2D Magnetic Materials

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FNSNF SWISS NATIONAL SCIENCE FOUNDATION

GRAPHENE FLAGSHIP

Outline

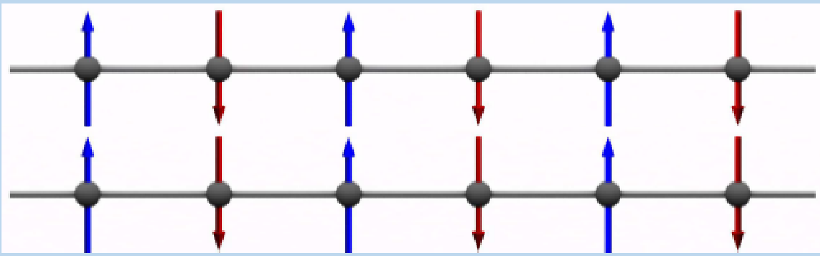
- *Short Introduction*
- *Semiconducting CrI_3 --- Ferromagnet or layered antiferromagnet?*
  - *- Bulk*
  - *- Kerr, Scanning magnetometry, an transport on multilayers*
- *Semiconducting AFM $CrCl_3$ --- Weak anisotropy & Spin-Flop*
  - *- Anisotropy, Spin-Flip & Spin-Flop*
  - *- Phase diagrams & Quantitative analysis*
- *More on AFM…(only one slide)*
- *van der Waals tunneling spin valves in Fe_3GeTe_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

Interlayer: Antiferromagnetic | Ferromagnetic

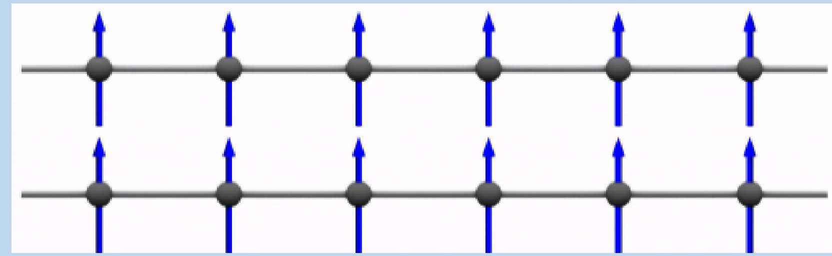
Intralayer: Ferromagnetic

Interlayer Antiferromagnetic — $J<0; J_L>0$



$CoPS_3$ Ref[1]
$MnPS_3$ Ref[2-5]
$NiPS_3$ Ref [6-8]

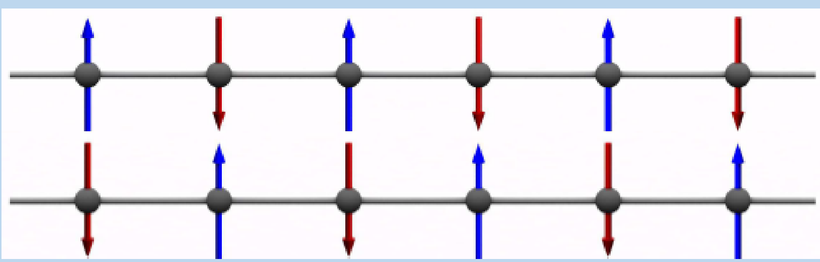
Interlayer Ferromagnetic — $J>0; J_L>0$



CrI_3 (bulk) Ref [9,10]
$CrBr_3$ (bulk, few layers) Ref[11,12]
$Cr_2Ge_2Te_6$ Ref[13,14]
Fe_3GeTe_2 Ref[15,16]
VSe_2 Ref[17-19]

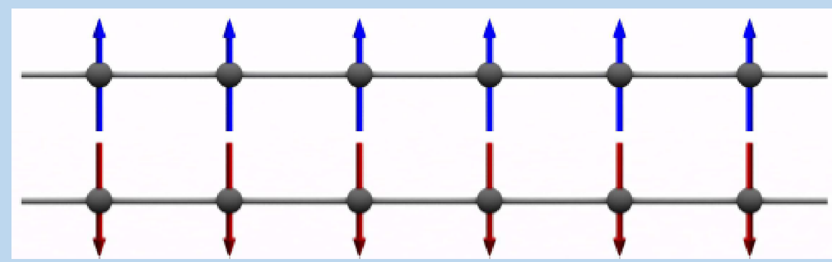
Intralayer: Antiferromagnetic

Interlayer Antiferromagnetic — $J<0; J_L<0$



$FePS_3$ Ref[20,21]
$MnPSe_3$ Ref[35]

Interlayer Ferromagnetic — $J>0; J_L<0$



CrI_3 (few layers) Ref[22]
$CrCl_3$ (bulk) Ref[37]

Green – semiconductor materials; orange - metallic

How can we probe magnetism in atomically thin crystals?
What do experimental probes really probe?

