Evidence for surface spin structures from first order reversal curves in magnetic topological semimetals

A.A. Avakyants,¹ N.N. Orlova,¹ A.V. Timonina,¹ N.N. Kolesnikov,¹ and E.V. Deviatov³

¹Institute of Solid State Physics of the Russian Academy of Sciences, Chernogolovka, Moscow District, 2 Academician Ossipyan str., 142432 Russia
(Dated: June 8, 2022)

We study magnetization reversal and first order reversal curves for two different magnetic topological semimetals, Co₃Sn₂S₂ and Fe₃GeTe₂, in a wide temperature range between 80 K and 180 K. For the magnetization hysteresis loops, we observe strong temperature dependence of the initial (low-temperature) step-like magnetization switchings, so asymmetric regions of slanted magnetization appear above 140 K. Usually, similar behavior is ascribed to appearance of the second, temperature-induced magnetic phase. However, first order reversal curve analysis shows two-phase behavior even at lowest temperatures of our experiment. While the bulk ferromagnetic phase is of high temperature dependence, the second magnetic phase demonstrates perfect temperature stability below the Curie temperature. We connect the robust second phase with the surface spin textures, which are inherent for magnetic topological semimetals, so the excellent temperature stability is due to the topological protection of the semimetal surface states. This conclusion is also supported by the characteristic bow-tie magnetic hysteresis loops.

PACS numbers: 71.30.+h, 72.15.Rn, 73.43.Nq

INTRODUCTION

Recent interest to topological semimetals is mostly connected with Fermi arc surface states, which are known for Dirac, Weyl, and nodal-line semimetals [1]. All of them are characterized by band touching in some distinct nodes (or along a nodal line), which are the special points of Brillouin zone with three dimensional linear dispersion. Topologically protected Fermi arc surface states are connecting projections of these nodes on the surface Brillouin zone.

Most of experimentally investigated WSMs, were noncentrosymmetric crystals with broken inversion symmetry [1]. In contrast, there are only a few candidates of magnetically ordered materials for the realization of WSMs [2,3]. Recently, giant anomalous Hall effect was reported [6,7] for the kagome-lattice ferromagnet Co₃Sn₂S₂, as an indication for the existence of a magnetic Weyl phase [1]. Fermi arcs were directly visualized for Co₃Sn₂S₂ by scanning tunneling spectroscopy [8]. Also, three-dimensional Fe₃GeTe₂ (FGT) is a unique candidate for the ferromagnetic nodal-line semimetal [9], hosting spin-polarized Fermi arc surface states [10].

Intriguing spin properties of Weyl semimetals make it attractive material for spin investigations. Complex spin textures appear [11–13] in WTe₂ due to the strong spin and momentum correlation [14] (spin-momentum locking) in topological semimetals. Spin- and angle-resolved photoemission spectroscopy data indeed demonstrate surface Fermi arcs with nearly full spin polarization [15–18]. Surface topological textures (skyrmions) are also visualized in some magnetic semimetals by STM, Lorenz electron microscopy, and magnetic force microscopy [14,21]. Recent investigations show topological protection of skyrmion structures due to their origin from the spin-polarized topological surface states [22].

Thus, any magnetic topological semimetal consist of two correlated spin-ordered systems, which are the magnetically ordered bulk and the spin-polarized surface textures. On the other hand, similar two-component magnetic systems are known for the artificial objects like ferromagnetic multilayers, e.g., for Co/Pd [23], Pt/Co/Ta [24,26], and Ir/Fe/Co/Pt [27] multilayer films. In these objects, nonmagnetic layers are of strong spin-orbit coupling, so magnetic skyrmions appear due to broken inversion symmetry at the interface between the ferromagnetic nonmagnetic layers. Multilayers demonstrate two independent magnetization processes [28], inverted hysteresis [29], exchange bias [30] and spin-valve effect [31,32]. The magnetic textures are also responsible for the atypical magnetization dynamics, i.e., for the bow-tie magnetic hysteresis [33] in these systems.

Due to the obvious similarity with the ferromagnetic multilayers, it is reasonable to study magnetization dynamics in magnetic topological semimetals. Recently, current-induced spin dynamics has been investigated in Weyl topological surface states [34,36], demonstrating strong similarity with spin-polarized transport in multilayers [37–40]. On the other hand, direct demonstration is still missing for the independent magnetization of bulk and surface magnetic systems for topological semimetals.

