Exchange Bias and Interface-related Effects in Two-dimensional van der Waals Magnetic Heterostructures: Open Questions and Perspectives

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The exchange bias (EB) effect is known as a fundamentally and technologically important magnetic property of a magnetic bilayer film. It is manifested as a horizontal shift in a magnetic hysteresis loop of a film subject to cooling in the presence of a magnetic field. The EB effect in van der Waals (vdW) heterostructures offers a novel approach for tuning the magnetic properties of the newly discovered single-layer magnets, as well as adds a new impetus to magnetic vdW heterostructures. Indeed, intriguing EB effects have recently been reported in a variety of low-dimensional vdW magnetic systems ranging from a weakly interlayer-coupled vdW magnet (e.g., Fe₃GeTe₂/CrCl₃, Fe₃GeTe₂/FePS₃, Fe₃GeTe₂/MnPS₃), to bilayers of two different vdW defective magnets (e.g., VSe₂/MoS₂), or to metallic ferromagnet/vdW defective magnet interfaces (e.g., Fe/MoS₂). Despite their huge potential in spintronic device applications, the physical origins of the observed EB effects have remained elusive to researchers. We present here a critical review of the EB effect and associated phenomena such as magnetic proximity (MP) in various vdW heterostructure systems and propose approaches to addressing some of the emerging fundamental questions.

Keywords: 2D magnets; van der Waals heterostructures; Exchange bias; Spintronics; Optospintronics; Spin-caloritronics; Opto-spin-caloritronics; Valleytronics

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1. Introduction

Understanding interfacial magnetism in magnetic heterostructures is the key to unlocking the door to novel applications in spintronics and magnetic devices [1][2][3][4][5][6]. In traditional heterostructure materials, interface properties are often strongly modified by lattice strain, intermixing, or charge transfer, so that the magnetic properties at the interface are generally different from that of the bulk [1][7][8]. In these heterostructures, the intriguing exchange bias (EB) effect, often viewed as a horizontal shift in the magnetic hysteresis loop subject to cooling of a magnetic bilayer film in the presence of a magnetic field, has been reported [9][10][11][12][13][14][15]. Understanding the EB mechanism enables the optimization and manipulation of the magnetic functionality of spintronic devices, but this goal remains challenging due to uncontrolled interface properties or poor interface quality of these systems [13][14][15]. In this context, exploiting the EB effect in van der Waals (vdW) magnetic heterostructures is of paramount importance [16][17][18] as the high-quality interfaces and weakly coupled interlayer interactions in these systems allow probing intrinsically interfacial magnetic coupling mechanisms [19][20][21][22] that govern EB behavior (Fig. 1).

The EB effect has been known since 1956 when Meiklejohn and Bean observed a horizontal shift in the magnetic hysteresis loop of ferromagnetic/antiferromagnetic (FM/AFM) Co/CoO core/shell nanoparticles cooled in the presence of an external magnetic field [23]. Since, EB has been extensively studied in several FM/AFM thin films and core/shell systems, and its practical implementation has been realized in commercial magnetic recording and other spintronic devices [9][10][11]. For instance, EB has proved its usefulness in pinning a magnetically hard reference layer in spin valve (SV) readback heads and MRAM memory circuits, as well as improving the overall thermal stability of small magnetic particles within magnetic disk media through their FM/AFM

interfacial coupling [24][25][26][27]. Despite these realized applications, the EB mechanism remains highly controversial [11][13]. In FM/AFM systems, the EB effect was initially ascribed to a unidirectional pinning of the FM layer by the adjacent AFM layer causing a shift in the switching field of the FM layer away from the H = 0 axis by an amount H_{EB} (the EB field) and is accompanied by an increase in the coercive field $(H_{\rm C})$ of the FM layer [9]. However, recent research has shown that the pinned uncompensated moments in FM/AFM systems generated by defects at the FM/AFM interface play a dominant role in determining the EB magnitude [28][29]. These disordered interfacial spins behave like "spin clusters" (SCs), which are analogous to spin glasses (SGs) at the FM/AFM interface. These SCs transmit the anisotropy from the AFM layer to the FM layer allowing for interactions via exchange coupling to the AFM and FM layers that gives rise to the coercivity of the FM layer [30][11]. Indeed, Berkowitz et al. found magnetically hard particles (e.g., CoFe₂O₄) at the FM/AFM interface in FeNi/CoO FM/AFM bilayers and attributed the EB effect and coercivity enhancement of the FM FeNi layer to the exchange coupling between the interfacial spins produced by the CoFe₂O₄ nanoparticles and those of the AFM (CoO) layer [31]. The authors also demonstrated that the interfacial spins produced by the FeNi layer did not contribute to the EB effect. In a recent review, Schuller *et al.* also revealed that the inner, uncompensated, pinned spins in the AFM layer play a crucial role in setting the EB magnitude in FM/AFM systems [29]. These arguments are supported by the experimental observations of the intrinsic EB effects in FM/SG interfaces (e.g., Co/CuMn [32] and La_{0.7}Sr_{0.3}MnO₃/LaNiO₃ [33]), and most recently in AFM/SG interfaces such as Fe_xNbS_2 [34]. In the case of Fe_xNbS_2 , the EB has been shown to set in the SG phase that arose in the disordered AFM layer, and both the AFM and SG parameters could be tuned to manipulate the EB magnitude [34]. In a similar perspective, the coexistence of ferromagnetism and geometric frustration intrinsic to the Kagome network of magnetic ions has recently been demonstrated to give rise to SG behavior and the EB effect in the ferromagnetic Weyl semimetal Co₃Sn₂S₂ [35]. Geometric spin frustration has also been shown to give rise to a large EB effect in the conductive, layered 2D metalorganic Kagome lattice compound Mn₃(C₆S₆) – which represents the first example of a topological SG showing EB [36]. These studies demonstrate that an AFM/FM interface is not the only condition that induces the EB effect and, in fact, EB is a more general phenomenon as other types of interfaces including ferromagnet/ferrimagnet FM/FIM, soft FM/hard FM, FIM/AFM, FIM/FIM, and AFM/dilute magnetic semiconductors (DMSs) have been reported to show EB characteristics as well [13][14]. To complicate matters, other effects, such as magnetic proximity (MP) [37][38][39][40][41][42] where magnetization from a ferromagnet penetrates a neighboring nonmagnetic material or affects the magnetic ordering of an adjacent magnetic material, that have been reported to impact EB in magnetically interfaced systems [43][44] are often ignored.

The recent discoveries of two-dimensional (2D) intrinsic magnetism in atomically thin layers of CrI₃ [45] and Cr₂Ge₂Te₆ [46] have triggered global attention due to their prospective applications in spin transistors, valleytronics, and quantum computing [3][4][5][6][47][48]. Subsequently, a wide range of 2D magnetic materials (with both intrinsic and extrinsic magnetism) have been realized in monolayers of VSe₂ [49], MnSe₂ [50], Cr₃Te₄ [51], Fe₃GeTe₂ [52], Fe₅GeTe₂ [53], and FePS₃ [54]. Most recently, tunable room-temperature ferromagnetism has been discovered in magnetically-doped transition metal chalcogenide (TMD) monolayers including chemical vapor deposition- (CVD-) grown monolayers of V-doped WSe₂ [55][56], V-doped WS₂ [57], and Fe-doped MoS₂ [58]. These TMD monolayers are also known as 2D dilute magnetic semiconductors and they have potential to revolutionize the fields of spintronics, opto-spintronics, and opto-spin-caloritronics [59][60]. Since these vdW materials are flexible and easily stacked together, assembling layers of different vdW magnetic materials, or a vdW material with a non-vdW material, can create novel heterostructures with atomically sharp interfaces and properties that would otherwise be absent in their individual components [41]. Interestingly, large EB effects have recently been observed in FM/AFM vdW interfaces such as oxidized Fe₃GeTe₂ [61], Fe₃GeTe₂/CrCl₃ [16], Fe₃GeTe₂/FePS₃ [62], Fe₃GeTe₂/MnPX₃ (*X*=S, Se) [17][18], and Fe₃GeTe₂/Ir₂₂Mn₇₈ [63], as well as in defective magnet (DM) vdW interfaces such as VSe₂/MoS₂ [64] and FM/vdW DM interfaces such as Fe/MoS₂ [65][66]. Owing to the reduced dimensionality, stacking and mechanical flexibility, and tunability of their EB field, these exchange-biased vdW heterostructures appear to be novel platforms for probing low-dimensional vdW nanomagnetism and for developing a new generation of vdW spintronic nanodevices. However, the physical origins of the EB and its association with other effects, such as the MP effect [62][67][68][69], are not fully understood. The following fundamental, important, and unanswered questions are emerging:

- *i.* What is the exact coupling mechanism between spins at the FM/AFM interface in FM/AFM vdW systems?
- *ii.* Does the EB effect in FM/AFM vdW systems originate from the direct FM/AFM interfacial coupling?
- *iii.* What do FM and AFM spins play roles in the EB effect in FM/AFM vdW systems?
- *iv.* Does type of AFM ordering affect the EB behavior in FM/AFM vdW systems?
- v. Is there a thickness limit of the AFM layer for inducing the EB effect in FM/AFM vdW systems?
- vi. Can an intermediate magnetically disordered phase be formed at the FM/AFM interface and induce the EB effect in FM/AFM vdW systems?
- vii. Can FM/SG or AFM/SG interfaces be formed during fabrication and induce the EB effect in vdW magnetic systems?

