2D Magnetic Materials

Alberto Morpurgo


Collaborations: A. Imamoglu, M. Kroner (ETH); P. Maletinsky, L. Thiel, M. Tschudin (Basel); N. Chepiga, F. Mila (EPFL); I. Martin (Argonne)

Materials: E. Giannini, D. Dumcenco (Geneva); D. Mandrus (Oak Ridge); T. Taniguchi, K. Watanabe (NIMS)
Outline

• Short Introduction

• Semiconducting CrI$_3$ --- Ferromagnet or layered antiferromagnet?
  - Bulk
  - Kerr, Scanning magnetometry, an transport on multilayers

• Semiconducting AFM CrCl$_3$ --- Weak anisotropy & Spin-Flop
  - Anisotropy, Spin-Flip & Spin-Flop
  - Phase diagrams & Quantitative analysis

• More on AFM... (only one slide)

• van der Waals tunneling spin valves in Fe$_3$GeTe$_2$
  - ideal interfaces of vdW materials

• Exfoliation gives access to more length scales: not only 2D materials
  - Helical magnets and topological transitions in Cr$_{1/3}$NbS$_2$
## Vast material portfolio

<table>
<thead>
<tr>
<th>Antiferromagnetic</th>
<th>Interlayer</th>
<th>Ferromagnetic</th>
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<tbody>
<tr>
<td>( \text{Antiferromagnetic} ) ( J&lt;0; J_L&gt;0 )</td>
<td>\text{Ferromagnetic} ( J&gt;0; J_L&gt;0 )</td>
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<td>\text{Ferromagnetic}</td>
<td>\text{CoPS}_3 \text{ Ref}^{1} \text{ MnPS}_3 \text{ Ref}^{2-5} \text{ NiPS}_3 \text{ Ref}^{6-8} \text{ CrI}_3 \text{ (bulk) Ref}^{9,10} \text{ CrBr}_3 \text{ (bulk, few layers) Ref}^{11,12} \text{ Cr}_2\text{Ge}_2\text{Te}_6 \text{ Ref}^{13,14} \text{ Fe}_3\text{GeTe}_2 \text{ Ref}^{15,15} \text{ VSe}_2 \text{ Ref}^{17,19} \text{ FePS}_3 \text{ Ref}^{20,21} \text{ MnPSe}_3 \text{ Ref}^{35} \text{ CrI}_3 \text{ (few layers) Ref}^{22} \text{ CrCl}_3 \text{ (bulk) Ref}^{37} \text{ Green – semiconductor materials; orange - metallic}</td>
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Basic Concepts of low-D magnetism

Heisenberg model

\[ H = \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - D \left( S_z^2 \right) \]

Ferromagnetism --- \( J_{ij} < 0 \) (AF more complex but “similar”)

**Mean-field:** FM state with \( \mathbf{M} \propto \sum \langle \mathbf{S}_i \rangle \neq 0 \) (always \( T < T_c \))

**Elementary excitations:** spin waves \( E(k) = \hbar \omega(k) \propto |k|^2 \) (if \( D=0 \))

(1 magnon = 1 spin flip)

**Fluctuations:** \( \langle \delta \mathbf{M} \rangle \propto T \int_0^{BZ} \frac{dk}{\frac{\hbar \omega(k)}{e^{\frac{kT}{kT}} - 1}} \rightarrow T \int_0 k^{(d-1)} dk \rightarrow \frac{d \leq 2}{\infty} \)

**Anisotropy:** \( \frac{kT \ll D}{\hbar \omega(k) \propto \Delta + |k|^2} \) \( \langle \delta \mathbf{M} \rangle \propto T e^{-\frac{\Delta}{kT}} \int k^{(d-1)} dk \rightarrow 0 \)

From full rotational symmetry to “Ising” = bypass Mermin-Wagner
...but what is interesting for 2D materials

1) Semiconductor physics coupled to magnetism:
   - How does the spin couples to the electron states in the bands?
   - Which states does the spin configuration affect?

\[ H = \sum J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - D \left( S_z^2 \right) \]

How are J and D “coupled”
to the band states?

