Hysteresis features of the transition-metal dichalcogenides VX₂
(X = S, Se, and Te)

E Vatansever, S Sarikurt and R F L Evans
1 Department of Physics, Dokuz Eylül University, TR-35160, Izmir-Turkey
2 Department of Physics, University of York, YO10 5DD, York-United Kingdom
E-mail: erol.vatansever@deu.edu.tr

Keywords: magnetic hysteresis, Monte Carlo simulation, two-dimensional materials

Abstract
Very recently, it has been shown that vanadium dichalcogenides (VX₂, X = S, Se and Te) monolayers show intrinsic ferromagnetism, and their critical temperatures are nearly to or beyond room temperature. Hence, they would have wide potential applications in next-generation nanoelectronic and spintronic devices. In this work, being inspired by a recent study we systematically perform Monte Carlo simulations based on single-site update Metropolis algorithm to investigate the hysteresis features of VX₂ monolayers for a wide range of temperatures up to 600 K. Our simulation results indicate that, both remanence and coercivity values tend to decrease with increasing temperature. Furthermore, it is found that hysteresis curves start to evolve from rectangular at the lower temperature regions to nearly S-shaped with increasing temperature.

1. Introduction

In recent years, two-dimensional (2D) monolayers such as boron nitride (BN) [1], silicene [2], germanene [3], arsenene and antimonene [4], phosphorene [5] and transition metal dichalcogenides (TMDs) [6–8] have attracted considerable attention beyond graphene due to their remarkable structural, electronic, optical and magnetic properties. Among these 2D materials, TMDs have extensive and growing application areas ranging from electronics to energy storage [9–14].

Most of the primitive TMDs are non-magnetic and these materials could gain magnetic properties by applying strain or introducing transition metal atoms, point defects or non-metal element adsorption [15–20]. In recent years, the effect of tensile strain on magnetic moments of monolayered MX₂ (M = V, Nb; X = S, Se) structures have been demonstrated by several researchers [21–23]. These studies pointed out that electronic and magnetic properties can be manipulated by applying a biaxial compression or tensile strain. Due to existing intrinsic ferromagnetism and semiconducting properties in VX₂ (X = S, Se and Te) monolayer structures, it is not necessary to expose these materials under the effect of tensile strain or to doping of the monolayer structure with either transition metals or non-metallic atoms [24, 25]. So, TMDs such as pristine VX₂ monolayers could be fabricated without either applying strain or introducing transition metal atoms or native defects.

In the 1970s, bulk VS₂ was synthesized for the first time [26]. A few-layer VS₂ [7, 24, 27–31] has been synthesized in both hexagonal (H–VS₂) and trigonal (T–VS₂) structures while the bulk and few-layer VSe₂ [32–34] and bulk VTe₂ [35] can only be successfully synthesized in the trigonal structure. As far as we know, the synthesis of monolayer VX₂ (X = S, Se and Te) has not been experimentally demonstrated to date.

Electronic and magnetic properties of VX₂ monolayers (X = S, Se and Te) have been investigated in numerous studies using first-principles calculations based on density functional theory (DFT) [21, 23–25, 27, 29, 36–46]. For example, Ma et al [21] reported that pristine 2D VX₂ (X = S, Se) monolayers exhibit magnetic ordering and that they have two stable magnetic structures, one being ferromagnetic (FM) while the other is antiferromagnetic (AFM). They performed calculations to obtain the magnetic behaviour of the ground state for VX₂ monolayers and found out that the ground states of both structures are FM. This ground state characteristic has been explored in various studies [21, 25, 40, 41, 44].
According to the results of first-principles calculations, it has been previously stated that the total magnetic moment has the main contribution from V atoms while X atoms only give a small contribution to the magnetism of VX₂ (X = S, Se). In the case of VS₂, the magnetic moment values have been obtained as 0.486 μ_B [21], 0.51 μ_B [24], 0.858 μ_B [40] on each V atom and −0.026 μ_B [21], 0.03 μ_B [24], 0.047 μ_B [40] on each S atom. In the VSe₂ and VTe₂ case, the magnetic values have been reported as 0.680 μ_B [21], 0.951 μ_B [40] per V atom, 0.048 μ_B [21], 0.062 μ_B [40] per Se atom, and 0.986 μ_B [40] per V atom, 0.096 μ_B [40] per Te atom, respectively.

