Review

Unconventional Magnetism in Layered Transition Metal Dichalcogenides

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Abstract: In this contribution to the MDPI Condensed Matter issue in Honor of Nobel Laureate Professor K.A. Müller I review recent experimental progress on magnetism of semiconducting transition metal dichalcogenides (TMDs) from the local-magnetic probe point of view such as muon-spin rotation and discuss prospects for the creation of unique new device concepts with these materials. TMDs are the prominent class of layered materials, that exhibit a vast range of interesting properties including unconventional semiconducting, optical, and transport behavior originating from valley splitting. Until recently, this family has been missing one crucial member: magnetic semiconductor. The situation has changed over the past few years with the discovery of layered semiconducting magnetic crystals, for example CrI_3 and VI_2 . We have also very recently discovered unconventional magnetism in semiconducting Mo-based TMD systems 2H-MoTe_2 and 2H-MoSe_2 [Guguchia et. al., *Science Advances* 2018, 4(12)]. Moreover, we also show the evidence for the involvement of magnetism in semiconducting tungsten diselenide 2H-WSe_2 . These results open a path to studying the interplay of 2D physics, semiconducting properties and magnetism in TMDs. It also opens up a host of new opportunities to obtain tunable magnetic semiconductors, forming the basis for spintronics.

Keywords: transition metal dichalcogenides; magnetic semiconductor spintronics

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1. Introduction

Spintronics, or spin-based electronics, is one of the promising next generation information technology [1,2]. It makes use of the quantum property of electrons, such as spin, as information carriers and possesses potential advantages of speeding up the data processing, high circuit integration density, and low energy consumption. Magnetic semiconductors, combining the properties and advantages of both magnets and semiconductors, form the basis for spintronics. Not only ferromagnetic semiconductors, but also antiferromagnetic semiconductors were proposed to be natural candidates for integrating spintronics and traditional microelectronic functionalities in a single material [2]. All semiconductor spintronic devices act according to the following simple scheme: information is stored (written) into spins as a particular spin orientation; the spins, being attached to mobile electrons, carry the information along a wire; and the information is read and processed at a terminal. However, spintronics applications require novel magnetic semiconducting materials with high-temperature ferromagnetic or antiferromagnetic ordering of spins, which would simultaneously enable the conventional tunability of electronic properties and spintronic functionalities. Moreover, the materials should be produced as very stable thin layers to be incorporated in the devices.

Along these lines, transition metal dichalcogenides (TMDs), a family of two dimensional (2D) layered materials such as graphene, have appeared as the most promising platform due to their exciting mechanical, electronic and optoelectronic properties [3–9]. TMDs share the same formula, MX_2 , where M is a transition metal and X is a chalcogen ion. They have a layered structure and crystallize in several polytypes, including 2H-, 1T-, 1T'- and T_d -type lattices. Much interest is focused on the cases where the transition metal M is either Molybdenum (Mo) or Tungsten (W). Hence, the 2H forms of these compounds are semiconducting and can be mechanically exfoliated to a monolayer. The unique properties of the TMDs, especially in the monolayer form, have triggered a wealth of device applications such as: magnetoresistance and spintronics, high on/off ratio transistors, optoelectronics, valley-optoelectronics, superconductors and hydrogen storage. Many of these interesting properties arise due to the strong spin-orbit interaction present in these materials arising from the presence of the heavy metal ion. While there are many studies focused on the spin-orbit coupling and the interesting consequences for electrical and optical properties in these materials, there are very limited, and mostly theoretical, studies on the intrinsic magnetism [10–17]. Theoretical work shows that, in the absence of crystalline imperfections, the Mo-based TMDs are nonmagnetic.

Combining a wealth of different technique, in particular the muon-spin rotation/relaxation (μ SR) technique, we discovered novel magnetism in these very stable semiconducting materials: molybdenum ditelluride ($MoTe_2$) and molybdenum diselenide ($MoSe_2$) [9]. The results are published in a journal of the American Association for the Advancement of Science [9]. Here, I provide a short review of the previous results, show the new data for tungsten diselenide (2H-WSe₂) and discuss the importance of the presence of magnetism in semiconducting TMDs.

