Creating and detecting ferro- and antiferromagnetic order in 2D materials by proximity effects

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Abstract

We propose an efficient way of detecting the magnetic state of bilayer CrI$_3$ via proximity effect, which can be generalized to other two-dimensional van der Waals magnets. In addition, we discuss the optical magnetization switching in CrI$_3$. First-principles calculations, together with a minimal tight binding Hamiltonian, reveal proximity exchange splittings of few meV in transition-metal dichalcogenides (TMDC) MoSe$_2$ and WSe$_2$ on mono- and bilayer magnetic insulator CrI$_3$ substrates. The magnitudes of proximity exchange and band offsets can be tuned by applying realistic transverse electric fields across the heterostructures. Most strikingly, the proximity exchange originates only from the ferromagnetic (FM) CrI$_3$ layer closest to the TMDC, as we find by comparison of mono- and bilayer CrI$_3$ substrates. Even though the bilayer CrI$_3$ can be in an antiferromagnetic (AFM) state with zero net magnetization, one can read out the magnetic state (FM or AFM) via proximity coupled two-dimensional materials, not necessarily TMDCs, on both sides of the bilayer CrI$_3$.

Keywords

transition-metal dichalcogenides, transition-metal trihalides, van der Waals heterostructures, magnetic proximity effect

Introduction

Two-dimensional (2D) materials and their hybrids are highly relevant nowadays for a variety of physical fields, dealing with electronics, spintronics, optics and magnetism. For example, graphene has excellent charge and spin transport properties, but lacks a band gap for transistor applications. Recently, the 2D ferromagnets MnSe$_2$, CrGeTe$_3$, and CrI$_3$ have been demonstrated to exist. These ferromagnetic monolayers are perfectly suited for nanoelectronic devices, such as magnetic sensors. Another class of materials are 2D semiconducting TMDCs, which have a band gap in the optical range, and are already used for optospintronic experiments, as proposed by first-principles calculation prediction.

Considering optical selection rules for TMDCs, one finds spin-valley coupling: the helicity selective optical excitation of carriers with different spins in different valleys, at the same excitation energy. By an exchange field one can break the time-reversal symmetry of the TMDC, the degeneracy of the valleys, and introduce valley polarization, relevant for the field of valleytronics. By an external magnetic field, the valley splitting rises roughly linear with $0.1 - 0.2$ meV/T, such that large fields are required to get a sizable effect.

Fortunately, the field of proximity effects is under intense investigation at the moment. Experiments and theory show, for example,
that graphene can borrow different properties from a variety of substrates, be it spin-orbit coupling (SOC) or magnetism. Therefore, a much better perspective to achieve large valley polarization in TMDCs is by the proximity exchange effect. Indeed, placing the TMDC on a magnetic substrate, it was shown that one can reach giant valley splittings ranging from few to hundreds of meV. In particular, first-principles calculations predict that EuO or MnO can give 200 – 300 meV, while experiments on EuS gives 2.5 meV of valley splitting.

Recent measurements show a few meV of proximity exchange also in TMDC/CrI$_3$ heterostructures. CrI$_3$ is especially interesting, because the monolayer is a FM, while bilayer CrI$_3$ shows AFM coupling, in contradiction to the existing theory, predicting a FM state for the low temperature phase. Astonishingly, the magnetization of the CrI$_3$ can be tuned optically, thereby influencing proximity exchange and the photoluminescence (PL) spectrum of the TMDC. In addition, the magnetism in few layer CrI$_3$ can be controlled by gating and external magnetic fields, opening a new path for gate controlled devices, such as spin-filter tunnel junctions, and AFM spintronics.

Here, we investigate the proximity exchange coupling in TMDC/CrI$_3$ heterostructures from first-principles. We find that the magnetic insulator substrate couples weakly to the TMDC, due to the van der Waals nature of the crystals. While preserving the characteristic electronic band structure of the TMDC, in addition, the proximity exchange coupling splits the conduction (CB) and valence band (VB) of the TMDC by roughly 5 meV, and together with the intrinsic SOC of the TMDC, we observe a lifting of the valley degeneracy. We employ a minimal model Hamiltonian, suitable for TMDC/CrI$_3$ heterostructures, and extract realistic proximity exchange parameters that can be used for further studies of, e.g., excitonic effects. We also show that experimentally accessible transverse electric fields of some V/nm, can tune the exchange parameters by few meV.