- viii. What is the role of magnetic proximity of the FM layer on the EB effect in FM/AFM vdW and related systems?
- *ix.* Does charge transfer play a role in mediating the magnetism and the EB effect in *FM/AFM vdW systems*?
- *x.* What is the role of interlayer spin coupling on the EB effect in FM/AFM vdW systems?
- xi. Can the EB effect be tuned to occur at room temperature in vdW magnetic systems?
- xii. Can the EB effect be tuned by external stimuli (electrical field, strain) in vdW magnetic systems?

This review aims to provide a thorough analysis on EB and related phenomena in recently reported vdW heterostructures and related systems. Emphasis will be placed on an intrinsic vdW ferromagnet Fe₃GeTe₂ and its heterostructures (Fig. 1). Effects of oxidization, capping layer, and substrate on the magnetism and EB in Fe₃GeTe₂ and its heterostructures are found significant and need careful attention [70][71][72][73][74]. We raise several important questions and propose approaches to addressing those questions. Perspective applications of these and related heterostructures in the emerging fields of spintronics, opto-spintronics, spin-caloritronics, opto-spin-caloritronics, valleytronics, and quantum computation are assessed and proposed. Finally, concluding remarks and an outlook for the future research in this exciting and ever rapidly expanding research field are laid out.

2. Exchange Bias and Related Phenomena

2.1. Weakly Interlayer-Coupled vdW Ferromagnets

Among the recently discovered 2D intrinsic ferromagnets [75], Fe₃GeTe₂ appears to be one of the most promising candidates for spintronics applications [6][52][76][77][78][79][80] as it orders

ferromagnetically at high Curie temperature ($T_{\rm C} \sim 207$ K in bulk and ~ 130 K in monolayer), which can be enhanced to above room temperature upon ionic liquid gating (e.g., $T_{\rm C} \sim 310$ K in trilayer [76]). Fe₃GeTe₂ is a layered material, and its lattice and spin structure are illustrated in Fig. 2a. This material belongs to the P63/mmc space group with one Fe₃Ge layer sandwiched by two Te layers. The separation between two adjacent monolayers is ~2.95 Å. The valence states of Fe₃GeTe₂ can be viewed as $(Te^{2-})(Fe_1^{3+})[(Fe_1^{2+})(Ge^{4-})](Fe_1^{3+})(Te^{2-})$ with inequivalent Fe_1^{3+} and Fe_{11}^{2+} sites within the Fe₃Ge plane [76]. Bulk Fe₃GeTe₂ often possesses a large out-of-plane magnetic anisotropy with respect to the vdW planes (Fig. 2a), and the significant strength of this anisotropy stabilizes longrange ferromagnetic order in the monolayer limit. It has been reported that mechanically exfoliated crystals of Fe₃GeTe₂ (monolayer and a few layers) have their bulk magnetic characteristic preserved [52][76]. The Curie temperature of Fe₃GeTe₂ varies significantly with thickness when the number of layers is less than ~10 but remains almost unchanged for thicker films. However, the T_C of this material in the 2D limit can be largely increased by ionic liquid gating [76]. Unlike CrI₃ [45] and MnSe₂ [50], Fe₃GeTe₂ exhibits relatively weak interlayer exchange coupling [52] and hosts a large Berry curvature responsible for its anomalous Hall effect [81].

It is of practical importance to recall that Fe₃GeTe₂ can be easily oxidized when exposed to air, so particular attention must be paid while characterizing the magnetic properties of this material [70]. This matter has also urged researchers to investigate effects of oxidization on the magnetism in mechanically exfoliated crystals of Fe₃GeTe₂. Recently, Gweon *et al.* reported a robust and sizable EB effect in Fe₃GeTe₂ crystals when the flakes were mechanically exfoliated and annealed in air at 100 °C for 30 min [61]. Annealing was performed to facilitate the formation of an oxide layer on the FM layer (Fig. 2b). The authors hypothesized that this oxide layer would be antiferromagnetic and its interfacial coupling with the pre-existing FM layer would induce the EB effect (Fig. 2c,d). The authors observed a similar temperature dependence of EB field (H_{EB}) and coercive field (H_C) for annealed Fe₃GeTe₂ samples with two different thicknesses (17 and 38 nm, in Fig. 2d), and that the value of H_{EB} remained large even at a FM thickness of ~100 nm. Their observations seem to suggest that the EB effect occurs mainly at the interface between the oxide layer and the outer FM layer while the interior FM layer played a minor role, which is a reasonable assumption given the weak interlayer magnetic exchange interaction between vdW FM layers within the Fe₃GeTe₂ film. This intriguing feature distinguishes exchange-biased vdW magnetic heterostructures from conventional non-vdW magnetic bilayers exchange [10].

However, the underlying origin of the observed EB effect in oxidized Fe₃GeTe₂ remains elusive. As noted above, an FM/AFM interface does not necessarily induce an EB effect. In annealed Fe₃GeTe₂ samples, the magnetic nature of the oxide phase is unknown (i.e., What are the chemical composition and the thickness of this oxide layer?), and whether this phase is magnetically ordered or comprises disordered spins analogous to "spin clusters" or SGs [71][72][82][83]. It should also be noted in Fig. 2b that the oxide layer was not uniform over the surface of the FM layer, and the presence of the AlO₂ capping layer on top of the oxide layer could also affect the magnetic property of the oxide layer and hence the EB effect. Indeed, the presence of a Pt top layer or WTe_2 on Fe_3GeTe_2 has been shown to alter the magnetic domain structure of Fe₃GeTe₂ [71][72]. Energy Dispersive Spectroscopy (EDS) mapping revealed a strong variation in Fe content across the FM/oxide interface suggesting a possible formation of a less magnetically ordered or magnetically disordered Fe_{3-x}GeTe₂ phase in addition to an iron oxide phase (e.g., FeO, Fe₃O₄, γ -Fe₂O₃), which could also be formed in Fe₃GeTe₂ samples during annealing [70]. The EB effect could thus occur at the Fe₃GeTe₂/Fe_{3-x}GeTe₂ interface, and the iron oxide layer could act as a pinning layer. These open questions warrant further systematic studies. For example, it is essential to anneal Fe₃GeTe₂ at different temperatures and/or for different times to vary the thickness of the oxide layer and investigate its influence on the magnetic coupling between the FM and oxide layers and, consequently, the EB effect. It would be valuable to know at what thickness of oxide layer the EB effect disappears as this could explain the absence of an EB effect in unannealed Fe₃GeTe₂ [61] whose oxide layer could be too thin to result in a strong exchange coupling between the FM and oxide layers. In this case, thicker oxide layers may allow a probe of the chemical composition and spin structures in the oxide phase (Fe_{3-x}GeTe₂ and/or iron oxide phase) by means of Mössbauer, x-ray magnetic circular dichroism (XMCD), neutron diffraction (ND), scanning tunneling microscopy (STM), and spin-polarized STM measurements to grant deeper insight into the magnetic interfacial coupling mechanism and EB origin. Interfacing a clean (non-oxidized) Fe₃GeTe₂ layer with a thin iron oxide layer (~2-5 nm) to create a Fe₃GeTe₂/rion oxide heterostructure would also be interesting to understand the role of the iron oxide phase (FeO, Fe₃O₄, γ -Fe₂O₃), if present, on the magnetism and the EB effect in oxidized Fe₃GeTe₂ samples, as well as in its heterostructures, as will be discussed below.