Here, we study magnetization reversal and first order reversal curves for two different magnetic topological semimetals, Co₃Sn₂S₂ and Fe₃GeTe₂, in a wide temperature range between 80 K and 180 K. For the magnetization hysteresis loops, we observe strong temperature dependence of the initial (low-temperature) step-like magnetization switchings, so asymmetric regions of
A slanted magnetization appears above 140 K. Usually, similar behavior is ascribed to appearance of the second, temperature-induced magnetic phase. However, first-order reversal curve analysis shows two-phase behavior even at lowest temperatures of our experiment. While the bulk ferromagnetic phase is of high temperature dependence, the second magnetic phase demonstrates perfect temperature stability below the Curie temperature. We connect the robust second phase with the surface spin textures, which are inherent for magnetic topological semimetals, so the excellent temperature stability is due to the topological protection of the semimetal surface states. This conclusion is also supported by the characteristic bow-tie magnetic hysteresis loops.

SAMPLES AND TECHNIQUES

Co$_3$Sn$_2$S$_2$ single crystals were grown by the gradient freezing method. Initial load of high-purity elements taken in stoichiometric ratio was slowly heated up to 920°C in the horizontally positioned evacuated silica ampule, held for 20 h and then cooled down to the ambient temperature at the rate of 20 degree/h. The obtained ingot was cleaved in the middle part. The Laue patterns confirm the hexagonal structure with (0001) as cleavage plane. Fe$_3$GeTe$_2$ single crystals were grown by the two-stage iodine transport from the initially synthesized Fe$_3$GeTe$_2$ compound. The electron probe microanalysis of cleaved samples and X-ray diffractometry of powdered samples confirmed the stoichiometric composition of the crystals.

To confirm Co$_3$Sn$_2$S$_2$ and Fe$_3$GeTe$_2$ crystals quality, magnetoresistance measurements were also performed in standard Hall bar geometry for the reference samples with normal (Au) leads. The specific feature of time reversal symmetry breaking in topological semimetals is a large anomalous Hall effect (AHE), which manifests itself as non-zero Hall conductance in zero magnetic field. AHE can be understood in a topological-insulator-multilayer model, where the two-dimensional Chern edge states form the three-dimensional surface states. We have demonstrated a large anomalous Hall effect for the reference samples, which indicates a magnetic topological phase.

To investigate magnetic properties of small Co$_3$Sn$_2$S$_2$ and Fe$_3$GeTe$_2$ single crystal flakes, we use Lake Shore Cryotronics 8604 VSM magnetometer. It is equipped with nitrogen flow cryostat, which allows measurements below Curie temperatures of Co$_3$Sn$_2$S$_2$ and Fe$_3$GeTe$_2$ (177 K and 220 K, respectively).

Since Co$_3$Sn$_2$S$_2$ and Fe$_3$GeTe$_2$ are of layered crystal structure, we use small flakes, which are obtained by a mechanical cleavage from the initial single crystals. A flake is mounted to the magnetometer sample holder by a low temperature grease, which has been tested to have a negligible magnetic response. The flake’s surface can be rotated in magnetic field, also, we perform centering and saddling procedures to establish correct sample position in the cryostat.

We investigate sample magnetization by the standard method of the magnetic field gradual sweeping between two opposite saturation values to obtain hysteresis loops at different temperatures. Apart from the hysteresis measurements, we perform first order reversal curve (FORC) analysis, which is of growing popularity nowadays. FORC is known as a powerful tool to investigate the domain state of the sample and the nature of magnetic interactions in the material. It provides information on the magnetic reversal mechanism, which can not be obtained from standard hysteresis loops.