Gao et al [24] have experimentally demonstrated that ultrathin VS₂ nanosheets with less than five layers represent room temperature FM behavior combined with weak antiferromagnetism. According to the results obtained from the experiment performed at room temperature, the nanosheet displays clear hysteresis in the low applied field regime. They also carried out magnetization versus magnetic field (M-H) curve measurement for temperature range from 50 K to 300 K and for all different temperature values they observed the pronounced S-shaped curve, which is a characteristic of ferromagnetism [47, 48]. They revealed that the saturation magnetization and coercive field decrease with increase of temperature. Furthermore, they verified their experimental results that point out the ferromagnetic ground state by performing total energy calculations.

Kan et al [23] studied the comparative stability of both H- and T-structures of VS₂ monolayer using DFT with generalized gradient approximation (GGA) functionals. They conclude that H-structure has a direct semiconducting character with a small band gap of 0.187 eV whereas T-structure has a metallic character [21, 27, 29, 49] and H-structure is more stable than the T-structure. They also obtained the semiconductor character of H-structure of VS₂ monolayer using GGA plus on-site Coulomb interaction U (GGA+U, U = 3 eV) and Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional. The band gap energies were calculated as E_{gap} = 0.721 eV and E_{gap} = 1.128 eV in respective order. Besides these results, Kan et al also pointed out that both structures are magnetic and T-structure of VS₂ monolayer has lower magnetism (0.43 μ_B per unit cell) in comparison with H-structure (1 μ_B per unit cell). In a previous study by Zhang et al [29], for the bulk structures the total magnetic moments of hexagonal and trigonal VS₂ were estimated as 0.85 μ_B and 0.31 μ_B, respectively. Due to the difference between magnetic moment values of T and H-structures, it can be deduced that both monolayer and bulk H-VS₂ structures exhibit greater magnetism than T-structures and so the magnetic moment significantly depends on the crystal structure. More recently, Fuh et al [25] reported that H-VX₂ monolayer structures have indirect energy band gap with respective small band gap energies of 0.05, 0.22, and 0.20 eV using GGA DFT functionals. They also considered different exchange-correlation functionals such as GGA+U (U = 2 eV) and HSE06 hybrid functional to examine the electronic band structure of H-VX₂ monolayers. In addition, they performed GW calculation method to get an accurate value of the semiconducting band gap. The respective energy band gaps were reported as E_{gap} = 1.334, 1.2, 0.705 eV for VS₂, VSe₂ and VTe₂. Furthermore, Huang et al [43] and Zhanget al [44] performed electronic band structure calculations for H-VS₂ monolayer by using GGA+U (0 ≤ U ≤ 4eV) and Local Density Approximation (LDA)+U (0 ≤ U ≤ 5 eV), respectively and HSE06 functional. They all found out that H-VX₂ monolayer structures are semiconductors.

On the other hand, Fuh et al [23] also performed Monte Carlo simulations and obtained the Curie-temperatures as 292, 472, and 553 K for VS₂, VSe₂, and VTe₂ monolayers, respectively. The Curie temperature values obtained using mean field theory are reported by Pan [40] as follows: 309 K for VS₂, 341 K for VSe₂ and 618 K for VTe₂ monolayers. These Curie temperatures reveal that the unique ferromagnetic character can be achieved close to or well beyond the room temperature.

In this paper, we comprehensively investigate the temperature dependencies of remanence magnetization, coercivity and hysteresis behaviors of monolayer H-VX₂ (X = S, Se, and Te) structures using Monte Carlo simulations with single-site update Metropolis algorithm. The recent theoretical and experimental studies have clearly pointed out the favorable magnetic ground states, magnetic moment values and Curie temperature values of related monolayer structures. We believe that our Monte Carlo simulation results obtained in this work may be beneficial for both experimental and theoretical point of views.