Key to understand: transport, optical properties, thickness evolution

Can we expect large effects? From neutrons J & D typically \( \sim 1 - 2 \) meV

2) Electrostatic doping expected to have large effects

3) “Other” magnetic length scales;
   “2D version” of phenomena known in 3D
   ....
$\text{Crl}_3$

a bulk van der Waals ferromagnetic semiconductor
$T_c = 61 \text{ K}$

Soft bulk ferromagnet

What's up at 51 K?

Bulk susceptibility
Extremely unstable in air:

*Thin crystals (even 50 nm) dissolve in a few minutes*
Layer–dependent ferromagnetism in a van der Waals crystal down to the monolayer limit

Bevin Huang1, Genevieve Clark2, Efrén Navarro-Moratalla3, Dahlia R. Klein3, Ran Cheng4, Kyle L. Seyler1, Ding Zhong1, Emma Schmidgall1, Michael A. McGuire5, David H. Cobden1, Wang Yao6, Di Xiao4, Pablo Jarillo-Herrero3 & Xiaodong Xu2

Magneto-optical Kerr effect to probe magnetism

Hysteretic Kerr rotation angle as expected for ferromagnets
How to measure magnetization of 2D materials?

**Scanning magnetometry of 2D magnets**

**Single-spin magnetometer:**

Maletinsky’s group

- Magnetic field Zeeman-splits states of NV-center
- Energy of splitting gives magnetic field
- Narrow microwave absorption line determines energy splitting → local B-field
- From fringing field reconstruct M

**Example**

2L and 3L CrI3 on same flake

Fringing field only on 2L

M(2L) = 0
M(3L) ~ 16 μB/nm²
Direct observation of layered antiferromagnetism

In all even multilayers: $M = 0$

In all odd multilayers: $M \sim 16 \mu_B/nm^2$

Sign of exchange coupling depends on strain?

Why bulk is FM and multilayers are AFM?

Magnetic state may depend on structure

L. Thiel, Z. Wang, AM, P. Maletinsky Science 2019
Kerr-effects in double gated CrI$_3$ bilayer devices

Opposite polarity = E-field

Same polarity = n accumulation

Mak & Shan groups
Nat Mat 17, 406 (2018)
Nat Nano 13, 549 (2018)

...But...
1) In which states does the charge go?
2) How much charge is accumulated?

Electron accumulation:
Turns AFM into FM

Magnetoelectric effect
Devices for transport measurements

In-plane transport = field-effect transistor

Thin CrI$_3$ as tunnel barrier between graphene contacts

Example of tunnel barrier device

Optical microscope

With contacts

Atomic force microscope
**In-plane and vertical transport**

**In-plane transport** = field-effect transistor

**Vertical transport** = tunnel barrier

Below 150 K: too insulating

Works down to the lowest T
Tunneling Magnetoresistance

New phenomenon:
10’000 % magnetoresistance due to magnetic states of the tunnel barrier
Different Magnetic States in Atomically Thin CrI$_3$

Steps also visible in Kerr effect
(with A. Imamoglu, M. Kroner @ETH)

Magnetoresistance onset is NOT at ferromagnetic transition ($T_c = 61$K)

Questions:
- Multilayer-to-bulk transition?
- Do we expect large MR in all layered antiferromagnets?