2.2. Ferromagnetic vdW/Antiferromagnetic vdW Interfaces

To explore the EB effect in FM/AFM vdW heterostructures, Zhu *et al.* stacked the FM Fe₃GeTe₂ with the AFM CrCl₃ with different thicknesses of CrCl₃ [16]. CrCl₃ is an insulating antiferromagnet with a Néel temperature of ~20 K. It is a layered material exhibiting an in-plane magnetic anisotropy (Fig. 3a) [84]. The advantages of this material include easy exfoliation and chemical robustness, which enable a systematic study of the effect of varying thickness of CrCl₃ on the magnetism and EB effect in Fe₃GeTe₂/CrCl₃ heterostructures [16]. Anomalous Hall effect (AHE) measurements (Fig. 3c) revealed sizeable EB effects in these heterostructures (Fig. 3d,e). Relative to bare Fe₃GeTe₂ (thickness, 30 nm), the Fe₃GeTe₂ (30 nm)/CrCl₃ (15 nm or 45 nm) heterostructures were reported to exhibit an enhanced coercivity that increased significantly when the thickness of the

CrCl₃ flake increased from 15 to 45 nm (Fig. 3e). However, the EB field was observed to be maximal for a critical thickness of CrCl₃ (~20 nm) while above and below which the EB field decreased significantly. Indeed, this thickness-dependent H_{EB} trend is rather different from those reported for non-vdW FM/AFM systems [10]. Further, the authors observed an appearance and enhancement of the EB effect at temperatures below the Néel temperature of the AFM CrCl₃. The effect of the cooling field (H_{CF}) on the EB field was also investigated, which showed a strong suppression of the EB effect for $H_{CF} > 1$ T at which the AFM state was fully converted into the FM state. Accordingly, the origin of the EB effect in Fe₃GeTe₂/CrCl₃ heterostructures was attributed to FM/AFM interfacial coupling. As noted above, however, a sizeable EB effect was also observed in oxidized Fe₃GeTe₂ [61] and such an oxide layer could be naturally formed on the surface of Fe₃GeTe₂ during Fe₃GeTe₂/CrCl₃ formation. If the oxide phase was present between the Fe₃GeTe₂ and CrCl₃ layers and behaved as "spin clusters", then the AFM CrCl₃ could act as a pinning layer and the EB mechanism would be different from what was proposed. Another point is that the EB effect disappeared at ~120 K for oxidized Fe₃GeTe₂, while it vanished at a much lower temperature of ~20 K for the Fe₃GeTe₂/CrCl₃ heterostructure. This suggests that the oxide layer, if it did exist in that heterostructure, would be very thin and its spin configuration could be impacted by the presence of CrCl₃, which would alter interfacial spin coupling and hence the EB effect. To further clarify this, it would be essential to investigate the EB effect in a heterostructure composed of an intentionally oxidized (annealed) Fe₃GeTe₂ layer and the CrCl₃ layer and compare these results with those reported for the oxidized Fe_3GeTe_2 sample and the $Fe_3GeTe_2/CrCl_3$ heterostructure. On the other hand, the large enhancement of H_C in the Fe₃GeTe₂/CrCl₃ heterostructure [16] relative to bare (oxidized) Fe₃GeTe₂ [61] could suggest a significant dual MP effect induced by the FM layer (Fe₃GeTe₂) on the AFM layer (CrCl₃) and vice versa. MP and its impact on magnetism and EB should thus be systematically investigated in these heterostructures. In addition, charge transfer between Fe_3GeTe_2 and $CrCl_3$ could give rise to the enhanced magnetism in Fe_3GeTe_2 and hence the EB effect in the $Fe_3GeTe_2/CrCl_3$ heterostructure, which should also be investigated further.

In another study, Zhang et al. reported on the large enhancement of coercive field, Curie temperature, and EB effect in Fe₃GeTe₂/FePS₃ and FePS₃/Fe₃GeTe₂/FePS₃ heterostructures [62]. Unlike CrI₃ and CrCl₃, FePS₃ is an Ising-type AFM material with both intra- and inter-layer AFM ordering (Fig. 4a) [54]. It belongs to the class of cation-ordered, CdCl₂-type, low-dimensional layered magnetic materials and is a Mott insulator. Bulk FePS₃ undergoes AFM ordering at $T_N \sim 115$ K, which is lower than the Curie temperature of bulk Fe₃GeTe₂ ($T_C \sim 230$ K) (Fig. 4b). The formation of FM/AFM Fe₃GeTe₂/FePS₃ heterostructures resulted in a large enhancement of magnetism (T_C and H_{C} in Fe₃GeTe₂, as well as the appearance of an EB effect (Fig. 4c,d). Magneto-optic Kerr effect (MOKE) measurements indicated that T_C increased from 150 K for the mechanically thinned Fe_3GeTe_2 crystal (thickness, 8.2 nm) to 180 K for its heterostructure $Fe_3GeTe_2/FePS_3$ where the thickness of the FePS₃ layer was about 6 nm. The corresponding increase in H_C by 100 % from 2000 to 4000 Oe was also reported. However, it has remained unknown, from the MOKE experiments, if the saturation magnetization (M_S) of Fe₃GeTe₂ increased when the Fe₃GeTe₂/CrCl₃ interface formed. Unlike the case of the Fe₃GeTe₂/CrCl₃ interface, a double-shifted hysteresis loop feature was observed for the Fe₃GeTe₂/FePS₃ heterostructure (Fig. 4d). Interestingly, relative to the Fe₃GeTe₂/FePS₃ heterostructure (one interfacial magnetic coupling), the magnetism (T_C and H_C) and EB effect were further enhanced in the FePS₃/Fe₃GeTe₂/FePS₃ heterostructure (double interfacial magnetic coupling) in which an additional AFM layer of FePS₃ (the same thickness) was stacked on the other surface of the Fe₃GeTe₂ flake (Fig. 4e,f). In this tri-layer heterostructure, a step-like magnetization behavior in the M-H loop was also observed (Fig. 4f). The origins of the enhanced magnetism and EB effect were attributed to FM/AFM interfacial coupling that was mediated by the MP effect. It was suggested that the presence of the AFM FePS₃ layer pinned surface spins within the FM Fe₃GeTe₂ layer causing the H_C of the FM layer to increase. However, the MOKE data (Fig. 4c) revealed a noticeable increase in M_S and a decrease in magnetic anisotropy in the Fe₃GeTe₂/FePS₃ heterostructure when compared to bare Fe₃GeTe₂. While the MP effect indeed plays an important role in mediating the magnetism and EB effect in Fe₃GeTe₂/FePS₃ and FePS₃/Fe₃GeTe₂/FePS₃ heterostructures, the underlying origins of the observed EB and MP effects remain unclear and warrant further studies. As noted earlier, oxidization of mechanically exfoliated Fe₃GeTe₂ flakes could occur during sample preparation and its effect on the magnetism and EB was not examined in that work [62]. To elucidate this, it would be necessary to perform a systematic comparative study of the magnetic and EB properties of both clean (non-oxidized) and oxidized (via annealing) Fe₃GeTe₂/FePS₃ heterostructures. Varying FePS₃-thickness in such Fe₃GeTe₂/FePS₃ heterostructures would also be essential to address the open questions regarding the effects of type of AFM ordering, interlayer coupling, and reduced dimensionality on the magnetism and EB behavior (the doubleshifted hysteresis behavior). Another effect that was not considered in the work [62] is "charge transfer" that could occur at the $Fe_3GeTe_2/FePS_3$ interface and give rise to the enhanced magnetism and EB field in this heterostructure.

In an extended study, Dai *et al.* also observed enhanced magnetism and EB effect in FM/AFM Fe₃GeTe₂/MnPX₃ (X = Se and S) heterostructures (Fig. 5) [17]. Bulk MnPS₃ has a monoclinic structure with the point group of C_2h (2/m). In MnPS₃, each Mn atom is surrounded by six S atoms and connected to two P atoms above and below the Mn plane (Fig. 5a). Unlike bulk FePS₃, bulk MnPS₃ exhibits Heisenberg-type AFM ordering with a Néel temperature of 78 K [85]. The magnetic moments of Mn in MnPS₃ are ferromagnetically coupled across the vdW gap to its inter- and intra-

layer nearest neighbor. Although bulk MnPS₃ and MnPSe₃ share a similar crystal structure (Fig. 5a), their magnetic characteristics are quite different, especially at low temperatures (Fig. 5b,c). Bulk MnPSe₃ exhibits Ising-type AFM ordering with a T_N of 74 K. The magnetic moments of Mn in this material are antiferromagnetically coupled to its inter- and intra-layer nearest neighbor, which is different from what was observed for bulk MnPS₃. While MnPS₃ possesses dominant out-of-plane magnetic moments, neutron scattering measurements have revealed that the majority of spins in MnPSe₃ are in-plane. Spin-orbit coupling has been found to be negligible in the former but significant in the latter. These differences could allow us to interpret different magnetic behaviors and the resulting EB effects between these two systems when each are stacked with Fe₃GeTe₂ to form corresponding Fe₃GeTe₂/MnPS₃ and Fe₃GeTe₂/MnPSe₃ heterostructures (Fig. 5b-d). Given that the thickness of each flake (Fe₃GeTe₂, MnPS₃, and MnPSe₃) was 23 nm to form the heterostructures, the flakes on their own should exhibit bulk magnetic characteristics i.e., MnPS₃ and MnPSe₃ should order antiferromagnetically below 80 K. This appears to be in line with the strong development of the EB effect observed just below this temperature in the Fe₃GeTe₂/MnPS₃ and Fe₃GeTe₂/MnPSe₃ heterostructures (Fig. 5d). As compared to Fe₃GeTe₂/MnPS₃, larger values of H_C and H_{EB} were reported for Fe₃GeTe₂/MnPSe₃ at temperatures below ~120 K. This could be attributed to spin-orbit coupling that is more significant in MnPSe₃ than MnPS₃. Nonetheless, the two-step magnetization versus temperature behavior observed around 100 K in the case of MnPSe₃ remains questionable as a re-orientation of spins at the Fe₃GeTe₂/MnPSe₃ interface may occur around this temperature. This hypothesis must be examined and validated experimentally. There are also open questions about the effects of oxidization (the oxidized Fe₃GeTe₂ layer), interlayer coupling within the AFM layer, charge-transfer across the Fe₃GeTe₂/MnPX₃ (X = S, Se) interface, and the effects of reduced dimensionality on the magnetism of Fe_3GeTe_2 and hence the EB effect observed in these heterostructures [18].