Basic Concepts of low-D magnetism

Interaction — Anisotropy

Heisenberg model $H = \sum J_{ij}\, \boldsymbol{S}_i \cdot \boldsymbol{S}_j - D\,(S_z{}^2)$

Ferromagnetism --- J_{ij}<0 (AF more complex but "similar")

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

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

(1 magnon = 1 spin flip)

Fluctuations: $\langle \delta \boldsymbol{M} \rangle \propto T \int_0^{BZ} \frac{d\boldsymbol{k}}{e^{\frac{\hbar\omega(\boldsymbol{k})}{kT}} - 1} \xrightarrow{k\to 0} T \int_0 \frac{k^{(d-1)} dk}{k^d} \xrightarrow{d\,\leq\,2} \infty$

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

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?*

$$H = \sum J_{ij} \boldsymbol{S}_i \cdot \boldsymbol{S}_j - D\,({S_z}^2)$$

How are J and D "coupled" to the band states ?

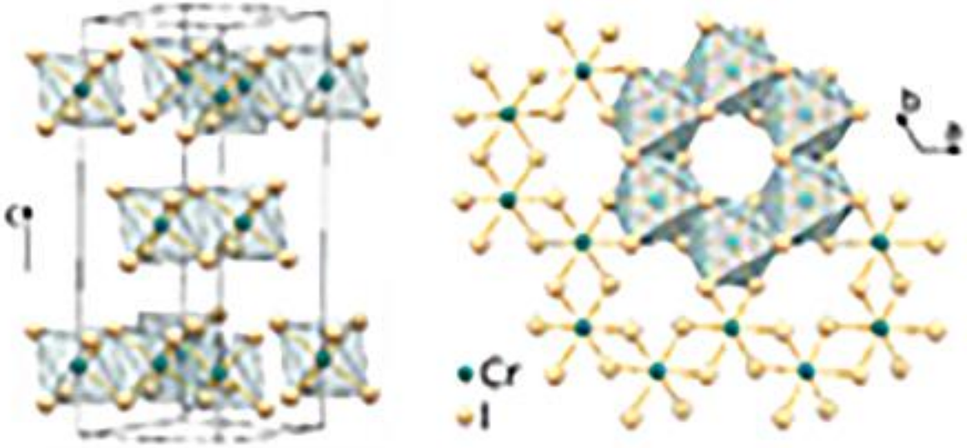
Key to understand: transport, optical properties, thickness evolution

Can we expect large effects? *From neutrons J & D typically ~ 1 – 2 meV*

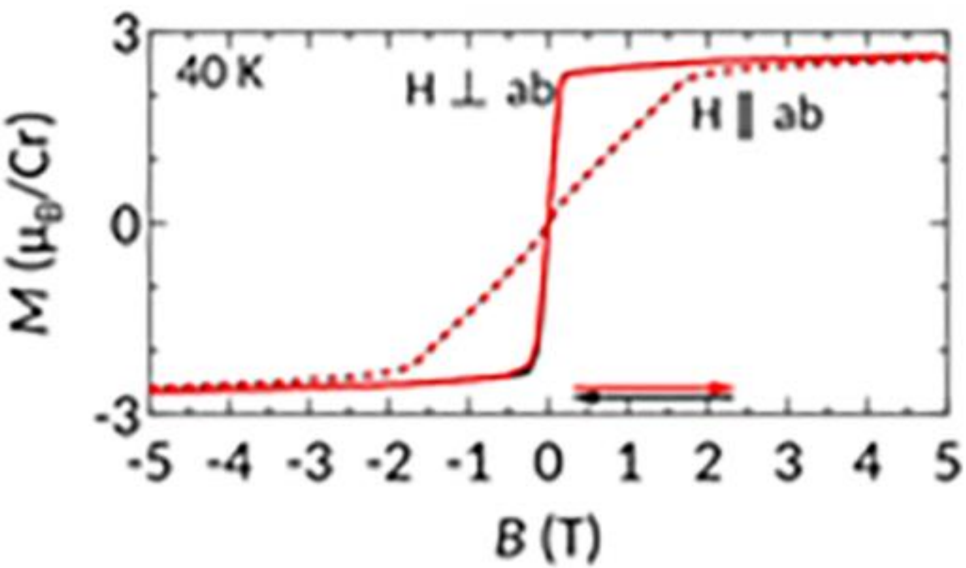
2) Electrostatic doping expected to have large effects

3) "Other" magnetic length scales;
"2D version" of phenomena known in 3D
….