2. μ SR Technique: Very Sensitive Microscopic Magnetic Probe

The acronym μ SR stands for muon spin rotation, or relaxation, or resonance, depending respectively on whether the muon spin motion is predominantly a rotation (more precisely a precession around a magnetic field), or a relaxation towards an equilibrium direction, or a more complex dynamics dictated by the addition of short radio frequency pulses.

It is noteworthy that Prof. K. Alex Müller realised the importance and the strength of the μ SR technique in the studies of high temperature superconductors (HTSs) at the very early stage of the era of high- T_c cuprates, as demonstrated in the pioneering papers [18–20]. Indeed, this technique allows us to study fundamental problems related to superconductivity [8,21–29].

Besides superconductivity, positive muons implanted into a sample serve as an extremely sensitive local probe to detect small internal magnetic fields and ordered magnetic volume fractions in the bulk of magnetic materials. μ SR can distinguish the volume fraction effect from the ordered moment size and thus, it is a particularly powerful tool to study the thermal or quantum evolution of both magnetic moment and magnetically ordered volume fraction in solid materials [30–33]. μ SR is also valuable for studying materials in which magnetic order is random or of short range. This makes μ SR a perfectly complementary technique to scattering techniques such as neutron diffraction, which is used to determine crystallographic and magnetic structures. Moreover, the μ SR technique has a unique time window (10^{-4} s to 10^{-11} s) for the study of magnetic fluctuations in materials, which is complementary to other experimental techniques such as neutron scattering, NMR, or magnetic susceptibility. With its unique capabilities, μ SR should be considered to play a leading role in determining magnetic phase diagrams and elucidating the quantum evolution from the paramagnetic to magnetic state in the semiconducting TMDs, which are interesting due to both fundamental and practical aspects. A brief introduction to the μ SR technique [34–36] is given below.

The μ SR method is based on the observation of the time evolution of the spin polarization $\vec{P}(t)$ of the muon ensemble. A schematic layout of a μ SR experiment is shown in Figure 1a–c. In a μ SR experiments an intense beam ($p_\mu = 29$ MeV/c) of 100 % spin-polarized muons is stopped in the sample (see Figure 1a). Currently available instruments allow essentially a background free μ SR measurement at ambient pressure [37]. The positively charged muons thermalize in the sample at interstitial lattice

sites, where they act as magnetic microprobes. In a magnetic material the muons spin precess in the local field B_μ at the muon site with the Larmor frequency $\nu_\mu = \gamma_\mu / (2\pi) B_\mu$ (muon gyromagnetic ratio $\gamma_\mu / (2\pi) = 135.5 \text{ MHz T}^{-1}$). The muons μ^+ implanted into the sample will decay after a mean life time of $\tau_\mu = 2.2 \text{ }\mu\text{s}$, emitting a fast positron e^+ preferentially along their spin direction. Various detectors placed around the sample track the incoming μ^+ and the outgoing e^+ (see Figure 1a). When the muon detector records the arrival of a μ in the specimen, the electronic clock starts. The clock is stopped when the decay positron e^+ is registered in one of the e^+ detectors, and the measured time interval is stored in a histogramming memory. In this way a positron-count versus time histogram is formed (Figure 1b). A muon decay event requires that within a certain time interval after a μ^+ has stopped in the sample an e^+ is detected. This time interval extends usually over several muon lifetimes (e.g., $10 \text{ }\mu\text{s}$). After a number of muons has stopped in the sample, one obtains a histogram for the forward (N_{e+F}) and the backward (N_{e+B}) detectors as shown in Figure 1b, which in the ideal case has the following form:

$$N_\alpha^{e^+}(t) = N_0 e^{-\frac{t}{\tau_\mu}} (1 + A_0 \vec{P}(t) \hat{n}_\alpha) + N_{bgr}. \alpha = F, B \quad (1)$$

Here, the exponential factor accounts for the radioactive muon decay. $\vec{P}(t)$ is the muon-spin polarization function with the unit vector $\hat{n}_\alpha$ ($\alpha = F, B$) with respect to the incoming muon spin polarization. N_0 is number of positrons at the initial time $t = 0$. N_{bgr} is a background contribution due to uncorrelated starts and stops. A_0 is the initial asymmetry, depending on different experimental factors, such as the detector solid angle, efficiency, absorption, and scattering of positrons in the material. Typical values of A_0 are between 0.2 and 0.3.