Most interesting is the case of a TMDC/bilayer-CrI$_3$ heterostructure, where only the FM CrI$_3$ layer closest to the TMDC is responsible for proximity exchange, even when the net magnetization of the bilayer CrI$_3$ is zero in the AFM state. We then propose a way to uniquely determine the magnetic state, via proximity coupled TMDC layers, on both sides of the CrI$_3$ bilayer. Furthermore, we discuss the magnetization switching in the TMDC/bilayer-CrI$_3$ heterostructure and speculate about a novel oscillatory magnetization switching for resonant optical excitation.

**Band structure**

To study proximity exchange effects, we set up a common unit cell for the TMDC/CrI$_3$ heterostructure (see Supporting Information). In Figs. 1(d,e), we show the geometry of the MoSe$_2$/CrI$_3$ heterostructure, as a typical structure. In Fig. 1 we show the calculated band structure with a fit to our model Hamiltonian (see Supporting Information) for MoSe$_2$/CrI$_3$ structure without SOC. We find that the bands of the TMDC are nicely preserved but with some proximity exchange present. The spin up CB, originating from the CrI$_3$, is located within the band gap of the TMDC, see Fig. 1(a). In experiments it was already shown that the spin polarized in-gap states from the CrI$_3$ quench the PL spectrum for one light helicity only, due to additional nonradiative relaxation processes. The energy gap of the full heterostructure is $\Delta E \approx 400$ meV, as defined in Fig. 1(a). The band edges of the TMDC can be almost perfectly described by our model Hamiltonian, as shown in Fig. 1(b,c). Due to proximity exchange, the bands are spin split by about 5 meV.

As a magnetic field or proximity exchange breaks time-reversal symmetry, we show the calculated band structure for MoSe$_2$/CrI$_3$ with SOC in Fig. 2. We find a very good agreement between the model Hamiltonian and the calculated bands around K and K' valley. The valley degeneracy is now broken, especially when comparing the CB edges at K and K' valley, see Fig. 2(b,c). Therefore, a TMDC/CrI$_3$ heterostruc-
In order to qualitatively extract the influence from the ferromagnetic substrate, we calculate the band structure of the TMDC/CrI₃ heterostructures and fit it to our low energy Hamiltonian (see Supporting Information). To obtain reasonable fit parameters we consider three situations. First, we calculate the band structure for the bare TMDC, removing the CrI₃, and check the SOC parameters for this situation, with the modified lattice constant used in the heterostructure geometry. This is crucial, because an increase in the lattice constant diminishes for example the band gap of the TMDC. Second, we calculate the band structure for the TMDC/CrI₃ heterostructures without SOC in order to obtain the proximity exchange splitting parameters. Finally, we calculate the band structure for the TMDC/CrI₃ heterostructures with SOC. In Tab. 1 we summarize the fit results for the three mentioned calculations.

Especially interesting are the proximity exchange parameters, being roughly 2 meV in magnitude, translating into about 10 T exchange field, in agreement with recent experiments. The calculation of the atomic magnetic moments reveals, that the magnetization direction of the TMDC is the same as in the I atoms, opposite to the Cr atoms, therefore giving negative proximity exchange parameters.
Table 1: Summary of fit parameters, calculated dipoles and distances for TMDC/CrI$_3$ systems. The orbital gap $\Delta$ of the spectrum and the Fermi velocity $v_F$. The parameters $\lambda_c$ and $\lambda_v$ describe the SOC splittings, and $B_c$ and $B_v$ are the proximity exchange parameters for CB and VB. The dipole of the structures is given in debye and the distance $d_{\text{TMDC/CrI}_3}$ is defined in Fig. (d). The individual columns are for calculations of the bare TMDC (B) with the modified lattice constant from the heterostructure, the heterostructure without SOC (noSOC) and with SOC.