2. Model and simulation details

We study hysteresis features of the VX₂ (X = S, Se and Te) monolayers on a hexagonal crystal structure under the influence of a magnetic field. The spin Hamiltonian of the considered systems can be written as follows:

\[ \mathcal{H} = -J_1 \sum_{\langle ij \rangle} S_i \cdot S_j - J_2 \sum_{\langle ij \rangle} S_i \cdot S_j - k \sum_i (S_{ix}^2 + S_{iy}^2) - g \mu_B H \sum_i S_{iz}. \]  

Here, S_i and S_j are the classical Heisenberg spins with unit magnitude at the site i and j in the system. J_1 and J_2 represent nearest neighbour (NN) and next-nearest neighbour (NNN) spin–spin couplings, respectively. \langle \cdots \rangle and \langle \langle \cdots \rangle \rangle denote the summation over the NN and NNN spin pairs through the system, respectively. k term corresponds to the magnetic anisotropy energy of the system, g, \mu_B and H are Landé–g constant, Bohr magneton and magnetic field terms, respectively. The first two summations are over the NN and NNN spin pairs while the last two
summations are over all of the lattice points in the system. We follow the [25] for the real values of the exchange couplings and magnetic anisotropy energy. We note that in table 2 and 4 of [25], the authors give the calculated magnetic anisotropy energies and exchange interaction parameters of VS₂, VSe₂ and VTe₂ monolayers, respectively.

We use Monte Carlo simulation with single site update Metropolis algorithm [50, 51] to understand the magnetic properties of the system on a \( L \times L \) hexagonal crystal structure. Here, \( L \) is the linear size of the hexagonal lattice, and it is fixed as 120 through this work. We select the boundary conditions such that they are periodic in all directions. The simulation process can be briefly summarized as follows. Magnetic hysteresis curves are generated over the 50 independent sample realizations. In each sample realization, the simulation starts at high temperature value using random initial spin configuration. It slowly cooled down until the temperature reaches a specific temperature value in the presence of a magnetic field \( H = 1 \) \( T \) applied in \( x \)-direction of the system. Then, using the obtained last spin configuration as initial configuration, the decreasing branch of hysteresis curve is obtained by tracing the magnetic field from \( H \) to \( -H \). The decreasing branch of the hysteresis curve is complete when the applied field reaches \( H \) value. Similarly, using the spin configuration obtained after this process as initial configuration, the increasing branch of hysteresis curve is obtained by scanning the magnetic field from \( -H \) to \( H \). At each magnetic field step, the magnetization is collected over \( 5 \times 10^4 \) Monte Carlo per step (MCSS) after the first \( 10^4 \) MCSS are discarded for equilibration process. The instantaneous magnetization components of the system can be calculated using the formula \( M_\alpha = 1/N \sum_i S_{i\alpha} \). Here, \( N \) is the total number of the spins located on the hexagonal lattice, and \( \alpha = x, y \) and \( z \).

3. Results and discussion

In figure 1, we give thermal dependencies of the remanence magnetizations and coercivities of the VX₂ monolayers. As shown in figure 1(a), remanence magnetization treatments of the considered systems sensitively...
depend on the studied temperature value. In the lower temperature regions, VX$_2$ monolayers are in the strongly ferromagnetic phase. So, it is possible to observe bigger remanence values in this region. When the temperature is increased starting from relatively lower temperature, remanence magnetizations become to shift to the lower values. This is a consequence of the fact that increasing thermal energy tends to overcome the spin-spin interaction term between spin pairs and magnetic anisotropy energy in the system. As expected, if the temperature is increased further and is reached to a characteristic value, remanence magnetization tends to

![Figure 2. Effects of the temperature on the hysteresis curves of the (a) VS$_2$, (b) VSe$_2$, and (c) VTe$_2$ monolayers. All curves are measured under the field cooling $H_{FC} = 1$ T applied in parallel directions with respect to the VX$_2$ monolayers.](image-url)
vanish. When one compares the obtained remanence magnetizations as a function of the temperature for VX2 monolayers, one can easily see that VTeX2 has much higher remanence value than the those found in other two materials. As given in figure 1(b), we also investigated the coercivity dependence on temperature for VX2 monolayers. It is possible to state that much more energy originating from external field is needed to reverse the sign of magnetization at the relatively lower temperature regions where VX2 monolayers display strong ferromagnetic character. When the temperature is increased starting from lower temperature regions, coercive field values start to decrease. Actually, this is an expected result since an increment in the temperature gives rise to the occurrence of more fluctuating behavior in the system, so coercive field gets narrower with increasing temperature value. These comments are also valid for all three monolayers studied here. If one compares the coercivity curves of VX2 monolayers, one can see that VTeX2 has a much higher coercivity value than those found in the other two materials. It should be mentioned here that according to the [25], Curie temperatures of the (a) VS2, (b) VSe2 and (c) VTeX2 monolayers are 292 K, 472 K and 553 K respectively. Our Monte Carlo results regarding the hysteresis features of VX2 monolayers illustrate that it is possible to observe finite remanence and coercivity treatments nearly or well beyond room temperature. These findings also support the previously reported Curie temperatures mentioned above.