Since the positrons are emitted predominantly in the direction of the muon spin which precesses with ω_μ , the forward and backward detectors will detect a signal oscillating with the same frequency. In order to remove the exponential decay due to the finite life time of the muon, the so-called asymmetry signal $A(t)$ is calculated (see Figure 1c):

$$A(t) = \frac{N_{e+F}(t) - N_{e+B}(t)}{N_{e+F}(t) + N_{e+B}(t)} = A_0 P(t), \quad (2)$$

where $N_{e+F}(t)$ and $N_{e+B}(t)$ are the number of positrons detected in the forward and backward detectors, respectively. The quantities $A(t)$ and $P(t)$ depend sensitively on the spatial distribution and dynamical fluctuations of the magnetic environment of the muons. Hence, these functions allow us to study interesting physics of the investigated system.

In μSR experiments two different magnetic field configurations are used: (i) Transverse field (TF) μSR involves the application of an external field perpendicular to the initial direction of the muon spin polarization. The muon spin precesses around the transverse field, with a frequency that is proportional to the size of the field at the muon site in the material. (ii) In the longitudinal field (LF) configuration the magnetic field is applied parallel to the initial direction of the muon spin polarization. The time evolution of the muon spin polarization along its initial direction is measured in this configuration. Measurements are often carried out in the absence of external magnetic field, a configuration called zero-field (ZF) μSR . In this configuration the frequency of an obtained μSR signal is proportional to the internal magnetic field, from which the size of the ordered moment and thus the magnetic order parameter is calculated. The capability of studying materials in zero external field is a big advantage over other magnetic resonance techniques.

If the local magnetic field $\vec{B}(\vec{r})$ at the muon site is pointing under an angle θ with respect to the initial muon spin polarization, the decay positron asymmetry is given by [33]:

$$A(t) = A_0 [\cos^2(\theta) + \sin^2(\theta) \cos(\gamma_\mu B t)], \quad (3)$$

where A_0 is the maximal value of the asymmetry. Further assuming that the random fields are isotropic and each component can be represented by a Gaussian distribution of width Δ/γ , then a statistical average of this distribution yields:

$$A(t) = A_0 \left[\frac{1}{3} + \frac{2}{3} e^{-\Delta^2 t^2 / 2} (1 - \Delta^2 t^2) \right], \quad (4)$$

This function was first obtained in a general stochastic treatment of Kubo and Toyabe [38]. The form of the distribution of internal magnetic fields influences the form of the μ SR signal [30,31,33]. Thus, by analysing the observed muon-spin time evolution, the magnetic field distribution inside the sample can be obtained. For clarity, Figure 1d–f shows the expected time evolution of the muon spin polarisation for three different cases of magnetically ordered polycrystalline sample: fully magnetic and magnetically homogeneous (d), full volume magnetic and inhomogeneous (e) and phase separation between magnetic and paramagnetic regions (f). The muons stopping in the homogeneous sample will sense the same magnetic field and their spin will precess around the internal field and the μ SR signal is characterised by maximum amplitude and zero depolarisation (Figure 1d). If there is an inhomogeneous static internal field in the sample, different muons will precess at slightly different frequencies. This leads to a progressive dephasing of the μ SR signal, and the oscillations in the μ SR time spectra will be damped (see Figure 1e). In some cases the signal is strongly damped, so that the oscillation will not be observed, and the resulting muon spin polarization will be averaged out to zero. Then, at a magnetic phase transition, if no wiggles are observed in the μ SR signal, one expects a drop in the effective initial asymmetry from A_0 in the paramagnetic state to $A_0 = 1/3$ in the ordered state [30]. However, this effect could also be due to fluctuations of the internal field. μ SR is capable of distinguishing between these two possibilities by performing an LF- μ SR experiment. In a longitudinal field inhomogeneous line broadening and fluctuations lead to different μ SR time spectra. Since muons stop uniformly throughout a sample, and the amplitudes of the μ SR signals arising from the different regions of the sample are proportional to the volume of the sample occupied by a particular phase, the presence of paramagnetic regions will result in the reduction of the signal amplitude as shown in Figure 1f. This schematics is a simple illustration of the fact that μ SR is capable to provide quantitative information on coexisting and competing phases in a material.