|                  | MoSe$_2$/CrI$_3$ | WSe$_2$/CrI$_3$ |
|------------------|------------------|------------------|
| dipole [Debye]   | 0.103            | 0.156            |
| distance [Å]     | 3.506            | 3.497            |
| calculation      | B                | noSOC            | SOC               |
| $\Delta$ [eV]    | 1.302            | 1.305            | 1.301             |
| $v_F$ [$10^5$m/s] | 4.591            | 4.579            | 5.683             |
| $\lambda_c$ [meV]| -9.647           | -                | 13.90             |
| $\lambda_v$ [meV]| 94.56            | -                | 241.79            |
| $\lambda_R$ [meV]| -                | -                | -                 |
| $B_c$ [meV]      | -2.081           | -1.592           | -2.223            |
| $B_v$ [meV]      | -1.454           | -1.426           | -1.446            |

for a net CrI$_3$ magnetization pointing along positive $z$-direction towards the TMDC.

Including SOC in the heterostructure calculations, we find the parameters to be barely different than those from the individual calculations for the bare TMDCs or for the heterostructures without SOC. Therefore, combining the model Hamiltonian, the SOC parameters from the bare TMDC monolayer, and the exchange parameters from the heterostructure calculation without SOC, already suffices to get a reasonable low energy band structure which can be used for further studies of, e.g., excitonic effects.$^{69}$ Our fit shows that the Rashba parameter is not necessary to capture the essentials of the band structure for the TMDC/CrI$_3$ stacks, because there is no in-plane component of the spin expectation value present around the band edges.

**Gate tunable proximity exchange**

Motivated by recent experiments,$^{22,25,26}$ showing the electric field control of magnetism in few layer CrI$_3$, and the optical tuning of proximity exchange in TMDC/CrI$_3$ heterostructures,$^{59}$ we perform additional calculations for our heterostructures, where we apply a transverse electric field across the geometry.

![Figure 3](image_url) Figure 3: (Color online) Fit parameters as a function of transverse electric field for TMDC/CrI$_3$ heterostructures for calculations without SOC. (a) The orbital gap $\Delta$ of the spectrum, (b) the Fermi velocity $v_F$, (c) the dipole of the heterostructure, (d,e) the proximity exchange parameters $B_c$ and $B_v$ and (f) the band gap $\Delta E$, as defined in Fig. (a).

As calculations without SOC already give reasonable proximity exchange parameters, we neglect SOC for the electric field study. In Fig.
we show the fit parameters as a function of a transverse electric field for TMDC/CrI₃ heterostructures calculated without SOC. We find that the gap parameter Δ, as well as the Fermi velocity $v_F$, are barely affected by external electric fields. The dipole of the heterostructure depends linearly on the electric field. By applying an electric field, the band offsets can be changed. The band gap ΔE of the heterostructure, defined in Fig. 1(a), shrinks linearly with applied electric field. This tunability of the band offsets can be very important, when studying interlayer excitons. Imagine electrons located in the CrI₃ layer coupled to holes in the TMDC layer. As we apply an electric field, we tune the band gap ΔE, possibly affecting the lifetime of interlayer excitons. Especially interesting is the fact that the CB states, originating from the CrI₃, are spin polarized, see Fig. 1(a), which then gives additional valley control, depending on the magnetization of the CrI₃, due to spin-valley coupling in the TMDC. Most important, the two exchange parameters $B_c$ and $B_v$ can be tuned by the external electric field. In general, the proximity exchange increases, when the electric field is tuned from negative to positive values, which enables the gate control of proximity exchange.