Similar results on MR
Science 360, 1214 (2018) Xu’s group
360, 1218 (2018) Jarillo-Herrero’s group
Tunneling: Fowler-Nordheim regime

\[ \ln \frac{I}{V^2} \sim -\frac{8\pi\sqrt{2m*\phi_B^3/2}}{3hqV} d \]

Barrier height depends on magnetic state

Assuming \( m^* = \text{free-electron mass} \)

Barrier height:
- \( B = 0 \) \( \sim 250 \text{ meV} \)
- \( B = 2T \) \( \sim 170 \text{ meV} \)

Change in barrier height: 50 – 100 meV

But exchange integrals 2-3 meV...

\[ H = \sum J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - D (S_z^2) \]
Phase diagram of CrCl$_3$ from tunneling MR

CrCl$_3$: weakly anisotropic layered antiferromagnet with in-plane spins

Z. Wang, M. Gibertini, AM et al Submitted
Energy scales and magnetic states of an antiferromagnet

Exchange = $J$; \[ E = J \vec{S}_1 \cdot \vec{S}_1 \]
Anisotropy = $K$; \[ E = -KS_z^2 \]
Zeeman = $\mu B$; \[ E = -\mu \vec{B} \cdot \vec{S} \]

**Bulk**

**Strong anisotropy = Large $K$**

\[ \Delta E \sim -\mu B + J \]
Spin-flip transition

**Weak anisotropy = Small $K$**

\[ \Delta E \sim -\frac{\mu B}{J} \mu B + K \]
Spin-flop transition
**Even-odd effect in weakly anisotropic AFM multilayers**

\[ \text{CrCl}_3 = \text{layered antiferromagnet with weakly anisotropic easy easy plane} \]

\[ B = 0 \]

**Even-N**

- \( \vec{S}_1 \)
- \( \vec{S}_2 \)

\[ B \sim \sqrt{JK} \]

Just like in the bulk

Energy balance:

\[ \Delta E \sim - N \frac{\mu B}{J} \mu B \]

Spin-flop transition at \( B \sim 0 \)

**Odd-N**

- \( \vec{S}_1 \)
- \( \vec{S}_2 \)
- \( \vec{S}_3 \)

\[ B \sim J/N \]

Energy balance:

\[ \Delta E \sim - N \frac{\mu B}{J} \mu B + \mu B \]

Net magnetization for odd \( N \)

Spin-flop transition at \( B \sim J/N \)
Compare with CrI$_3$

Perpendicular field

In-plane field

Strong uniaxial anisotropy in CrI$_3$
Spin alignment occurs different in in-plane and perpendicular field
$\text{Fe}_3\text{GeTe}_2$: a van der Waals ferromagnetic metal
**Gate-tunable room-temperature ferromagnetism in two-dimensional Fe$_3$GeTe$_2$**

Yuanbo Zhang’s group @ Fudan

Thickness evolution (ML $T_c$ ~ 20 K)

- **Gate-driven Li intercalation**

- MOKE: ML $T_c$ ~ 130 K

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**Two-dimensional itinerant ferromagnetism in atomically thin Fe$_3$GeTe$_2$**

Xiadong Xu’s group @ Seattle

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**Hall Resistance**

- 1L
- 2L
- 3L
- 4L
- 6L
- 50L

**$T_c$ vs. Temperature**

- Paramagnetic
- Ferromagnetic

**$\mu_0 H_T (T)$ vs. $V_g (V)$**

- $T = 10$ K

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**Magnetic Calculated Density (MCD) (a.u.)**

- $\mu_0 H (mT)$

- 153 K
- 146 K
- 134 K
- 130 K
- 126 K
- 121 K
- 117 K
- 110 K
- 100 K
- 90 K
Tunneling Spin Valves

Parallel magnetization

Anti-Parallel magnetization

Conventional ferromagnetic metal films with hBN tunnel barrier

Magnetic tunnel junctions with monolayer hexagonal boron nitride tunnel barriers

M. Piquemal-Banci, 1 R. Galceran, 1 S. Caneva, 2 M.-D. Martin, 2 R. S. Weatherup, 2 P. R. Kidambi, 2 K. Bouzehouane, 1 S. Xavier, 3 A. Anane, 1 F. Petroff, 1 A. Fert, 1 J. Robertson, 2 S. Hofmann, 2 B. Dlubak, 1 and P. Seneor 1