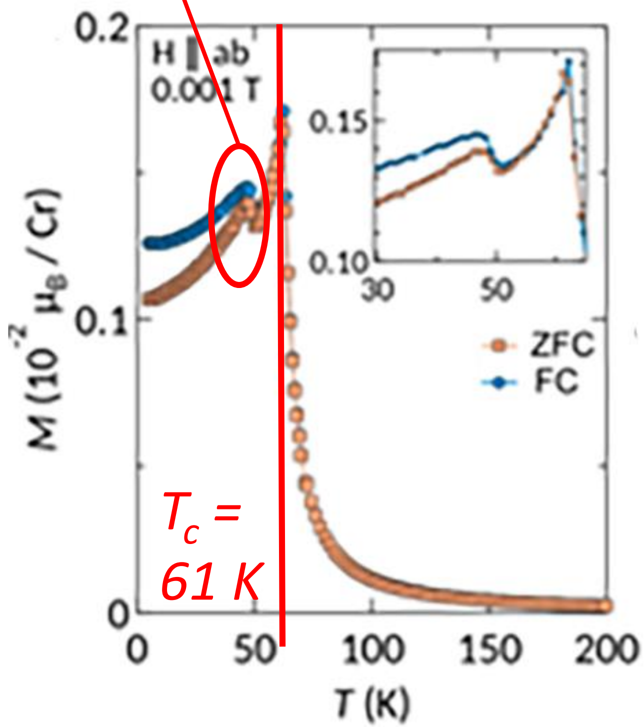
CrI_3
a bulk van der Waals ferromagnetic semiconductor



Soft bulk ferromagnet

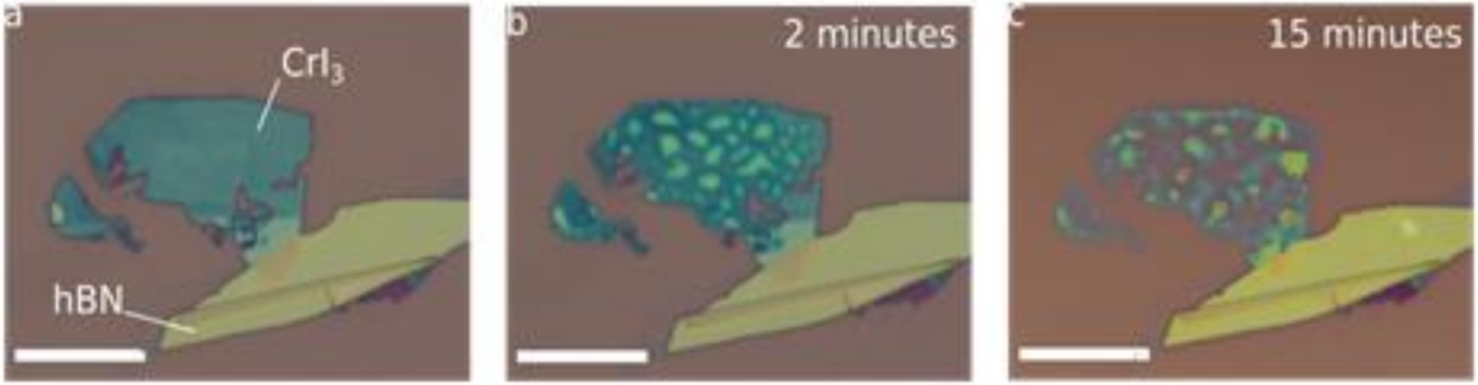


What's up at 51 K?