Figure 1. Principle of a μ SR experiment. (a) Overview of the experimental setup. Spin polarized muons with spin S_μ antiparallel to the momentum p_μ are implanted in the sample placed between the forward (F) and the backward (B) positron detectors. A clock is started at the time the muon goes through the muon detector (M) and is stopped as soon as the decay positron is detected in the detectors F or B. (b) The number of detected positrons N_F and N_B as a function of time for the forward and backward detector, respectively. (c) The so-called asymmetry (or μ SR) signal is obtained by essentially building the difference between N_F and N_B . (d–f) Schematic illustration of the magnetically homogeneous (i.e., full volume magnetic) (d), inhomogeneous (full volume magnetic, but with domains) and phase separated (i.e., part of the volume magnetic and part paramagnetic) polycrystalline samples and the corresponding μ SR spectra. The 1/3 non-oscillating μ SR signal fraction originate from the spatial averaging in powder samples where 1/3 of the magnetic field components are parallel to the muon spin and do not cause muon spin precession. Figure 1a–c is from [39,40].

3. Results

As we showed in our previous work, a spontaneous muon spin precession with a well-defined frequency was observed for both 2H-MoTe₂ and 2H-MoSe₂ at low temperatures (structural representation of the hexagonal 2H structure is shown in Figure 2). Moreover, muon spin precession was also observed for W-based TMD semiconductor 2H-WSe₂. The observation of a spontaneous muon spin precession is a clear signature of the occurrence of a static magnetic state in these

semiconducting systems at low temperatures. Figure 3 shows the comparison of zero-field μ SR time spectra, recorded at $T = 5$ K, between semimetallic orthorhombic T_d -MoTe₂ and semiconducting hexagonal 2H-MoTe₂ samples. It is interesting that while 2H-MoTe₂ showed coherent oscillations and thus the static magnetism, T_d -MoTe₂ gave a typical paramagnetic response from the whole sample volume. This indicates that static magnetism was a property for semiconducting 2H phase (Figure 2). The precession frequency was proportional to the local internal field $\mu_0 H_{int}$ at the muon site, which is shown in Figure 4a as a function of temperature for both 2H-MoTe₂ and 2H-MoSe₂ samples. A few points for 2H-WSe₂ were also shown. There was a smooth increase of $\mu_0 H_{int}$ below $T_M \simeq 40$ K and 100 K for 2H-MoTe₂ and 2H-MoSe₂, respectively. The internal field reached the saturated value of $\mu_0 H_{int} \simeq 200$ mT and 300 mT at low temperatures, for 2H-MoTe₂ and 2H-MoSe₂, respectively. For 2H-WSe₂, an even higher internal field value of $\mu_0 H_{int} \simeq 350$ mT was observed. A higher value of T_M and $\mu_0 H_{int}$ for 2H-MoSe₂ and 2H-WSe₂ as compared to values for 2H-MoTe₂ might be related to the distinct magnetic structures in these systems.

Although μ SR measurements revealed the homogeneous internal magnetic fields in 2H-MoTe₂ and 2H-MoSe₂ below $T_M \simeq 40$ K and 100 K, respectively, we observed that short-range (inhomogeneous) magnetism occurred at much higher temperatures. Figure 4b displays the paramagnetic fraction V_{PM} as a function of temperature for both samples. In MoTe₂, at 450 K, V_{PM} exhibited nearly a maximum value and decreases with decreasing temperature and tends to saturate below 300 K. This $\sim 30\%$ reduction of V_{PM} can arise for few different reasons and it was most likely due to the presence of a muonium fraction. In muonium, a bound state formed by a positive muon and an electron, may form in semiconductors [41]. In the bound state, the muon is much more sensitive to magnetic fields than as a free probe, because its magnetic moment couples to the much larger electron magnetic moment, thus amplifying the depolarization effects. Therefore, even small variations of the internal magnetic field may cause the loss of asymmetry such as that observed in 2H-MoTe₂ at high temperatures. However, there was an additional decrease of V_{PM} starting below $T_M^{onset} \sim 180$ K, which was due to the appearance of inhomogeneous short-range magnetism and V_{PM} continued to reduce until it reached the minimum value $V_{osc} \simeq 0.1$ at the long-range magnetic ordering temperature $T_M \simeq 40$ K, below which zero-field μ SR showed a well defined uniform internal magnetic field. This implies that the long range magnetic order was achieved only below $T_M \simeq 40$ K, while the short range magnetism appeared at higher temperature $T_M^{onset} \sim 180$ K. The same was also observed in MoSe₂, i.e., the short range magnetism appeared below $T_M^{onset} \sim 250$ K, while the long-range order was achieved below $T_M \simeq 100$ K. The onset temperature of short range magnetism in 2H-WSe₂ was close to the one for 2H-MoSe₂ (see Figure 4b). This suggests the presence of magnetic correlations in 2H-MoSe₂ and 2H-WSe₂ almost at room temperature, which may render TMDs useful for novel optoelectronics–spintronics applications. Moreover, we determined that hydrostatic pressure [42,43] had a significant effect on the magnetic properties of these materials. Namely, we saw a large suppression of both the magnetically ordered fraction and the magnetic order temperature T_M of 2H-MoTe₂ as a function of pressure (Figure 4c). The magnetism was nearly fully suppressed within 2.5 GPa. On the other hand, 2H structure remained stable up to much higher pressure of $p \sim 11$ GPa (the results will be reported elsewhere), which implies that the suppression of magnetism in 2H-MoTe₂ did not originate from the structural modifications. This strong pressure dependence of magnetism is very encouraging, because it indicates that one can have quantum control, in addition to thermal control, over the magnetic properties.