Final investigation has been devoted to determine the influences of the temperature on the hysteresis loops corresponding to remanence and coercivity features depicted in figure 1. In this regard, we represent hysteresis curves for (a) VS2, (b) VSe2 and (c) VTeX2 monolayers for varying values of the temperature, as shown in figures 2(a)–(c). At first glance, shapes of the curves qualitatively resemble to each other. The hysteresis curves measured for all VX2 monolayers clearly reveal the ferromagnetism character. In addition to these, their shapes explicitly depend on the studied temperature. For example, rectangular-shaped hysteresis curves obtained at the relatively lower temperature regions evolve into S-shape with increasing temperature. By comparing figures 2(a)–(c) we observe that VSe2 and VTeX2 monolayers evince ferromagnetism above room temperature.

4. Conclusion

In conclusion, we perform a detailed Monte-Carlo simulation based on the Metropolis algorithm to understand the hysteresis properties of the VX2 monolayers. For this aim, we obtain hysteresis curves for a wide range of temperature, up to 600 K. All curves are measured under the field cooling $H_{FC} = 1T$ applied in parallel directions with respect to the VX2 monolayers. Results obtained in this study suggest that both coercivity and remanence values significantly depend on the studied temperature. In other words, both parameters decrease prominently with increasing temperature. Moreover, it is found that hysteresis curves start to evolve from rectangular shaped observed at the lower temperature regions to nearly S-shaped as the temperature is further increased.

Acknowledgments

The numerical calculations reported in this paper were performed at TÜBİTAK ULAKBIM (Turkish agency), High Performance and Grid Computing Center (TRUBA Resources).