In a recent study, Fu *et al.* predicted EB and quantum anomalous Hall (QAH) effects in CrI₃/MnBi₂Te₄ FM/AFM heterostructures [86]. Recall that bulk MnBi₂Te₄ is an A-type topological AFM that exhibits a quantized Hall resistance when an applied external magnetic field exceeds the critical field of the spin-flop transition (> 6 T) [86]. Thus, strong interfacial coupling between the FM monolayer of CrI₃ and the AFM MnBi₂Te₄ layer was predicted to induce the EB effect, which could change electronic states near the Fermi level. The EB mechanism would then originate from the long Cr-*e*_g orbital tails that are strongly hybridized with Te *p* orbitals and an out-of-plane surface magnetic ordering in MnBi₂Te₄ would be induced via MP to the FM CrI₃ monolayer. These interesting predictions should be validated experimentally. In this regard, it would also be interesting to interface MnBi₂Te₄ or similar [87] [88] with other types of vdW magnets such as Fe₃GeTe₂ or Fe₅GeTe₂, and further explore EB and QAH effects in those heterostructures.

2.3. Ferromagnetic vdW/Antiferromagnetic non-vdW Interfaces

Exchange biased non-vdW magnetic systems have been extensively explored for applications in spintronic devices based on spin-orbit torque (SOT)-driven magnetization switching [89]. Owing to their atomically flat surfaces and 2D magnetic properties, there has been a growing interest in exploring vdW magnetic materials for use in SOT-based spintronic devices [5][6]. Alghamdi *et al.* created heterostructures consisting of 5-nm Pt films sputtered onto the surfaces of ~20 nm exfoliated Fe₃GeTe₂ flakes and measured the second harmonic Hall responses as the applied magnetic field rotated the magnetization of Fe₃GeTe₂ in the plane [90]. They achieved a large SOT efficiency and attributed it to the atomically flat Fe₃GeTe₂/Pt interface. The SOT efficiency of the Fe₃GeTe₂/Pt heterostructure is comparable with that of the best heterostructures comprising non-vdW

ferromagnetic metals and is greater compared to those based on non-vdW ferrimagnetic insulators, which makes this heterostructure an attractive candidate for use in highly efficient spintronic nanodevices. By adding an AFM layer of Ir₂₂Mn₇₈ (IrMn) in between the Fe₃GeTe₂ and Pt layers (Fig. 6a), Zhang et al. recently observed both EB and SOT effects in the Fe₃GeTe₂/IrMn/Pt heterostructure (Fig. 6b,c) [63]. A large EB effect (up to 895 Oe) was achieved in this heterostructure (Fig. 6b), which is greater than what has been observed in previously reported bilayers including Fe₃GeTe₂/CrCl₃ [16], Fe₃GeTe₂/FePS₃ [62], and Fe₃GeTe₂/MnPX₃ (X = S, Se) [17]. Relative to the Fe₃GeTe₂/Pt heterostructure, a larger SOT-driven magnetization switching performance was achieved for the Fe₃GeTe₂/IrMn/Pt heterostructure (Fig. 6c). Nonetheless, effects of the oxidization layer of Fe₃GeTe₂ on the SOT efficiency in the Fe₃GeTe₂/Pt and Fe₃GeTe₂/IrMn/Pt heterostructures, as well as on the large EB coupling in the Fe₃GeTe₂/IrMn/Pt heterostructure, have remained questionable. It would thus be essential to investigate this effect in both clean and oxidized Fe₃GeTe₂/Pt heterostructures by annealing the Fe_3GeTe_2 flakes to form an oxidization layer on their surfaces before depositing the top Pt layer. Other vdW magnetic systems have recently been explored for SOT-based device applications [5][6] and further studies are needed to examine if interfacing these vdW magnets with other materials can enhance the SOT efficiency and the EB effect, as well as utilize their combined functionalities for modern spintronics.

2.4. Ferromagnetic vdW/Ferromagnetic non-vdW Interfaces

While most recently discovered intrinsic 2D vdW magnets exhibit ferromagnetic ordering well below room temperature and possess a rather weak magnetic signal in the 2D limit, interfacing a 2D vdW magnet with a 3D non-vdW ferromagnet has proved an alternative and effective approach to enhance the magnetic property of a 2D vdW magnet via MP induced by the 3D non-vdW ferromagnet and vice versa [67]. However, a clear understanding of the magnetic interfacial coupling

mechanism in these hybrid structures is lacking. Chen et al. deposited a 6-nm Ni layer on exfoliated monolayer and bilayer Fe₃GeTe₂ flakes (and also on an exfoliated $Cr_2Ge_2Te_6$ flake) to create Fe₃GeTe₂/Ni (and Cr₂Ge₂Te₆/Ni) heterostructures and investigated their magnetic properties using spin torque ferromagnetic resonance (FMR) [67]. It is worth mentioning that relative to the bare Ni film, the presence of the Fe₃GeTe₂ or Cr₂Ge₂Te₆ layer increased the perpendicular magnetic anisotropy (PMA) and magnetic damping of the adjacent Ni film. The PMA effect became stronger when the Fe₃GeTe₂ thickness increased from monolayer to bilayer highlighting the important role of interlayer magnetic coupling. The observation of such an enhanced effect at room temperature also suggests that the presence of the Ni layer could significantly enhance the magnetic ordering within Fe₃GeTe₂ or Cr₂Ge₂Te₆ via their magnetic interfacial coupling despite the fact that the Curie temperatures of Fe₃GeTe₂ and Cr₂Ge₂Te₆ are well below room temperature. These findings are of practical importance and may provide an effective approach for utilizing 2D magnets in modern spintronic devices that operate at ambient temperature. However, the exact nature of the interfacial spins (i.e., their spin textures) and their couplings to Fe spins located within each layer are unknown in these hybrid systems. The case could become even more complicated if the oxidized Fe₃GeTe₂ layer-possibly formed during the exfoliation of Fe₃GeTe₂ crystals or during the deposition of the Ni layer on the Fe₃GeTe₂ flake-was present in between the Fe₃GeTe₂ and Ni layers. Further studies are needed to clarify this effect. Since oxidized Fe₃GeTe₂ flakes could exhibit an EB effect, it would be necessary to create oxidized Fe₃GeTe₂/Ni heterostructures and investigate impacts of EB on the magnetic property of the Ni layer, as well as on the spin transport across the Fe₃GeTe₂/Ni interface. Reducing the thickness of the Ni layer to 2D would also allow one to create novel 2D Fe₃GeTe₂/Ni heterostructures with potentially emerging new magnetic functionalities. It has been shown that $MnBi_{8}Te_{13}$ is an intrinsic topological ferromagnetic insulator whose interlayer interaction and surface state can be modulated upon photoexcitation [91]. Interfacing a 2D vdW magnet like Fe₃GeTe₂ or Fe₅GeTe₂ with this type of magnetic topological insulator could also create a novel heterostructure whose interfacial magnetism can be tuned by external stimuli such as light. Such heterostructures would be an interesting subject for future research, and the knowledge of which will lay a foundation for the development of modern 2D spintronic devices.