The FORC analysis consists of magnetization $M$ recording as a two-dimensional map with the reversal field $H_r$ and demagnetization field $H$ as $x$ and $y$ coordinates, respectively. Before every FORC curve, the magnetization is stabilized at some fixed positive saturation field $H_s$. As a second step, the field is changed to the chosen reversal field $H_r$, then the demagnetization curve $M(H)$ can be recorded toward the positive magnetic fields. For the next FORC curves, the starting point $H_s$ is shifted to the lower magnetic field, so the FORC density $\rho(H, H_r)$ can be calculated as a second derivative

$$\rho = -\frac{1}{2} \frac{\partial^2 M(H, H_r)}{\partial H \partial H_r}.$$ 

The obtained $\rho(H, H_r)$ map is usually redrawn in $(H_u, H_c)$ coordinates, where $H_u = \frac{1}{2}(H + H_r)$ and $H_c = \frac{1}{2}(H - H_r)$. The FORC density distribution $\rho(H_u, H_c)$ is known to be convenient for analysis. For example, closed contours are usually associated with single-domain regime, while multi-domain material gives open contours that diverge towards the $H_u$ axis. Vertical shift of $\rho(H_u, H_c)$ structures characterizes strength of exchange interaction. Which is of primary importance for us, multiple FORC density $\rho(H_u, H_c)$ structures correspond to multiple magnetic phases in the material.

EXPERIMENTAL RESULTS

Fig. (a) shows the hysteresis loops for a thick (0.56 mg mass) Co$_3$Sn$_2$S$_2$ sample at low temperatures (80 K, 100 K, 120 K and 135 K). Here and below, the curves are obtained after zero-field cooling, the magnetic field is normal to the flake’s surface, i.e. along the Co$_3$Sn$_2$S$_2$ easy axis direction. The sample orientation is verified by the angle dependence of magnetization in Fig. (b) for high external magnetic field $H$=15 kOe.

Hysteresis loops are of strictly rectangular shape with step-like magnetization switching in Fig. (a),
which confirms the single domain magnetic structure of Co$_3$Sn$_2$S$_2$. The coercive field ($H_c$) is about 1 kOe, as it is expected for a hard magnetic Co$_3$Sn$_2$S$_2$ material. At the lowest 80 K temperature, the hysteresis loop is shifted to the negative magnetic fields, as it has also been shown in Ref. [50], this asymmetric shift can be removed by multiple cycling of the external field or by temperature increase above 90 K. The coercive field and the saturated magnetization value are monotonically diminishing with temperature in Fig. 1 (a).

To our surprise, the hysteresis loops show complicated temperature dependence above 140 K, see Fig. 2 (a). For every hysteresis branch, a region of slanted magnetization dependence appears, which is not symmetric in respect to the zero magnetic field. This slanted region accompanies the usual step-like magnetization switching of initially (at low temperatures) rectangular hysteresis loop, so it corresponds to the independent magnetization processes. First traces of the effect can be seen at 135 K in Fig. 1 (a). The width of the slanted region is increasing with temperature, so the step-like magnetization switching is shifted across the zero fields. This hysteresis loop type is known as the so called inverted hysteresis [51, 52]. The magnetization loops are completely suppressed above the Curie temperature, see the linear 180 K curves in Fig. 2 (a).

The inverted hysteresis is a fingerprint of material with two independent magnetic phases, e.g. realized in artificial ferromagnetic multilayer structures [52]. It reflects the phase interaction in this case, so one magnetic phase provides a bias field to the second one [51]. In Fig. 2 (a), one phase switches magnetization by sharp steps, while another phase shows the slanted hysteresis loop with low coercitivity. It seems, that the phases are of strongly different temperature dependences: the coercive field is significantly suppressed for the rectangular monodomain loop, while the temperature-stable slanted one is of the same slope and width, so it clearly appears only at high temperatures, cp. Figs. 1 (a) and 2 (a).

Fig. 2 (b) shows qualitatively similar behavior for much smaller (0.01 mg) Co$_3$Sn$_2$S$_2$ single-crystal sample. The saturated magnetization level is of two orders of magnitude smaller in this case, but we clearly observe the slanted region and the inverted hysteresis at high temperatures, above 155 K in this case.

Multiple magnetic phases can be directly observed in FORC measurements [48, 49]. Fig. 3 shows initial FORC diagrams (a,c,e) and calculated FORC-densities $\rho(H_a, H_c)$ (b,d,f) for 100 K, 135 K, 150 K temperatures, respectively.

