J.E. Greedan, Journal of Solid State Chemistry 140, 7 (1998).
49 H. Daubric, R. Berger, J. Kliava, G. Chastanet, O. Nguyen, and J.-F. Létard, Phys. Rev. B 66, 054423 (2002).
50 M. Shirai, N. Yonemura, T. Tayagaki, K. Kan‘no, and K. Tanaka, Journal of Luminescence 94–95, 529 (2001).
51 K. Morigaki, J. Phys. Soc. Jpn. 18, 733 (1963).
52 J.T. Vallin and G.D. Watkins, Phys. Rev. B 9, 2051 (1974).
53 N.Y. Garces, N.C. Giles, L.E. Halliburton, K. Nagashio, R.S. Feigelson, and P.G. Schunemann, Journal of Applied Physics 94, 7567 (2003).
Supplementary Information
Enhanced Magnetization from Proton Irradiated Bulk van der Waals Magnet CrSiTe$_3$

L. M. Martinez$^1$, Y. Liu$^2$, C. Petrovic$^2$, L. Shao$^3$, Q Wang$^4$, S. R. Singamaneni$^{15}$

$^1$Department of Physics, The University of Texas at El Paso, El Paso, Texas 79968, USA
$^2$Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, New York 11973, USA
$^3$Department of Nuclear Engineering, Texas A&M University, College Station, TX 77845, USA
$^4$Department of Physics and Astronomy, West Virginia University, Morgantown, WV 26506, USA

Fig. S1: SRM profile for proton irradiated CST crystal
Fig. S2: Curie-Weiss (CW) fits for pristine (a) and irradiated (b) CST crystals.
Fig. S3: XPS survey scans for both pristine (a) and irradiated (b) CST crystals

Fig. S4: Raman spectra collected from pristine (shown in black) and irradiated (shown in blue) CST crystals