2.5. Ferromagnetic vdW/Defective Magnetic vdW Interfaces

2D vdW transition metal dichalcogenides (TMDs), such as TX_2 monolayers (T = Mo, W; X =S, Se, Te), are at the heart of many important device applications such as field-effect transistors, photodetectors, photon emitters, spintronics, valleytronics, and quantum computers [3][60][92][93]. Recent studies have shown that the magnetic or magneto-optical property of a non-magnetic TMD can be induced or enhanced by stacking it with a vdW magnet [72][94][95][96]. This is a direct consequence of the MP effect induced by the vdW magnet [37]. Given the fact that the MoS₂ monolayer exhibits a large spin splitting and an out-of-plane spin polarization, sandwiching the MoS_2 monolayer in between two ferromagnetic (Fe, FeNi, or Co) electrodes has been predicted to promote the spin injection and enhance the magnetoresistance (MR) up to 300% [97]. However, only a 0.4% MR ratio was experimentally achieved in the NiFe/MoS₂/NiFe spin valve (SV) structure [98]. This low value could arise from the presence of a non-uniform interface between the non-vdW NiFe and vdW MoS₂ layers. To overcome this, Lin et al. created a novel vdW interface comprising Fe₃GeTe₂ and MoS_2 layers and both of which were mechanically exfoliated from their bulk crystal counterparts [99]. They showed that monolayer MoS_2 acted as a conducting interlayer in the Fe₃GeTe₂/MoS₂/Fe₃GeTe₂ structure [99], and an enhanced MR ratio of 3.1% was achieved at 10 K in this SV structure (Fig. 7), which is about 8 times greater than that of the NiFe/MoS₂/NiFe structure [98]. A large tunneling MR effect (up to 41%) has recently been achieved in a Fe₃GeTe₂/InSe/Fe₃GeTe₂ structure. This effect can be attributed to the presence of a pinhole-free tunnel barrier at the Fe₃GeTe₂/InSe interface. These observations pinpoint the importance of a flat interface, which can only be formed between vdW materials, and the superior advantages of the vdW heterostructures for SV-based spintronics. Nonetheless, there are several open questions that need to be addressed. First, the underlying origin of the MR enhancement in these SV structures is not fully understood. It should be recalled that Fe_3GeTe_2 flakes could become oxidized on their surface during mechanical exfoliation, so it is essential to examine the effect of Fe₃GeTe₂ oxidization on the spin injection and hence MR behavior in Fe₃GeTe₂/MoS₂/Fe₃GeTe₂ [99] and Fe₃GeTe₂/InSe/Fe₃GeTe₂ structures [100]. It remains unclear if the asymmetry observed in the MR curves was caused by the presence of the oxidized surface layer of Fe₃GeTe₂ that could be antiferromagnetically coupled to the interior layer of Fe₃GeTe₂. It is also essential to examine if the MR enhancement in these SV structures could be driven by the MP effect of the ferromagnetic Fe_3GeTe_2 layer onto the MoS₂ monolayer. While a defect-free MoS_2 monolayer is known to be diamagnetic in nature, in practice, most CVD-grown MoS₂ monolayers have been reported to exhibit defect-induced weak ferromagnetic ordering even at room temperature due to the presence of S and Mo vacancies [101]. This means that magnetic interfacial coupling between Fe_3GeTe_2 and MoS_2 could be significant, thus affecting the MR behavior in this SV structure. In the context of the MP effect, it is very important to know how the magnetic domain structure of Fe₃GeTe₂ varies when Fe₃GeTe₂ is placed in close contact with a 2D-TMD like monolayer MoS₂. Indeed, Lorentz transmission electron microscopy measurements on the Fe₃GeTe₂/WTe₂ heterostructure have evidenced the effect of a WTe₂ bilayer on the magnetic domain structure of the mechanically exfoliated Fe_3GeTe_2 flake [72]. The labyrinth-like magnetic domain structure observed in the Fe₃GeTe₂ flake (30 layers) was transformed to an aligned and stripe-like magnetic domain structure when the Fe_3GeTe_2 flake was interfaced with the WTe₂ layer. Such a difference in the magnetic domains identifies a significant interfacial coupling between the Fe₃GeTe₂ and WTe₂ layer that contributes to the strong Dzyaloshinskii-Moriya interaction (DMI) in the Fe₃GeTe₂/WTe₂ heterostructure [71]. In this case, spin orbit coupling proximity could play an important role. Since Fe₃GeTe₂ is a metal, and MoS₂ a semiconductor, the conductivity mismatch between these two materials could promote charge transfer across the Fe₃GeTe₂/MoS₂ interface thus mediating the overall magnetism of the Fe₃GeTe₂/MoS₂/Fe₃GeTe₂ heterostructure. Meanwhile, charge transfer-mediated magnetism has recently been reported in several vdW and non-vdW magnetic heterostructures [102]. Zhong *et al.* demonstrated that the spin-dependent charge transfer between monolayer WSe₂ and bi/trilayer CrI₃ in WSe₂/CrI₃ heterostructures is dominated by the interfacial CrI₃ layer due to which the MP effect impacts the magnetic and magneto-optic response of the heterostructure differently [41]. These hypotheses need experimental and theoretical validation.

2.6. Ferromagnetic non-vdW/Defective Magnetic vdW Interfaces

Although it has remained challenging to form uniform interfaces between a non-vdW magnetic material and a non-magnetic or defective magnetic vdW materials like TMDs, a large body of work on these heterostructures has been reported [66][103][104][105]. This challenge could arise from the fact that the surface of a non-vdW magnetic material is quite rough (surface roughness of a few nm) compared the thickness of a vdW monolayer (less than 1 nm). DFT calculations performed on a 2D Fe/MoS₂ heterostructure have shown that the Fe atoms on MoS₂ are ferromagnetically coupled with each other with a magnetic moment of ~2.0 μ_B /atom [66]. Monte Carlo simulations with Heisenberg spin Hamiltonians have predicted a high Curie temperature of 465 K, and this 2D Fe/MoS₂ heterostructure exhibits a half-metallic characteristic. However, these predictions have not been experimentally validated to date. It is also important to mention that the conductivity mismatch between the metal (Fe) and the semiconductor (MoS₂) could promote charge transfer across the

Fe/MoS₂ interface and the Fe layer could magnetize the MoS₂ monolayer via the MP effect-both of which were not included in these calculations. Effect of defects (e.g., S and Mo vacancies) on the magnetism of MoS_2 and the magnetic interfacial coupling between the Fe and MoS_2 layers were also not examined. The Fe/MoS₂ heterostructures with different thicknesses of Fe layers were hydrothermally synthesized and a noticeable EB effect was observed to occur at low temperatures in these samples [65]. The authors suggested a possible charge transfer from Fe to MoS₂ that induced magnetic moments that are antiferromagnetically coupled to the Fe spins. However, the mechanism of charge transfer that mediates the magnetism and the origin of the EB effect in these systems are not fully understood. Due to the nature of Fe/MoS_2 synthesis, Fe atoms could also be doped into the MoS₂ lattice, which would mediate the magnetism of MoS₂ and therefore give rise to the observed EB effect. This could be possible indeed as Fe-doped MoS₂ monolayers have been reported to show ferromagnetic ordering above room temperature [58]. In a relevant study, Wang et al. showed a strong hybridization between Mo/S atoms with Ni/Fe atoms in the FeNi/MoS₂ heterostructure and its significant impact on the electrical transport and spin transport in this bilayer [98]. The SV effect was observed at temperatures as high as 240 K with the largest MR ratio of 0.73% achieved at 20 K. This value of MR is about 9 times smaller than what was theoretically predicted (9%) for the same system. Such a large discrepancy between experiment and theory suggests other possible contributions (surface roughness, magnetic proximity, atomic diffusion, doping) to the magnetism, charge transport, and spin transport in the FeNi/MoS₂ system. Magnetic element specific x-ray photoemission electron microscopy (PEEM) of a Co/MoS_2 heterojunction revealed the formation of micron-sized magnetic domains on monolayer MoS_2 [106]. Meanwhile, x-ray photoelectron spectra evidenced the charge transfer from Co to S at the Co/MoS₂ interface. Relative to the Fe/MoS₂ heterostructure, a different ferromagnetic behavior was observed for the Co/MoS₂ heterostructure,

which could be attributed to a different orbital hybridization effect at the Co/MoS₂ interface. This could also explain the enhanced SV effect (the largest MR ratio of 8% at 4 K) reported for the Co/WS₂ heterostructure [103] as well as the enhanced spin Seebeck effect (SSE) in the $Ni_{81}Fe_{19}/WS_2/Pt$ heterostructure [107]. On the other hand, a giant MR effect (~30%) has been observed in the MoS₂ monolayer upon its direct contact with the ferrimagnetic substrate YIG in the YIG/MoS_2 heterostructure [104]. This value of MR is one order of magnitude greater than that reported for the MoS₂/CoFe₂O₄ heterostructure. The giant MR effect has been attributed to interfacial spin accumulation due to the YIG layer. Using spin-resolved photoluminescence spectroscopy (SRPS) and magnetic circular dichroism (MCD), Tsai *et al.* revealed room temperature ferromagnetic ordering in MoS₂ induced by the MP effect of YIG [94], and that the MP-induced spins are antiferromagnetically coupled to the YIG spins (Fig. 8). Charge transfer has also been proposed to occur at the YIG/MoS_2 interface and act as the mediator of the magnetism in the heterostructure. A large enhancement of the SSE has also been reported in YIG/monolayer WSe₂/Pt heterostructures [108]. The MP effect of YIG on the WSe_2 monolayer magnetism has been shown to impact spin transport and hence the spin-to-charge conversion efficiency in YIG/monolayer WSe₂/Pt [105]. These studies yield further insights into spin manipulation in non-vdW magnet/vdW 2D-TMD heterostructures, but also raise open questions regarding the underlying origins of MP-mediated interfacial magnetism.