The multi-phase behavior can be easily seen even at 100 K from the raw curves in Fig. 3 (a). For a simple rectangular hysteresis loop, one should expect the FORC diagram as two horizontal lines at positive and negative $M(H)$ saturation levels with multiple step-like switchings between them at positive magnetic fields. The multiple steps are due to the FORC procedure [46, 47] with incomplete magnetization for some intermediate values of the reversal field $H_r$. This expected behavior can indeed be seen in Fig. 3 (a), but there is an additional set of FORC curves with finite slope. This type of FORC curves usually corresponds to the slanted hysteresis loop, i.e. it indicates an additional magnetic phase even at 100 K. At higher temperatures, the first set of the curves strongly depends on temperature, see Fig. 3 (a,c,e), in good correlation with the rectangular loops dependence.
in Fig. 2(a). In contrast, the second (slanted) set of FORC curves is practically independent of temperature, the slope and width are nearly constant, which also confirms temperature-stable magnetic phase.

The FORC-density patterns directly shows two magnetic phases in Fig. 3(b,d,f). For a single-phase monodomain sample, one should expect a set of \( \rho(H_u, H_c) \) peaks, which corresponds to the step-like switchings in the raw FORC data. The peak positions at negative \( H_u \) values confirm ferromagnetic interaction for this phase \([18, 19]\). We obtain additional structures (thick green lines) in Fig. 3(b,d,f), as it should be expected for the constant slope FORC curves in the raw diagrams (a,c,e). Since multiple structures in FORC density is a fingerprint of multiple magnetic phases in a material \([18, 19]\), two magnetic systems are present in the \( \text{Co}_3\text{Sn}_2\text{S}_2 \) single-crystal even at lowest temperatures.

The described two-phase behavior is not unique for the \( \text{Co}_3\text{Sn}_2\text{S}_2 \) topological material. Two-phase behavior can also be observed for a topological nodal-line semimetal FGT, as depicted in Fig. 4 for the 0.04 mg flake. FGT single crystals are mostly in multidomain regime, as reflected by slanted hysteresis loop in Fig. 4(a) and (b). However, the width of the loop is diminished around zero \( M \) in comparison with the nearly-saturated \( M \) values, as it is highlighted in the insets. This shape of the hysteresis loop is known as the bow-tie loop, it is usually ascribed \([23, 24, 26, 27]\) to the skyrmions \([20, 21]\), i.e. to an additional magnetic phase in the sample. Every phase corresponds to its own slanted loop with specific slope, so the sum gives the bow-tie loop shape. Two independent slopes can also be seen in the raw FORC diagram in Fig. 4(c).

**DISCUSSION**

Similar magnetization behavior is known for different structures with two decoupled magnetic subsystems, e.g. for ferromagnetic multilayers \([28, 53, 54]\) or materials with two magnetic phases \([52, 50]\). Also, it has been reported for multilayer structures with topological spin textures (surface skyrmions) \([23, 24, 27]\). The inverted hysteresis corresponds to the antiferromagnetic interfacial coupling between the magnetic phases \([51, 52, 57]\), which provides the exchange bias field.

We wish to mention, that the observed results can not originate from two connected flakes of \( \text{Co}_3\text{Sn}_2\text{S}_2 \): in the latter case, the hysteresis loop would be a sum of two rectangular ones, arbitrary shifted in magnetic field and magnetization level \([28, 54]\), as we indeed observe for a reference two-crystal sample. Thus, Fig. 2 supports the presence of two magnetic phases in \( \text{Co}_3\text{Sn}_2\text{S}_2 \) single-crystals with independent magnetization behavior.

In principle, coexistence of two magnetic phases has been anticipated for \( \text{Co}_3\text{Sn}_2\text{S}_2 \) from \( M(T) \) measurements in fixed magnetic fields \([50, 58, 59]\) and from the AHE hysteresis \([50]\). While the first phase is obviously the ferromagnetic bulk, the existence of the second phase was explained by disorder effects, e.g. by the regions of antiferromagnetic order \([58]\) or even spin-glass state \([70]\).