Figure 2. Structural representation of the hexagonal 2H structure for MoTe₂: (a) Side view. (b) Top view.

Figure 3. Zero-field (ZF) muon-spin rotation (μ SR) time spectra for the single crystal samples of T_d -MoTe₂ and 2H-MoTe₂ recorded at $T = 5$ K. The data for 2H-MoTe₂ is from Guguchia et. al., Science Advances 4: eaat3672 (2018).

The presence of magnetism in MoTe₂ and MoSe₂ was substantiated by temperature dependent macroscopic magnetisation measurements (see Figure 5a,b). A large difference between zero-field cooled (ZFC) and field-cooled (FC) magnetic moments was seen for both samples. The samples showed a combination of a temperature-independent diamagnetism, small van Vleck-type paramagnetism (which is determined by the energy separation of bonding and anti-bonding states $E_a - E_b$. $E_a - E_b$ is proportional to the band gap E_g) and a magnetic contribution that onset near 230 K and 180 K for MoSe₂ and MoTe₂, respectively. The difference between the FC and ZFC response suggests that different magnetic domains tended to cancel out (anti-align) after ZFC. If we do field-cooling, then the domains align. The onset temperatures of hysteresis 230 K and 180 K for MoSe₂ and MoTe₂, respectively, were close to the temperature T_M^{onset} below which μ SR experiments showed the appearance of inhomogeneous magnetism (see Figure 4b). This means that below T_M^{onset} some small magnetic domains (droplets of magnetic order) formed, which produced inhomogeneous magnetic fields and resulted in the absence of coherent oscillations in the μ SR signal. Instead, the various magnetic fields produced in the sample gave rise to a strong damping of the muon asymmetry, which we clearly d at $T_M^{onset} = 180$ K in MoTe₂ and $T_M^{onset} = 250$ K in MoSe₂. μ SR observed homogeneous magnetism below $T_M \simeq 40$ K and 100 K for MoTe₂ and MoSe₂, respectively, and the anomalies (such as an additional

increase of the moment and of the difference) at around these temperatures could also be seen in magnetization data. We note that for the sample MoSe₂ the magnetic contribution dominated over the diamagnetism, gave rise to total positive moment. In contrast, for MoTe₂ diamagnetism dominated over the magnetic contribution. Assuming that the core diamagnetism is nearly the same in these materials, this difference might be related to a distinct magnetic structures of MoTe₂ and MoSe₂. Separation between ZFC and FC curves, observed at low temperatures, does not necessarily indicate the ferromagnetic (FM) order. It could be consistent with the canted antiferromagnetic (AFM) structure, i.e., AFM structure with some weak net FM moment. Since magnetic contribution dominates over the diamagnetism in MoSe₂, its magnetic structure most likely exhibits larger net FM moment than the one for MoTe₂.

Figure 4. (a) Temperature dependence of the internal field $\mu_0 H_{int}$ of 2H-MoTe₂, 2H-MoSe₂ and 2H-WSe₂ as a function of temperature. (b) The temperature dependence of the paramagnetic fraction for 2H-MoTe₂, 2H-MoSe₂ and 2H-WSe₂. Arrows mark the onset and long-range ordered temperatures for magnetism. (c) Magnetic transition temperature T_M and magnetic volume fraction V_M for 2H-MoTe₂ as a function of pressure. Figure is adapted from Guguchia et. al., Science Advances 4: eaat3672 (2018).