2.7. Defective Magnetic vdW Interfaces

Although there is an ongoing debate on the origin of the observed ferromagnetism in metallic VSe₂ monolayers [49][109][110][111][112][113][114][115], recent studies have suggested both intrinsic and extrinsic sources of magnetism in these films [109][113][115]. While decoupling intrinsic magnetism from defect-induced (extrinsic) magnetism is a challenging task, the latter

contributes more significantly to the magnetism of this 2D system [109][115]. Because bulk MoS₂ exhibits, in addition to its diamagnetic background, a relatively weak ferromagnetic ordering at RT due to S and Mo vacancies or defects, its magnetism and interfacial coupling with the VSe₂ layer have been shown to enhance the saturation magnetization and coercivity of the VSe₂/MoS₂ system (Fig. 9a) as compared to the VSe₂/HOPG system in which HOPG is purely diamagnetic [49]. The large enhancement of M_S and H_C in MoS₂/VSe₂ (Fig. 9b) due to the exchange interaction between the VSe₂ and MoS₂ layers raises an important question: *Can this FM/FM interaction lead to an exchange bias effect*?

Kalappattil et al. recently observed a sizable EB effect in the monolayer VSe₂/single crystal MoS₂ heterostructure (see Fig. 9b,c), which is absent in the case of the VSe₂/HOPG system [64]. The EB field as large as 310 Oe was achieved at 10 K. It is worth mentioning that the enhancements of both saturation magnetization (M_S) and coercivity (H_C) in the field-cooled M-H loop compared to the zero-field-cooled *M*-*H* loop at low temperatures (see, for example, Fig. 9b). This indicates that the cooling magnetic field could strengthen the MP-driven interfacial coupling between the MoS_2 and VSe₂ layers. The magnetic field enhanced MP effect could also facilitate long-range FM ordering within each layer. Since the MoS₂ film was not fully covered by the VSe₂ layer, randomly oriented MoS₂ spins (spin clusters) that were not pinned by the magnetic region in VSe₂ could be rotated towards the external magnetic field direction. As a result, the saturation magnetization and coercivity values were enhanced in the VSe₂/MoS₂ heterostructure relative to its individual components [49]. Such a feature is interesting and rather different from that observed in FM/AFM non-vdW bilayers for which AFM susceptibility is zero resulting in no coercivity enhancement [10]. Fig. 9c shows the temperature dependence of H_{EB} and H_C . As temperature decreases, H_C started increasing as expected for a typical FM system. However, at temperatures below 100 K, $H_C(T)$ exhibited a slope change. An exponential increase in H_{EB} below 50 K is noticeable, and this could be attributed to the establishment of long-range ferromagnetic ordering in MoS_2 . Recently, Guguchia *et al.* demonstrated from muon spin rotation spectroscopy (mSR) and scanning tunneling microscopy (STM) measurements that MoX_2 (X = Se, Te) possesses low-temperature FM ordering (~50-100 K) arising from intrinsic Mo vacancies [116]. This, along with the MP effect of VSe₂ on the MoS₂ layer, led to a very strong exchange energy, which, in turn, caused the EB field and coercivity to increase in the VSe₂/MoS₂ heterostructure at low temperatures. The cooling field (H_{FC}) dependence of the EB field (H_{EB}) taken at 10 K indicated that H_{EB} first increased with an increase in cooling field, reached a maximum at a certain value of H_{FC} (~1 T), and finally decreased for larger values of H_{FC} . Such behavior is typical in SG/FM systems and shows the complex magnetic coupling and spin frustration at the VSe₂/MoS₂ interface. The observation of the sizeable EB effect in defective magnetic vdW TMD interfaces such as VSe₂/MoS₂ is surprisingly interesting, which once again points to the fact that the FM/AFM interface is not the only condition for inducing the EB effect. The presence of a FM/SG interface or the coexistence of the FM and spin frustration could also lead to the EB effect. Nonetheless, several questions remain to be answered. For instance, it is unclear how spins of V atoms and spins induced by defects (Se vacancies) are coupled to MoS₂ spins (either Mo- or S-vacancy induced) at VSe₂/MoS₂ interfaces and contribute to the EB effect. Recall that in the VSe₂/MoS₂ system, the presence of the VSe₂ layer with a larger work function of ~4.5 eV (as compared to ~4.1 eV for the MoS₂ layer) leads to an accumulation of electrons in the VSe₂ layer and creates a depleted region in the MoS₂ side of the hetero-interface and the subsequent formation of a Schottky barrier. The accumulation of electrons in the VSe₂ layer could give rise to the enhanced ferromagnetism in this layer and, hence, contributes to the change in net magnetization of the VSe₂/MoS₂ heterostructure and hence the observed EB effect. Further studies are needed to verify this hypothesis. It would also be interesting to investigate how the interfacial magnetism and EB behavior in the VSe₂/MoS₂ heterostructure are altered when the thickness of the MoS₂ film is reduced to a few layers or the monolayer limit. Since the net magnetization of the VSe₂ film can be tuned by controlling Se-vacancy concentration [109], it would also be interesting to examine if the EB field of the VSe₂/MoS₂ heterostructure could be tuned by varying the magnetization of the VSe₂ layer. Given the fact that other TMDs, such as Se-deficient WSe₂ and TiSe₂ monolayers, could exhibit ferromagnetic ordering even at room temperature, it would be a worthwhile endeavor to explore the interfacial magnetism and EB effect in WSe₂/MoS₂ and TiSe₂/MoS₂ heterostructures. Engineering of atomic defects for tunable interfacial magnetism and EB would also offer a promising platform for 2D van der Waals spintronics [117].

3. Perspective applications

Magnetic anisotropy plays a crucial role in the applications of magnetic materials in spintronic devices. In magnetic heterostructures, tailoring exchange magnetic anisotropy (also known as interface anisotropy) has proved its usefulness in improving magnetic functionality and hence the performance of a spintronic device [18][63] [77][83] [118][119] [120][121][122]. We highlight below the important effects that MP-mediated exchange magnetic anisotropy may have on spin configurations, spin-transport, thermo-spin-transport, and valleytronic properties of 2D van der Waals magnet-based heterostructures, which are open to a wide range of important technological applications (Fig. 11).

3.1 Spintronics and opto-spintronics

Spin valve structures form the basis of spintronic devices. In these magnetic junctions, the quality of interfaces between the ferromagnetic electrodes and the spacing layer plays a decisive role in the magnetoresistance effect [3]. While poor interfaces are main concerns for non-vdW material-based SV devices, this issue can be overcome by using vdW materials because of their atomically flat

interfaces. Indeed, Song *et al.* have shown a giant tunneling magnetoresistance effect (~19,000%) at low temperatures in a novel vdW heterostructure in which an atomically thin CrI₃ was sandwiched between graphene contacts [123]. Zhou *et al.* theoretically demonstrated an extremely large tunneling magnetoresistance of 846% at room temperature in a vdW MoS₂/VSe₂/MoS₂ magnetic tunneling junction (MTJ) [124]. Because of the strong spin Hall conductivity of MoS₂, SOT is appropriate for magnetization switching of the VSe₂ layer. However, this prediction needs experimental validation. Large SV effects have been experimentally achieved in Fe₃GeTe₂-based vdW systems such as Fe₃GeTe₂/MoS₂/Fe₃GeTe₂ [99], Fe₃GeTe₂/WS₂/Fe₃GeTe₂ [125], Fe₃GeTe₂/InSe/Fe₃GeTe₂ [126], Fe₃GeTe₂/h-BN/Fe₃GeTe₂[127], and Fe₃GeTe₂/graphite/Fe₃GeTe₂ [128]. These proof-of-concept devices demonstrate a promising perspective towards proximitized vdW materials for use in energyefficient 2D vdW spintronics.

Owing to atomically flat vdW interfaces, the highly efficient SOT and magnetization switching of Fe₃GeTe₂, Cr₂Ge₂Te₆, and CrI₃ have also been achieved [79][63][90][129][130][131]. Alghamdi *et al.* have shown that the SOT efficiency achieved in Fe₃GeTe₂/Pt is comparable with that of the best heterostructures containing 3D ferromagnetic metals and much larger than that of heterostructures containing 3D ferrimagnetic insulators [90]. It is anticipated that proximitized vdW heterostructures may also provide better electrical manipulation and notable thermal perturbations that allow a lower analytical current for switching magnetization as compared to non-vdW magnetic junctions in SOT-mediated magneto-resistive memory devices [79][132][133][134]. While the surface magnetism of ferromagnetic electrodes is important in both SV and SOT systems, recall the significant effect of oxidization on the surface magnetic property of mechanically exfoliated Fe₃GeTe₂. In particular, oxidized Fe₃GeTe₂ has been shown to exhibit the EB effect [61], and the effect that exchange anisotropy may have on the MR and SOT should be investigated systematically.

Research has shown that it is possible to use light via a femtosecond laser pulse to manipulate the ferromagnetism (both magnetization and magnetic anisotropy values) in 2D magnets and heterostructures [135]. Interestingly, light-driven ferromagnetism has been observed at room temperature in atomically thinned Fe₃GeTe₂ [135]. The effect has been attributed to the change in the electronic structure of Fe₃GeTe₂ due to optical doping. This important observation reveals a new perspective for optically controlling SV and SOT effects in Fe₃GeTe₂-based heterostructures or similar vdW heterostructures at room temperature, which has the potential to establish a new subfield of opto-spintronics. Future studies are needed to realize all of this.