It is well known, that AHE hysteresis well correspond to the \( M(H) \) magnetization reversal curves, so it is not surprising that the slanted region appears at similar temperatures in Fig. 2 and in Ref. \([50]\). However, our FORC measurements directly demonstrate multi-phase behavior even at lowest temperatures, with excellent temperature stability of this phase in comparison with the main ferromagnetic one in Fig. 3. Thus, the second phase does not appear at some specific temperature in our experiment and their robustness requires specific explanation. Also,
Figure 4. (Color online) Two-phase behavior for the 0.04 mg flake of a topological nodal-line semimetal FGT. (a,b) Bow-tie slanted hysteresis loops at 100 K and at 160 K, respectively, the width of the loop is diminished around zero $M$ in comparison with the nearly-saturated $M$ values, as it is highlighted in the insets. The bow-tie loop is usually ascribed to the skyrmions, i.e. to an additional magnetic phase in the sample. Every phase corresponds to its own slanted loop with specific slope, so the sum gives the bow-tie loop shape. (c) Two independent slopes can be also seen in the raw FORC diagram at 100 K. Width of the slanted region is increasing with magnetic field, which indicates two slopes in the original loop. Inset shows full-range FORC diagram, while the enlarged region is shown in the main (c) panel.

As a conclusion, we study magnetization reversal and first order reversal curves for two different magnetic topological semimetals, Co$_3$Sn$_2$S$_2$ and Fe$_3$GeTe$_2$, in a wide temperature range between 80 K and 180 K. For the magnetization hysteresis loops, we observe strong temperature dependence of the initial (low-temperature) step-like magnetization switchings, so asymmetric regions of slanted magnetization appears above 140 K. Usually, similar behavior is ascribed to appearance of the second, temperature-induced magnetic phase. However, first order reversal curve analysis shows two-phase behavior even at lowest temperatures of our experiment. While the bulk ferromagnetic phase is of high temperature dependence, the second magnetic phase demonstrates perfect temperature stability below the Curie temperature. We connect the robust second phase with the surface spin textures, which are inherent for magnetic topological semimetals, so the excellent temperature stability is due to the topological protection of the semimetal surface states. This conclusion is also supported by the characteristic bow-tie magnetic hysteresis loops.

ACKNOWLEDGEMENT

We wish to thank S.S Khasanov for X-ray sample characterization.