### Reading and writing magnetic states

Another feature which was especially observed in bilayer CrI₃ is the switching from FM to AFM coupled layers by gating. For the AFM state, there are two energetically degenerate states of the bilayer (first layer $\uparrow$, second layer $\downarrow$, or vice versa). Therefore, we calculate the band structure, with and without SOC, for MoSe₂ on top of bilayer CrI₃, which is stacked in the low temperature rhombohedral phase. We find a total energy difference of $E_{AFM} - E_{FM} \approx 24$ meV between the FM and the AFM state calculated without SOC of the whole TMDC/bilayer-CrI₃ stack, which contains four Cr atoms in our supercell. In agreement with previous calculations, we find that the FM state of the bilayer CrI₃ is energetically favorable compared to the AFM state in contrast to experiments. As before we fit the model Hamiltonian to the first-principles band structures. The results are summarized in Tab. 2. A naive expectation would be that, depending on the total magnetization of the bilayer CrI₃, we can enhance or reduce proximity exchange in the TMDC, compared to the monolayer CrI₃ case. We can see that the FM ($\uparrow\uparrow$) coupled bilayer gives almost no difference in the fit parameters compared to the monolayer case. By switching the magnetization to AFM ($\uparrow\downarrow$), the magnitude of the exchange parameters stay similar. Even though the AFM coupled bilayer CrI₃ has no net magnetization, we still find proximity exchange in the TMDC. We conclude that only the FM CrI₃-layer closest to the TMDC is responsible for the proximity exchange, which is truly a short range effect, in agreement with previous thoughts.

In the following, we propose a geometry, that can optically or electrically readout the magnetic state of bilayer CrI₃. Suppose that a bilayer CrI₃ has two proximity coupled TMDCs on both sides, see Fig. 4(a). The top (bottom)
Figure 4: (Color online) Optical and electrical readout of FM and AFM state. Sketch of the proximity exchange, originating only from the CrI$_3$ closest to the TMDC. The colors correspond to the magnetization direction of the atomic layers (↑ = red, ↓ = blue). Top (bottom) TMDC layer is coupled only to the top (bottom) layer of bilayer CrI$_3$. In the FM state (a), proximity exchange for both TMDCs is similar, while switching the magnetization in one of the CrI$_3$ layers, leads to an AFM state (b) and the proximity exchange in the corresponding TMDC switches sign. Proximity exchange of the TMDC can be detected (a) optically by PL or (b) electrically in magnetotransport.

TMDC couples only to the top (bottom) CrI$_3$ of the bilayer. If the bilayer CrI$_3$ is FM coupled, both TMDCs experience the same proximity exchange, see Fig. 4(a), which can be detected, e.g., optically via PL spectrum or electrically via characteristic magnetotransport phenomena. Especially when two different TMDCs are used, two distinct energy peaks can be seen in the PL spectrum, each of which is valley polarized, corresponding to the specific proximitization. By switching the magnetization of the top CrI$_3$ layer, see Fig. 4(b), which is experimentally possible via optics, magnetism or gating, the proximity exchange induced in the top TMDC also switches sign, resulting in the opposite valley polarization. Therefore, all possible magnetic states (FM or AFM) of the bilayer CrI$_3$ can be distinguished by detecting proximity exchange in the TMDC layers.

Recently, photoinduced magnetization switching of the CrI$_3$ layer underneath a TMDC was shown, by tuning the laser excitation power. The optical induced carrier density $n_o$ depends on the laser power, the excitation energy, the absorption coefficient and the area of the laser spot, as reported for semiconductor nanowires. The electrical gate induced magnetization switching occurs for threshold densities of $n_t \approx 2 \times 10^{13} \text{cm}^{-2}$. Obviously, magnetization switching in CrI$_3$ occurs, when the induced optical density satisfies $n_o \geq n_t$. However, as noted by Seyler et al., it is unclear what exactly contributes to $n_o$. We believe that the switching appears due to a combination of direct optical excitation in CrI$_3$ and from an indirectly induced exciton contribution transferred from the TMDC, see Fig. 5.

Figure 5: (Color online) Shining light on the heterostructure directly creates (i) an exciton density in the TMDC and (ii) carriers in the CrI$_3$ layer. The combination of direct optical excitation in CrI$_3$ and from an indirectly induced exciton contribution transferred from the TMDC, switches the magnetization of the top CrI$_3$ layer and induces transitions from the AFM ground state to a FM state of the bilayer CrI$_3$.