3.2 Spin-caloritronics and opto-spin-caloritronics

In a heavy metal (HM)/ferromagnet (FM) bilayer such as $Pt/Y_3Fe_5O_{12}$, the application of an external magnetic field and a temperature gradient in the FM layer can generate a pure spin current, which can then be converted into an electrical voltage via the inverse spin Hall effect (ISHE) due to the strong spin-orbit characteristic of the HM. Such phenomenon is now widely known as the spin Seebeck effect (SSE), which was first discovered in Pt/FeNi bilayers by Uchida *et al.* in 2008 forming the basis for the development of spin-caloritronic devices [136][137]. Recent research has shown the large anomalous Nernst effect (ANE) in Fe₃GeTe₂ to be a result of charge current driven by the temperature gradient [138]. It is likely that both SSE and ANE coexist in Fe₃GeTe₂, but no study has been made to decouple their relative contributions. In SSE and ANE systems, surface/interface magnetic anisotropy has been shown to play an important role [139][140]. As mentioned earlier, it is possible to manipulate the magnetic anisotropy of Fe₃GeTe₂ by light. This suggests a new possibility of optically controlling SSE and ANE in Fe₃GeTe₂ and its heterostructures. Further studies should be performed to validate this hypothesis.

On the other hand, the giant enhancement of SSE has been reported in a Pt/YIG bilayer by inserting a semiconducting TMD monolayer of WSe₂ [108]. In this context, the addition of a 2D-TMD magnetic semiconductor (e.g., V-doped WS₂ or V-doped WSe₂ monolayer [57][55][56]) has been proposed to reduce the conductivity mismatch between the HM and FM layers and enhance the spin mixing conductance across the HM/FM interface both resulting in further enhancement of the SSE in Pt/YIG [59]. Since the magnetization of a magnetic TMD monolayer (e.g., V-WS₂) has recently been demonstrated to be manipulated by varying the intensity of an irradiated light at low power [141], it is possible to use light to control the SSE in HM/magnetic 2D-TMD/FM heterostructures. This idea sparked a new research subfield named "opto-spin-caloritronics" [59]. In a similar perspective, exploring ultrafast magnetism in 2D-TMD magnets and heterostructures would also provide a novel platform for ultrafast opto-spin-caloritronics.

3.3 Valleytronics and spin-valleytronics

Valleytronics combines valley and electronics in a way that exploits local extrema, or "valleys," in the electronic band structure of a semiconductor like a TMD monolayer [3][142] [143]. This effect has been observed over a wide range of 2D-TMD semiconductors such as monolayers of WSe₂, WS₂, and MoS₂ [144][145][146]. The MP effect has recently been reported to enhance valley Zeeman splitting in these 2D-TMDs by interfacing them with magnetic materials that can fulfill the increasing requirements of spin-valleytronics [104][143][147][148]. Theoretical studies show that the magnetization can be induced in monolayer MoS₂ when interfaced with a magnetic metal like Ni [149] or a ferromagnetic TMD like EuS [150]. Recently, Zhao *et al.* experimentally demonstrated the use of a magnetic exchange field (MEF) from an EuS substrate to enhance valley splitting in monolayer WSe₂ [151]. More recently, Seyler *et al.* optically manipulated the magnetization of an ultrathin ferromagnetic insulator CrI₃ to tune MEF over a range of 20 T, thus

enabling a continuous control of the magnitude and sign of valley polarization and Zeeman splitting in monolayer WSe₂ [152]. However, these vdW magnets (EuS, CrI₃) order ferromagnetically at low temperature (below 100 K) hindering valleytronic devices from operating at room temperature. To realize their practical applications, the valley spin states should be controllable by magnetic field at room temperature. In this context, Kim *et al.* recently demonstrated that the interfacial anisotropy in a Fe₃GeTe₂/WSe₂ heterostructure can be controlled by varying adjacent layers of Fe₃GeTe₂, which leads to an appearance of multiple magnetic behaviors in a single channel [83]. This system is of potential interest for exploring spin valleytronics.

As a promising alternative, magnetic doping into 2D-TMDs has proved its usefulness in enhancing the valley Zeeman splitting at room temperature [153]. Li *et al.* demonstrated an enhanced valley Zeeman splitting at 300 K ($g_{eff} = -6.4$) in a Fe-doped MoS₂ monolayer relative to pristine MoS₂ [153]. The g_{eff} factor can also be tuned to -20.7 by increasing the Fe concentration, which has been attributed to the enhanced Heisenberg exchange interaction of Fe magnetic moments with MoS₂ through *d*-orbital hybridization. In this context, exploring the valley Zeeman splitting effect in the recently discovered room-temperature ferromagnetic V-doped TMD monolayers [56] would also be very interesting.

4. Concluding Remarks and Outlooks

This article has provided a critical review of exchange bias and related emerging phenomena over a wide range of heterostructure systems possessing magnetically coupled vdW/vdW and vdW/non-vdW interfaces. We show that while the EB effects observed in these heterostructures are sizable and interesting for spintronics applications, their origins and association with other effects such as MP and charge transfer are unclear and deserve further studies. Fe₃GeTe₂ is emerging as an excellent candidate for exploring 2D van der Waals spintronics. However, this material can be

oxidized easily when exposed to air thereby forming a surface layer that possesses a different magnetic order relative to its interior FM layer. While some have suggested that the formation of AFM ordering in this oxidized layer and its interface with the interior FM layer induce the EB effect, there is no solid evidence for the existence of AFM ordering and the resultant FM/AFM coupling. The situation becomes more complex when the EB effect has been reported in Fe₃GeTe₂-based heterostructures with various magnetic interfaces including Fe₃GeTe₂/CrCl₃ [16], Fe₃GeTe₂/FePS₂ [62], and Fe₃GeTe₂/MnPS₃ and Fe₃GeTe₂/MnPSe₃ [18]. Due to the uncontrolled oxidization effect and the undefined configuration of spins within the surface layer of Fe₃GeTe₂, the EB mechanism in these heterostructures cannot be simply attributed to FM/AFM coupling. Further studies on the effect of oxidization on the magnetism and EB in Fe₃GeTe₂ and its heterostructures are crucial. Other effects such as magnetic proximity caused by the FM layer (Fe₃GeTe₂) on the AFM spins of the adjacent layer (e.g., CrCl₃) at the FM/AFM interface and hence on the EB behavior have remained an open question. Since Fe₃GeTe₂ is metallic and CrCl₃ is semiconducting, there possibly exists "charge transfer" that occurs across this metal/semiconductor interface mediating the interfacial magnetism in this system, which should be investigated further. Given the fact that the EB effect has been observed in VSe₂/MoS₂ and Fe/MoS₂, it is reasonable to argue that the FM/AFM interface is not a necessary condition for achieving the EB effect in vdW magnetic heterostructures. Instead, interfacing a FM vdW material with a spin cluster or a SG vdW material could also result in a sizable EB effect [154]. In most cases, however, the large EB effect was observed at low temperature (below 100 K). Therefore, there is a pressing need for creating new heterostructure systems that can bring the large EB effect to room temperature. It is also necessary to develop new theoretical models that can better interpret the EB and associated effects in such heterostructures.

From a materials synthesis perspective, it is very challenging to obtain a clean and surface oxidization-free 2D Fe₃GeTe₂ from mechanical exfoliation of its single crystal. Consequently, the effect of oxidization on the magnetism and EB in Fe₃GeTe₂ and its heterostructures cannot be quantified. A possible solution to this problem is to employ molecular beam epitaxy (MBE) to grow clean Fe₃GeTe₂ films in high vacuum and cap the surfaces of the films with thin non-magnetic capping layers (e.g., Ta) to prevent or minimize the films from oxidization. Using this approach, it is also possible to create clean Fe₃GeTe₂-based heterostructures that would enable enhanced SV, SOT, ANE, and SSE effects. Nonetheless, the effect of the substrate on the magnetism of Fe₃GeTe₂ films should be taken into careful consideration [73][74].

Since the magnetism of Fe₃GeTe₂ can be controlled by external stimuli such as ionic gating [76] or light [135,155], it will be extremely interesting to explore electrical and/or optical manipulation of these effects to harness new applications in spintronics, opto-spintronics, spin-caloritronics, opto-spin-caloritronics, valleytronics, and opto-valleytronics. While Fe₃GeTe₂ orders ferromagnetically well below 300 K, its Fe-rich compounds (e.g., Fe₅GeTe₂) have recently been reported to show Curie temperatures near room temperature [53]. Future research may thus be focused on Fe₅GeTe₂ and its heterostructures, which have potential to fulfil the requirements of spintronic devices operating at ambient temperatures. Introducing the 2D magnetism into a TMD semiconducting monolayer by employing the magnetic proximity effect of an adjacent magnetic layer with high T_c such as a Fe₅GeTe₂ film may provide a novel strategy to achieve long-range magnetic interactions and boost the Curie temperature of TMDs to above room temperature without adding structural disorder to the TMD lattice. The exploration of SOT switching of 2D magnetic materials such as Fe₅GeTe₂ films with high Curie temperature ($T_c > 300$ K) will also benefit the application of SOT-based spintronic devices. Novel Fe₅GeTe₂-based heterostructures such as TMD/Fe₅GeTe₂-

(TMD = MoS₂, WS₂, WSe₂) can be designed and fabricated using the same MBE technique, and the MP effect induced by the Fe₅GeTe₂ layer on the TMD layer can be exploited to tune the spin and valley-polarization phenomena at room temperature [120][125][156][157]. The recent observation of the hysteretic magneto response of the exciton emission of quantum emitters in monolayer WSe₂ interfaced with Fe₃GeTe₂ has indeed demonstrated a new degree of freedom for spin and *g*-factor manipulation of quantum states [158].