ORCID iDs

E Vatansever @https://orcid.org/0000-0003-1222-3941

S Sarikurt @https://orcid.org/0000-0002-5373-4732

R F L Evans @https://orcid.org/0000-0002-2378-8203

References

[1] Han W-Q, Wu L, Zhu Y, Watanabe K and Taniguchi T 2008 Appl. Phys. Lett. 93 223103
[2] Vogt P, De Padova P, Quaresima C, Avila J, Frantzeskakis E, Asensio M C, Resta A, Ealel B and Le Lay G 2012 Phys. Rev. Lett. 108 155501
[3] Dávila M, Xian L, Cahangirov S, Rubio A and Lay G Le 2014 New J. Phys. 16 095002
[4] Zhang S, Yan Z, Li Y, Chen Z and Zeng H 2015 Angewandte Chemie 127 3155–8
[5] Liu H, Neal A T, Zhu Z, Luo Z, Xu X, Tománek D and Ye P D 2014 ACS Nano 8 4033–41
[6] Novoselov K, Jiang D, Schedin F, Booth T, Khotkevich V, Morozov S and Geim A 2005 Proc. Natl Acad. Sci. USA 102 10451–3
[7] Coleman J N et al 2011 Science 331 568–71
[8] Chhowalla M, Shin H S, Eda G, Li L-J, Loh K P and Zhang H 2013 Nature Chemistry 5 263–75
[9] Appel A M, DuBois D L and Rakowski DuBois M 2005 J. Am. Chem. Soc. 127 12717–26
[10] Karunadasa H I, Montalvo E, Sun Y, Majda M, Long J R and Chang C J 2012 Science 335 698–702
[11] Chang K and Chen W 2011 ACS Nano 5 4720–8
[12] Radisavljevic B, Radenovic A, Brivio J, Giacometti I and Kis A 2011 Nat. Nanotechnol. 6 147–50
[13] Wang Q H, Kalantar-Zadeh K, Kii A, Coleman J N and Strano M S 2012 Nat. Nanotechnol. 7 699–712
[14] Bhimanapati G R et al 2015 ACS Nano 9 11509–39
[15] Shidpour R and Manteghian M 2010 Nanoscale 2 1429–35
[16] He J, Wu K, Sa R, Li Q and Wei Y 2010 Appl. Phys. Lett. 96 082504
[17] Wang Z et al 2011 J. Mater. Chem. 21 171–80
[18] Li Y, Zhou Z, Zhang S and Chen Z 2008 J. Am. Chem. Soc. 130 16739–44
[19] Ma Y, Dai Y, Guo M, Niu C and Huang B 2011 Nanoscale 3 3883–7
[20] Ma Y, Dai Y, Guo M, Niu C, Lu J and Huang B 2011 Phys. Chem. Chem. Phys. 13 15546–53
[21] Ma Y, Dai Y, Guo M, Niu C, Zhu Y and Huang B 2012 ACS Nano 6 1695–701
[22] Zhou Y, Wang Z, Yang P, Zu X, Yang L, Sun X and Gao F 2012 ACS Nano 6 9727–36
[23] Kan M, Wang B, Lee Y H and Sun Q 2015 Nano Research 8 1348–56
[24] Gao D, Xue Q, Mao X, Wang W, Xu Q and Xue D 2013 J. Mater. Chem. C 1 5909–16
[25] Fuh H-R, Chang C-R, Wang Y-K, Evans R F, Chantrell R W and Jeng H-T 2016 Sci. Rep. 6 32623
[26] Murphy D W, Cross C, Di Salvo F and Waszczak J 1977 Measurement 16 3027–31
[27] Feng J, Sun X, Wu C, Peng L, Lin C, Hu S, Yang J and Xie Y 2011 J. Am. Chem. Soc. 133 17832–8
[28] Feng J, Peng L, Wu C, Sun X, Hu S, Lin C, Dai J, Yang J and Xie Y 2012 Adv. Mater. 24 1969–74
[29] Zhang H, Liu L-M and Lau W-M 2013 Journal of Materials Chemistry A 1 10821–8
[30] Rout C S, Kim B-H, Xu X, Yang J, Jeong H Y, Odkhuu D, Park N, Cho J and Shin H S 2013 J. Am. Chem. Soc. 135 8720–5
[31] Song C, Yu K, Yin H, Fu H, Zhang Z, Zhang N and Zhu Z 2014 J. Mater. Chem. C 2 4196–202
[32] Boscher N D, Blackman C S, Carmalt C J, Parkin I P and Prieto A G 2007 Appl. Surf. Sci. 253 6041–6
[33] Guzmán R et al 1997 J. Appl. Electrochem. 27 1207–11
[34] Thompson A, Scanlon J and Symon C 1980 Solid State Ion. 1 44–57
[35] Vinokurov A, Tyurin A, Emelina A, Gavrichev K and Zlovonov V 2009 Inorganic Materials 45 480–5
[36] Zhang Y and Wu X 2013 Phys. Lett. A 377 3154–7
[37] Gan L-Y, Zhang Q, Cheng Y and Schwingenschlögl U 2013 Phys. Rev. B 88 235310
[38] Pan H 2014 Sci. Rep. 4 5348
[39] Zhong M, Li Y, Xia Q, Meng X, Wu F and Li J 2014 Mater. Lett. 124 282–5
[40] Pan H 2014 The Journal of Physical Chemistry C 118 13248–53
[41] Wasey A H M A, Chakrabartty S and Das G P 2015 J. Appl. Phys. 117 064313
[42] Qu Y, Pan H, Kwok C T and Wang Z 2015 Nanoscale Research Letters 10 480
[43] Huang P-R, He Y, Pal H K and Kindermann M 2015 arXiv preprint arXiv:1501.00760
[44] Zhuang H L and Hennig R G 2016 Phys. Rev. B 93 034429
[45] Wang T, Li Y, Xia C, Zhao X, An Y and Dai X 2016 J. Mater. Chem. C 4 8111–20
[46] Luo N, Si C and Duan W 2017 Phys. Rev. B 95 205432
[47] Gao D, Li J, Li Z, Zhang Z, Zhang J, Shi H and Xue D 2010 The Journal of Physical Chemistry C 114 11703–7
[48] Wang C, Wu Q, Ge H, Shang T and Jiang J 2012 Nanotechnology 23 075704
[49] Ataca C, Sahin H and Ciraci S 2012 The Journal of Physical Chemistry C 116 8983–99
[50] Binder K 1979 Monte Carlo Methods in Statistical Physics (Berlin: Springer-Verlag)
[51] Newman M E J and Barkema G T 1999 Monte Carlo Methods in Statistical Physics (New York, USA: Oxford University Press)