Let us now speculate on a scheme, where magnetization switching happens solely due to the induced exciton density. If one resonantly ex-
cites the TMDC with circularly polarized light, addressing only one valley, one can switch the magnetization of the CrI$_3$ layer underneath. Thereby, the proximity exchange in the TMDC switches sign, the band gap in the corresponding valley changes, and the optical excitation in the TMDC is getting off resonance. Without the induced exciton density, the bilayer CrI$_3$ then relaxes back to its initial magnetic state. The TMDC is again in resonance, as the original band gap in the valley is restored, and the process starts anew, resulting in oscillatory magnetization switching. Especially materials with similar properties and a larger band gap than CrI$_3$ should be suitable to observe this effect, since the direct optical density is then decoupled from the indirect excitonic one.

Summary

In conclusion, we have shown that a CrI$_3$ substrate causes sizable proximity exchange in the TMDC. By applying experimentally accessible electric fields transverse to the geometry, we can tune band offsets and proximity exchange splittings. Finally, we have seen that proximity exchange originates only from the FM CrI$_3$-layer closest to the TMDC by investigating TMDC/bilayer-CrI$_3$ heterostructures. The short range proximity effect can be used to efficiently detect the magnetic state of bilayer magnetic insulator CrI$_3$. This concept can be generalized to other hybrid structures to detect the magnetic state of 2D van der Waals magnets.

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Supporting Information Available

The following files are available free of charge. Further details about the geometry, computational details and the model Hamiltonian.

Competing financial interest

The authors declare no competing financial interest.

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Supporting Information:
Creating and detecting ferro- and antiferromagnetic order in 2D materials by proximity effects

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The Supporting Information contains details about the used supercell geometry and the computational methods, as well as the model Hamiltonian used to fit the low energy bands of the TMDCs in the presence of proximity exchange.

Geometry and Computational Details

To study proximity exchange effects, we set up a common unit cell for the TMDC/CrI₃ heterostructure with the atomic simulation environment (ASE).¹ We choose a 2 × 2 supercell for the TMDCs (MoSe₂ and WSe₂) and a 1 × 1 cell of CrI₃. The lattice constants and strains are summarized in Tab. S1, for the individual monolayers. We can see that a maximum strain of roughly 3% is present for CrI₃, which is still an acceptable value for studying heterostructures, without altering the individual monolayer properties too much. Taking the geometry as explained, we end up with 20 atoms in the supercell. Our heterostructure is built such that a chalcogen atom of the TMDC is directly above a Cr atom of the CrI₃ layer (see Fig. 1 in the main manuscript). We do not consider other stacking configurations, as our results should be valid in general for TMDC/CrI₃ heterostructures and our main focus is on the qualitative influence of the substrate on the TMDC. For proper interlayer distances, we allow the atoms of the TMDC, as well as the Cr atoms in the CrI₃, to relax their z coordinates, while the I atoms are allowed to fully change their position in x, y, and z, because they form a distorted octahedral surrounding around the Cr-atoms.² The distances \( d_{\text{TMDC/CrI₃}} \) are about 3.5 Å, and of typical size for van der Waals systems.

Table S1: Lattice constants and strains for the subsystems used in the TMDC/CrI₃ heterostructures. The experimental \( a \) (exp.) lattice constants (Ref.³⁻⁵) and lattice constants used for the heterostructures \( a \) (het.) are given. The strain for each subsystem, is calculated as \( (a_{\text{het}} - a_{\text{exp}})/a_{\text{exp}} \).

|         | CrI₃  | MoSe₂ | WSe₂ |
|---------|-------|-------|-------|
| \( a \) (exp.) [Å] | 6.867 | 3.288 | 3.282 |
| \( a \) (het.) [Å] | 6.748 | 3.374 | 3.374 |
| strain [%] | -3.08 | 2.62  | 2.80  |