Figure 5. The temperature dependence of zero-field cooled (sample was cooled down to the base- T in zero magnetic field and the measurements were done upon warming) and field-cooled (the sample was cooled down to the base- T in an applied magnetic field and the measurements were done upon warming) magnetic moments for the polycrystalline samples of MoSe₂ (a) and MoTe₂ (b), recorded in an applied field of $\mu_0 H = 10$ mT. The arrows mark the onset of the difference between ZFC and FC moment as well as the anomalies seen at low temperatures. The Figure is from Guguchia et. al., Science Advances 4: eaat3672 (2018).

4. Summary and Discussion

The μ SR measurements establish 2H-MoTe₂, 2H-MoSe₂ and 2H-WSe₂ as intrinsic magnetic, moderate bandgap semiconductors [9]. The μ SR results demonstrate magnetic order below $T_M \simeq 40$ and 100 K for MoTe₂ and MoSe₂, respectively. These results came as a surprise since the previous theoretical work [11] and simple chemical bonding considerations indicate that the Mo atoms in these samples are in a nonmagnetic $4d^2$ configuration. To understand the origin of magnetism, we carried out [9] the detailed investigation of the presence of defects and examined their magnetic properties by combination of the high-resolution STM [44] and Hubbard corrected DFT+U calculations [45] for Mo-based systems. STM measurements demonstrate the presence of intrinsic dilute self-organized defects. Note that two major defects, i.e., metal-vacancies (Figure 6a) and chalcogen-antisites (Figure 6b) (where a molybdenum atom substitutes the Tellurium/Selenium atom) were found in these materials. The defect concentration is small (~ 0.5 –1%), but defects are found to have a large electronic impact. Moreover, DFT indicates that the chalcogen-antisite defects Mo_{sub} are magnetic, while metal-vacancy defects Mo_{vac} do not introduce a significant local moment. Although, DFT shows the magnetic defects in these systems, it is difficult to understand how the low-density of the chalcogen-antisite defects can give rise to homogeneous internal magnetic fields, observed in 2H-MoTe₂ and 2H-MoSe₂, indicative of long-range magnetic order. This may be possible if these defects have electronic coupling to the semiconductor valence electrons. The presence of such spin-polarized itinerant electrons would imply that these materials are dilute magnetic semiconductors. This idea may be partly supported by the recent report on the observation of hidden spin-polarized states in the bulk MoTe₂ [46]. Although the exact link between μ SR and STM/DFT results [9] in 2H-MoTe₂ and 2H-MoSe₂ is not yet clear, both results together constitute a first strong evidence concerning the relevance of magnetic order in the TMDs physics. Defect induced, layer-modulated magnetism was recently reported for ultrathin metallic system PtSe₂ [47]. Ferromagnetism is also observed in VSe₂ monolayers. However, this system is characterized by a high density of states at the Fermi level [48], which is different from the systems 2H-MoTe₂, 2H-MoSe₂ and 2H-WSe₂, showing good semiconducting behavior. Thus, they open up a host of new opportunities to obtain tunable magnetic semiconductors, forming the basis for spintronics. Recently, there have been several reports on magnetism in W-based TMDs from bulk magnetisation measurements. Namely, the formation of ferromagnetism was reported for Vanadium doped WS₂ [49] and WSe₂ [50,51] monolayers with a small amount (~ 0.5 –4%) of V-content and the materials was classified as a dilute-magnetic semiconductor. We note that the mechanism behind the

magnetic order in 2H-MoTe₂, 2H-MoSe₂ and 2H-WSe₂ with intrinsic magnetic defects and in WS₂ with incorporation of small amount of Vanadium could be similar. Besides Mo- and W-based TMDs, a very interesting magnetic semiconducting TMD system is CrI₃ [52]. Although the experimental investigations of bulk CrI₃ date back to the 1960s, the temperature dependent magnetic and structural properties have only recently been reported [53]. Standard magnetization measurements show that CrI₃ is an anisotropic ferromagnet below the $T_C = 61$ K, with its easy axis pointing perpendicular to the layers. Evidence for a second unexpected magnetic phase transition at $T = 50$ K is found both in the bulk and in atomically thin crystals of CrI₃ [52]. It is important to emphasize that neither the nature nor the details of the ensuing magnetic state in CrI₃ are currently understood. To date, the origin of the novel magnetic order in Mo/W-based TMDs and the nature of complex magnetism in CrI₃ is not understood. To fully exploit the magnetic properties of these TMD semiconductors, future works needs to address these important issues. It is essential to make use of pressure, strain, organic cation intercalation, light illumination [54], and particle irradiation as tuning parameters for bulk material to explore the precise role of itinerant carriers and the specific type of defects in the formation of magnetism in Mo- and W-based TMDs.