[1] N.P. Armitage, E.J. Mele, and A. Vishwanath, Rev. Mod. Phys. 90, 015001 (2018).
[2] X. Wan, A. M. Turner, A. Vishwanath, S. Y. Savrasov, Phys. Rev. B 83, 205101 (2011).
[3] M. Hirschberger, S. Kushwaha, Z. Wang, Q. Gibson, S. Liang, C. A. Belvin, B. A. Bernevig, R. J. Cava, N. P. Ong, Nat. Mater. 15, 1161-1165 (2016).
[4] G. Xu, H. Weng, Z. Wang, X. Dai, Z. Fang, Phys. Rev. Lett. 107, 186806 (2011).
[5] S. K. Kushwaha, Z. Wang, T. Kong, R. J. Cava, J. Phys. Condens. Matter. 30, 075701 (2018).
[38] M. Tsoi, A. G. M. Jansen, J. Bass, W.-C. Chiang, M. Seck, V. Tsoi, and P. Wyder, Phys. Rev. Lett., 80, 4281 (1998).
[39] M. Tsoi, A. G. M. Jansen, J. Bass, W.-C. Chiang, V. Tsoi and P. Wyder, Nature, 406, 46, (2000).
[40] J. A. Katine, F. J. Albert, R. A. Buhrman, E. B. Myers and D. C. Ralph, Phys. Rev. Lett., 84, 3149 (2000).
[41] O. O. Shvetsov, Yu. S. Barash, A. V. Timonina, N. N. Kolesnikov, E. V. Deviatov, JETP Letters, 115, 267 (2022). DOI: 10.1134/S0021364022100101
[42] For a review on AHE, see N. Nagaosa, J. Sinova, S. Onoda, A. H. MacDonald, and P. P. Ong, Rev. Mod. Phys. 82, 1539 (2010).
[43] F. D. M. Haldane, Phys. Rev. Lett. 93, 206602 (2004).
[44] S. Nakatsuji, N. Kiyohara, and T. Higo, Nature 527, 212 (2015).
[45] W. Schnelle, A. Leithe-Jasper, H. Rosner, F. M. Schapacher, R. Pöttgen, F. Pielnhofer and R. Weihrich, Physical Review B, 88, 144404 (2013).
[46] B. C. Dodrill, Magnetometry Measurements and First-Order-Reversal-Curve (FORC) Analysis, Lake Shore Cryotronics. www.lakeshore.com.
[47] Dustin A. Gilbert, Peyton D. Murray, Julius De Rojas, Randy K. Dumas, Joseph E. Davies and Kai Liu, Scientific Reports, 11, 4018 (2021).
[48] B. C. Dodrill, H. S. Reichard, and T. Shimizu, Lake Shore Cryotronics. Technical Note. www.lakeshore.com.
[49] B. C. Dodrill, Magnetometry Measurements of Nanomagnetic Materials, Advanced Materials: ThechConnect Briefs 2018 www.lakeshore.com.
[50] Ella Lachman, Ryan A. Murphy, Nikola Maksimovic, Robert Kealhofer, Shannon Haley, Ross D. McDonald, Jeffrey R. Long and James G. Analytis, Nature Communications, 11, 560 (2020).
[51] M. J. O’Shea and A.-L. Al-Sharif, Journal of Applied Physics 75, 6673 (1994).
[52] Mohammad Saghayezhian, Zhen Wang, Hangwen Guo, Rongying Jin, Yimei Zhu, Jiandi Zhang and E. W. Plummer Physical Review Research 1, 033160 (2019).
[53] T. R. McGuire and T. S. Plaskett, IEEE Transactions on Magnetics, 28, 2748-2750 (1992).
[54] S. Mark, C. Gould, K. Pappert, J. Wenisch, K. Brunner, G. Schmidt, and L. W. Molenkamp, Physical Review Letters, 103, 017204 (2009).
[55] Jesús G. Ovejero, Vanda Godinho, Bertrand Lacroix, Miguel A. García, Antonio Hernando, Asunció Fernández, Materials and Design, 171, 107691 (2019), https://doi.org/10.1016/j.matdes.2019.107691.
[56] Zhao-hua Cheng, Jun-xian Zhang and H. Kronmüller, Physical Review B, 68, 144417 (2003).
[57] J. Nogués, Ivan K. Schuller, Journal of Magnetism and Magnetic Materials, 192, 203 (1999).
[58] Z. Guguchia, J. A. T. Verezhiak, D. J. Gawryluk, S. S. Tsirkin, J.-X. Yin, I. Belopolski, H. Zhou, G. Simutis, S.-S. Zhang, T. A. Cochrane, G. Chang, E. Pomjakushina, L. Keller, Z. Skrzeczowska, Q. Wang, H. C. Lei, R. Khasanov, A. Amato, S. Jia, T. Neupert, H. Luetkens and M. Z. Hasan, Nature Communications, 11, 559 (2020).
[59] H.C. Wu, P.J. Sun, D.J. Hsieh, H.J. Chen, D. Chandrasekhar Kakarla, L.Z. Deng, C.W. Chu, H.D. Yang, Materials Today Physics, 12, 100189 (2020).
[60] Noam Morali, Rajib Batabyal, Pranab Kumar Nag, Enke Liu, Quman Xu, Yan Sun, Binghai Yan, Claudia Felser, Nurit Avraham, Haim Beidenkopf, Science 365, 1286 (2019).
[61] Qi Wang, Yuanfeng Xu, Rui Lou, Zhonghao Liu, Man Li, Yaobo Huang, Dawei Shen, Hongming Weng, Shancai Wang and Hechang Lei, Nature Communications, 9, 3681 (2018).
[62] Zhipeng Hou, Weijun Ren, Bei Ding, Guizhou Xu, Yue Wang, Bing Yang, Qiang Zhang, Ying Zhang, Enke Liu, Feng Xu, Wenhong Wang, Guangheng Wu, Xixiang Zhang, Baogen Shen, Zhifeng Zhang, Advanced Materials, 30, 1701144 (2017).
[63] Akira Sugawara, Tetsuya Akashi, Mohamed A. Kassem, Yoshikazu Tabata, Takeshi Waki, and Hiroyuki Nakamura, Physical Review Materials 3, 104421 (2019).