Finally, we note that the magnetism of 2D magnetic materials such as Fe₃GeTe₂ and V-doped TMDs is very sensitive to strain [159]. Therefore, it is possible to use mechanical strain to manipulate the exchange magnetic anisotropy field and spin dynamics in these systems if they are transferred or grown on flexible substrates [160]. This would open a new research direction in the field of 2D vdW straintronics.

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Figure captions

Figure 1. Schematic shows the magnetic proximity (MP) and exchange bias (EB) effects in a van der Waals magnetic heterostructure. Fe_3GeTe_2 represents an example of material that preserves a ferromagnetic ordering in the 2D limit and can be interfaced with other material such as MnPS₃ to induce both MP and EB effects.

Figure 2. (c) Crystal and magnetic structure of Fe₃GeTe₂; (b) Cross-sectional STEM image of a Fe₃GeTe₂ flake capped with an AlO_x (2.5 nm) passivation layer; (c) Temperature and cooling-field dependence of the out-of-plane M-H loops measured for the oxidized Fe₃GeTe₂ flake (t = 38 nm); (d) H_{EB} and H_C as functions of T for two different flake thicknesses of t = 17 nm (circle) and 38 nm (square). *Reproduced with permission from Gweon et al.*, *Nano Letters 21*, 1672 (2021).

Figure 3. (a) Side view of the structure of CrCl₃. (b) Color plot of normalized dI_t/dT as a function of in-plane magnetic field H_{in} and temperature *T*. AFM: layered antiferromagnetic. PM: paramagnetic. SP: Fully spin polarized. *Reproduced with permission from Cai et al.*, *Nano Letters 19, 3993 (2019);* (c) Schematic diagram of the whole device structure. Inset: Optical image of the CrCl₃(top)/Fe₃GeTe₂ heterostructure on top of the Pt Hall contacts. (d) Temperature-dependent magnitudes of the exchange-bias field ($|H_E|$) and coercivity (H_C) in the individual Fe₃GeTe₂(30 nm) and CrCl₃(15 nm, 45 nm)/Fe₃GeTe₂(30 nm) heterostructures. (e) R_{xy} -H loops for individual Fe₃GeTe₂(30 nm) and CrCl₃(15 nm, 45 nm)/Fe₃GeTe₂(30 nm) heterostructures, respectively, measured at 2.5 K. *Reproduced with permission from Zhu et al.*, *Nano Letters 20, 5030 (2020)*.

Figure 4. (a) Magnetic ordering in vdW Fe₃GeTe₂ and FePS₃ flakes; (b) Magnetic susceptibility as a function of temperature for Fe₃GeTe₂ (gray curve) and FePS₃ (orange curve) single crystals along the c-axis; (c) Comparison of the MOKE signals versus the magnetic field at 80 K for Fe₃GeTe₂ and FPS/FGT; (d) The domain of the Fe₃GeTe₂ and FePS₃ layers around the interface of Fe₃GeTe₂/FePS₃

under the different external magnetic fields; (e) Comparison of the MOKE signals versus the magnetic field at 80 K for bare Fe₃GeTe₂ and the FePS₃/Fe₃GeTe₂/FePS₃ heterostructure; (f) The magnetic domain of FePS₃/Fe₃GeTe₂/FePS₃ at three typical magnetic states. *Reproduced with permission from Zhang et al.*, *Advanced Materials 32*, 2002032 (2020).

Figure 5. (a) Crystal structures of the Fe₃GeTe₂/MnPS₃ and Fe₃GeTe₂/MnPSe₃ heterostructures; (b) Polar RMCD signal of Fe₃GeTe₂, Fe₃GeTe₂/MnPS₃, and Fe₃GeTe₂/MnPSe₃ measured at 10 K; (c) Temperature dependent coercive fields of the Fe₃GeTe₂ flake, Fe₃GeTe₂/MnPS₃, and Fe₃GeTe₂/MnPSe₃ heterostructures; (d) Temperature-dependent exchange bias fields of Fe₃GeTe₂/MnPS₃ and Fe₃GeTe₂/MnPSe₃ and Fe₃GeTe₂/MnPSe₃ heterostructures; (d) Temperature-dependent exchange bias fields of *ACS Appl. Mater. Interfaces 13, 24314 (2021).*

Figure 6. (a) Schematics of the Fe₃GeTe₂/(IrMn or Pt) bilayers. Cross-sectional STEM image of the Fe₃GeTe₂/IrMn device fabricated on a Si/SiO₂ substrate by the vacuum exfoliation approach. Optical image of the hall-bar device for transport measurements; (b) Dependence of R_{xy} on out-of-plane *H* for IrMn (2 nm)/Fe₃GeTe₂ devices (prepared in a high vacuum) measured at 2 K. A clear shift to the left (right) is observed for the field cooling under a field of p_1 (–1 T); (c) Hall resistance measured with a current of 66 mA and an external field of 3000 Oe applied in the *x*-*z* plane and at an angle *b* away from the *x* direction. *Reproduced with permission from Zhang et al., Appl. Phys. Lett. 118, 262406 (2021).*

Figure 7. (a) Schematic diagram of the Fe₃GeTe₂/MoS₂/Fe₃GeTe₂ spin valve encapsulated by a top h-BN capping layer (~50 nm thick). Junction resistance and MR vs magnetic field at 10 K. \downarrow and \uparrow denote the out-of-plane magnetizations alignment directions of the Fe₃GeTe₂ flakes; *Reproduced with permission from Lin et al. ACS Appl. Mater. Interfaces 12, 43921 (2020).* (b) The schematic diagram of the device and magnetotransport setup. An out-of-plane magnetic field was applied to control the magnetization of the two Fe₃GeTe₂ electrodes. Resistance as a function of the perpendicular magnetic field (R–B) of device A at a fixed current bias of 0.1 μ A at 10 K; *Reproduced with permission from Zhu et al. Adv. Mater. 2104658 (2021).* (c) Sample for Lorentz transmission electron microscopy measurements consisting of 2L WTe₂ and 30L Fe₃GeTe₂. Scale bar: 10 μ m. Typical labyrinth domain in 30L Fe₃GeTe₂ thin flakes. Scale bar: 2 μ m. From the aligned and stripe-like domain structures of the WTe₂/Fe₃GeTe₂, a Dzyaloshinskii–Moriya interaction energy is estimated to be ~1.0 mJ m⁻². Scale bar: 2 μ m. *Reproduced with permission from Wu et al. Nature Com. 11, 3860 (2020).*

Figure 8. (a) Raman spectra of YIG and the MoS₂ single layer on YIG. The Raman spectrum of single-layer MoS₂ reflects the signature E^{1}_{2g} and A_{1g} modes, which are associated with horizontal and vertical vibration modes as the insets; (b) Highlighted MCD spectra of YIG/MoS₂ and the reference MCDs of (c) YIG/Al₂O₃/MoS₂ and bare YIG. Arrows in (a) and (b) indicate antiferromagnetically coupled moments in YIG and MoS₂ based on the anti-symmetry of MCD. (d) Field-dependent MCD taken with a fixed photon energy at 2.95 and 1.97 eV, corresponding to the optical response of YIG and MoS₂, respectively. (e) Exchange between induced moments in MoS₂ assisted without/with BMP. The induced moments locate in the vicinity of sulfur vacancies enable the long-range magnetic interaction through BMP percolation. *Reproduced with permission from Tsai et al. Adv. Quantum Technol. 4, 2000104 (2021).*

Figure 9. (a) Schematic shows a bilayer heterostructure composed of monolayer VSe_2 and single crystal MoS₂; (b) Magnetic hysteresis loops in FC and ZFC regimes taken at 10 K for the VSe₂/MoS₂ bilayer; (c) Temperature dependence of exchange bias field (H_{EB}) and coercive field (H_C) of the VSe₂/MoS₂ bilayer; (d) Cooling field dependence of exchange bias field (H_{EB}) for the VSe₂/MoS₂ bilayer.

Figure 10. Schematic showing perspective applications (spintronics; opto-spintronics, spincaloritronics; opto-spin-caloritronics; valleytronics; spin-valleytronics) of van der Waals magnets and their heterostructures in which exchange magnetic anisotropy plays an important role.





