The electronic structure calculations and structural relaxation of our heterostructures are performed by means of density functional theory⁶ within Quantum ESPRESSO.⁷ Self-consistent calculations are done with the \( k \)-point sampling of \( 36 \times 36 \times 1 \) for TMDC/CrI₃ heterostructures. We perform open shell calculations that provide the spin polarized ground state with magnetization pointing in z-direction. We use an energy cutoff for charge density of 500 Ry, and the kinetic energy cutoff
for wavefunctions is 60 Ry for the scalar relativistic pseudopotential with the projector augmented wave method \(^8\) with the Perdew-Burke-Ernzerhof exchange correlation functional. \(^9\) In the cases where SOC is included, the fully relativistic version of the pseudopotentials are used. In addition we include the Hubbard correction for Cr atoms with \(U = 4\) eV. \(^10\) For the relaxation of the heterostructures, we add van der Waals corrections \(^11,12\) and use quasi-newton algorithm based on trust radius procedure. In order to simulate quasi-2D systems a vacuum of at least 20 Å is used to avoid interactions between periodic images in our slab geometry. Dipole corrections \(^13\) are also included to get correct band offsets and internal electric fields. Structural relaxations are performed until all components of all forces were reduced below \(10^{-3}\) [Ry/\(a_0\)], where \(a_0\) is the Bohr radius.

**Model Hamiltonian**

We want to describe proximity exchange effects that are due to the magnetic insulator substrate CrI\(_3\). Following an earlier work in this field, \(^14\) we introduce a minimal model Hamiltonian to describe the band structure of the TMDC close to K and K', in the presence of proximity exchange

\[
\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_\Delta + \mathcal{H}_{\text{soc}} + \mathcal{H}_{\text{ex}} + \mathcal{H}_R, \quad (S1)
\]

\[
\mathcal{H}_0 = h v_F s_0 \otimes (\tau \sigma_x k_x + \sigma_y k_y), \quad (S2)
\]

\[
\mathcal{H}_\Delta = \frac{\Delta}{2} s_0 \otimes \sigma_z, \quad (S3)
\]

\[
\mathcal{H}_{\text{soc}} = \tau s_z \otimes (\lambda_c \sigma_+ + \lambda_v \sigma_-), \quad (S4)
\]

\[
\mathcal{H}_{\text{ex}} = -s_z \otimes (B_c \sigma_+ + B_v \sigma_-), \quad (S5)
\]

\[
\mathcal{H}_R = \lambda_R (\tau s_y \otimes \sigma_x - s_x \otimes \sigma_y). \quad (S6)
\]

The valley index is \(\tau = \pm 1\) for K (K’) point and \(v_F\) is the Fermi velocity. The Cartesian components \(k_x\) and \(k_y\) of the electron wave vector are measured from K (K’). The pseudospin Pauli matrices are \(\sigma_i\) acting on the (CB, VB) subspace and spin Pauli matrices are \(s_i\) acting on the (↑, ↓) subspace, with \(i = \{0, x, y, z\}\). The parameter \(\Delta\) denotes the orbital gap of the spectrum. For short notation we introduce \(\sigma_\pm = \frac{1}{2} (\sigma_0 \pm \sigma_z)\). The parameters \(\lambda_c\) and \(\lambda_v\) describe the spin splitting for CB and VB, due to SOC, respectively. In the case when we have a ferromagnetic substrate, proximity exchange effects will be present with \(B_c\) and \(B_v\) describing the proximity induced exchange splittings of CB and VB. The Rashba SOC parameter \(\lambda_R\) is due to the presence of inversion asymmetry in the heterostructure. The four basis states we use are \(|\Psi_{\text{CB}}, \uparrow\rangle, \; |\Psi_{\text{VB}}, \uparrow\rangle, \; |\Psi_{\text{CB}}, \downarrow\rangle, \; \text{and} \; |\Psi_{\text{VB}}, \downarrow\rangle\). The wave functions are \(|\Psi_{\text{CB}}\rangle = |d_{xz}\rangle\) and \(|\Psi_{\text{VB}}\rangle = \frac{1}{\sqrt{2}} (|d_{z2}\rangle + i |d_{xy}\rangle)\), corresponding to CB and VB at K and K’, since the band edges are formed by different \(d\)-orbitals from the transition metal \(^15\) of the TMDC.

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