Figure 6. Schematic illustration of the metal-vacancy defect Mo_{vac} (a) and the chalcogen-antisite Mo_{sub} defect (b). Figure is adapted from Z. Guguchia et. al., Science Advances 4: eaat3672 (2018).

Previously, magnetic semiconductors have been synthesized in a range of thin film and crystal materials [55–57]. Much interest has been focused on the III-V (GaAs) [55,56] and I-II-V (LiZnAs) [57,58] semiconductor class, where a small concentration of some magnetic ions, in particular Mn^{2+} , can be incorporated by substituting for the group II (Zn^{2+}) and III (Ga^{3+}) cations of the host semiconductor. Numerous technical challenges in making uniform magnetic semiconducting materials have been overcome in recent years, but formidable challenges still remain in producing stable, high-quality materials with high T_M . For instance, GaMnAs has poor chemical solubility and can not be grown as a bulk material. Only MBE films are available and only as a p-type system. LiZnMnAs has high chemical solubility and can be grown as a bulk material. However, no films of LiZnMnAs are available. Our present systems offer an alternative route to synthesize magnetic semiconducting materials with the following advantages:

1. High quality bulk samples of Mo/W-based semiconducting TMDs can be grown. The systems can be doped to make both n-type and p-type semiconductors available.
2. The materials are cleavable down to a monolayer thickness and readily grown in large-area form. As it is well established in these materials, the bandgap is strongly dependent on the thickness, providing tunability over the semiconductor properties.
3. The chemical potential and electric field in thin films are easily tuned by electrostatic gates, opening the possibility to tune magnetism, as demonstrated in GaAs.

4. Finally, these materials can be easily layered by van der Waals heteroepitaxy, allowing the creation of unique new device concepts. For instance, one can grow the heterostructure of the magnetic TMDs (2H-MoTe₂, 2H-MoSe₂, 2H-WSe₂) and superconducting Weyl semimetal [3] (T_d-MoTe₂) or the heterostructure of the magnetic TMDs (2H-MoTe₂, 2H-MoSe₂, 2H-WSe₂) and topological insulator (TI) [59,60] (Bi₂Se₃) and study exotic magnetic/superconducting properties at the interface [61–63]. Even though the SC in the bulk can be topologically trivial, the robust Z₂ related topological states at the surface or at the interfaces is expected to feature helical or other exotic Cooper pairing due to spin-momentum locking [64], and the external magnet field induced vortex line can support Majorana fermions. When a topological insulator/metal is in contact with a ferromagnet, both time reversal and inversion symmetries are broken at the interface. An energy gap is formed at the TI surface, and its electrons gain a net magnetic moment through short-range exchange interactions. Magnetic/superconducting proximity effects at the interface between magnet and Weyl semimetal (Figure 7a) or magnet and topological insulators (Figure 7b) is considered to have great potential in spintronics as, in principle, it allows realizing the quantum anomalous Hall and topological magneto-electric effects. However, detailed experimental investigations of induced magnetism at the interfaces has remained a challenge. Low-energy μ SR [63,65] experiments, which allows to probe the magnetism and superconductivity as a function of distance from the free surface to the interface, will be crucial to address the interesting magnetic/superconducting aspects of the interfaces.

Figure 7. (a) Schematics of the heterostructure of the magnetic transition metal dichalcogenide (TMD) (2H-MoTe₂, 2H-MoSe₂, 2H-WSe₂) and superconducting Weyl semimetal (T_d-MoTe₂). (b) Schematics of the heterostructure of the magnetic TMD (2H-MoTe₂, 2H-MoSe₂, 2H-WSe₂) and topological insulator (Bi₂Se₃).

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Conflicts of Interest: The authors declare no conflict of interest.

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