APPLIED PHYSICS LETTERS 108, 102404 (2016)

Ideal behavior difficult to achieve
- Magnetization switching
- Tunnel barrier quality
- etc.

\[ TMR \, = \, \frac{R_{AP} - R_P}{R_{AP}} \, = \, \frac{2P_1P_2}{1 - P_1P_2} \]
Van der Waals Magnetic tunnel junction

$Fe_3GeTe_2 / hBN / Fe_3GeTe_2$

$Fe_3GeTe_2$: ferromagnetic for $T < T_c = 220 \, K$

Van der Waals Heterostructure = Tunneling spin valve

Measure TMR + anomalous Hall effect

$R_{Hall} = R_H H + R_A M$
$Fe_2GeTe_3/hBN/Fe_2GeTe_3 = Ideal TMR behavior$

TMR = 160 %

Polarization $P = 0.66$; Spin up/down $N_\uparrow = 83\%$ $N_\downarrow = 17\%$

Z. Wang, AM et al Nano Letters 2018
TMR & anomalous Hall conductivity = same T dependence

**Tunneling Magneto-Resistance**

**Anomalous Hall effect**

\[ R_{\text{Hall}} = R_H H + R_A M \]

Compare temperature dependence

Spin polarization at the surface proportional to bulk magnetization
$Co_{\frac{1}{3}}NbS_2$ a helical magnet with 48 nm pitch

Topological transitions:
states with different spin winding number

Controlling the Topological Sector of Magnetic Solitons in Exfoliated Cr$_{\frac{1}{3}}$NbS$_2$ Crystals
L. Wang,$^{1,2,*}$ N. Chepiga,$^3$ D.-K. Ki,$^1$ L. Li,$^4$ F. Li,$^5$ W. Zhu,$^5$ Y. Kato,$^6$ O. S. Ovchinnikova,$^7$
F. Mila,$^3$ I. Martin,$^8$ D. Mandrus,$^{4,9,10}$ and A. F. Morpurgo$^{1,*}$

PRL 118, 257203 (2017)
Direct observation by Lorentz microscopy

Magnetic structures coupled to transport: aligning spins lowers resistance
Spin structure of the anisotropic helimagnet $\text{Cr}_{1/3}\text{NbS}_2$ in a magnetic field

Benjamin J. Chapman, Alexander C. Bornstein, Nirmal J. Ghimire, David Mandrus, and Minhyea Lee

APPLIED PHYSICS LETTERS 105, 072405 (2014)

$$\mathcal{H} = \sum_i [-J s_i \cdot s_{i+1} - D \cdot (s_i \times s_{i+1}) - \mu_B B \cdot s_i + A(\hat{z} \cdot s_i)^2]$$

- Ferromag. exchange
- Dzyaloshinskii Moriya
- In-plane anisotropy

- Bulk well-understood
- Model parameters can be extracted quantitatively
Varying thickness: shorter/longer than magnetic pitch

Thickness determines the spin winding number at $B = 0 \, T$; It has no influence on the critical temperature.
Ramping up magnetic field: first order transitions between different topological sectors

- **Ground state has different winding numbers in different B ranges**
- **1st-order transitions between topological sectors** change the spin configuration throughout the crystal thickness
- **Hysteresis & abrupt magnetization jump** -> resistance jumps
Compare MR of bulk and crystals with $t > 48$ nm

Winding # = 1

Winding # = 2

B value at which $W_N \# 1 \rightarrow 0$ transition occurs

Winding # = 5
The magic of topology....

Drastic difference in the MR of Cr$_{1/3}$NbS$_2$

$t > 48 \text{ nm} \rightarrow \text{hysteretic MR}$

$t < 48 \text{ nm} \rightarrow \text{no hysteresis in MR}$
Conclusions

The game is on…

Green – semiconductor materials; orange - metallic