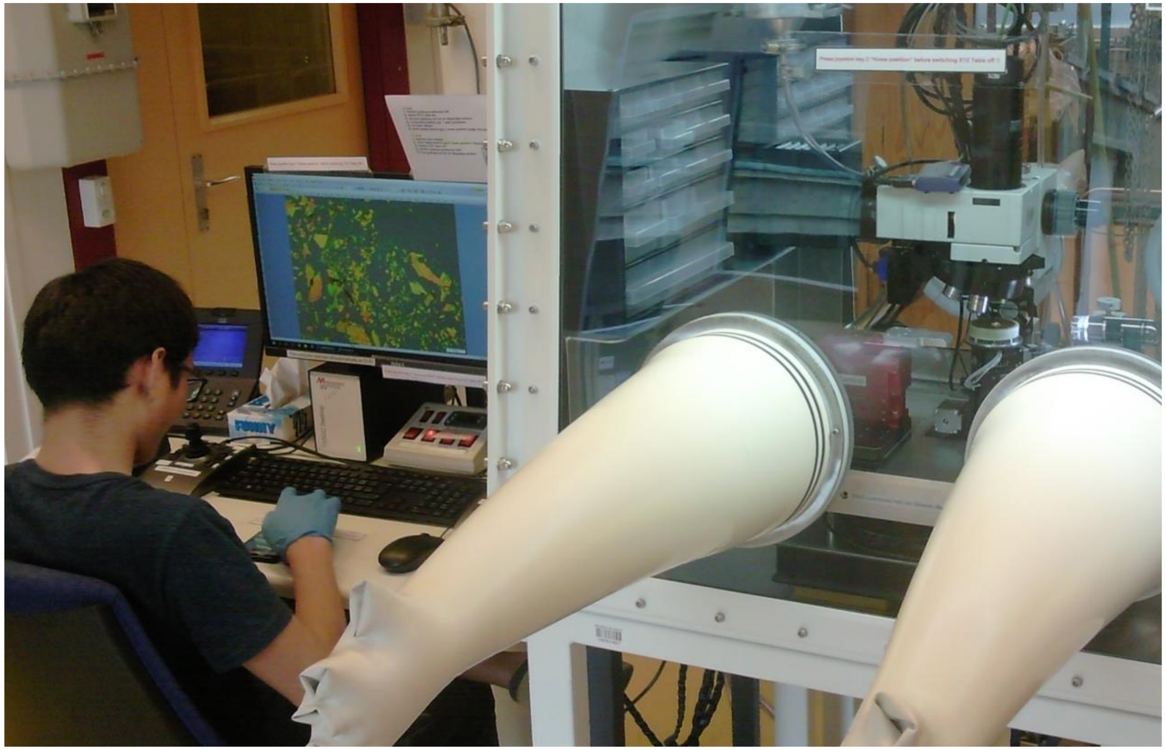
Bulk susceptibility

Exfoliating/processing/encapsulating in Glove box



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 Huang[1]*, Genevieve Clark[2]*, Efrén Navarro-Moratalla[3]*, Dahlia R. Klein[3], Ran Cheng[4], Kyle L. Seyler[1], Ding Zhong[1], Emma Schmidgall[1], Michael A. McGuire[5], David H. Cobden[1], Wang Yao[6], Di Xiao[4], Pablo Jarillo-Herrero[3] & Xiaodong Xu[1,2]

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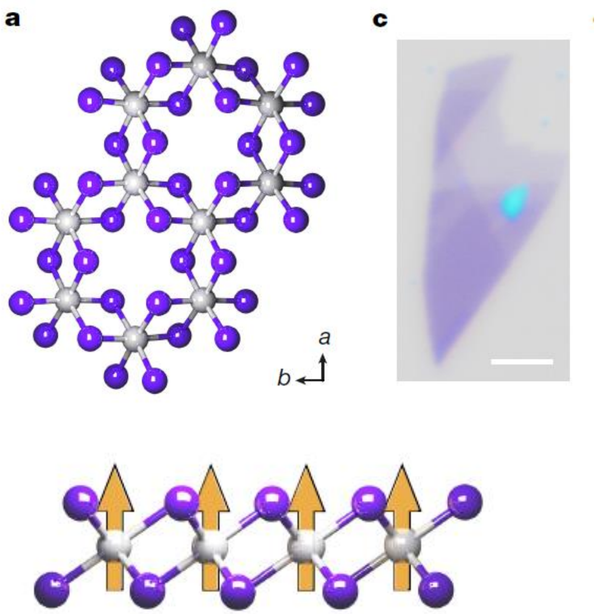
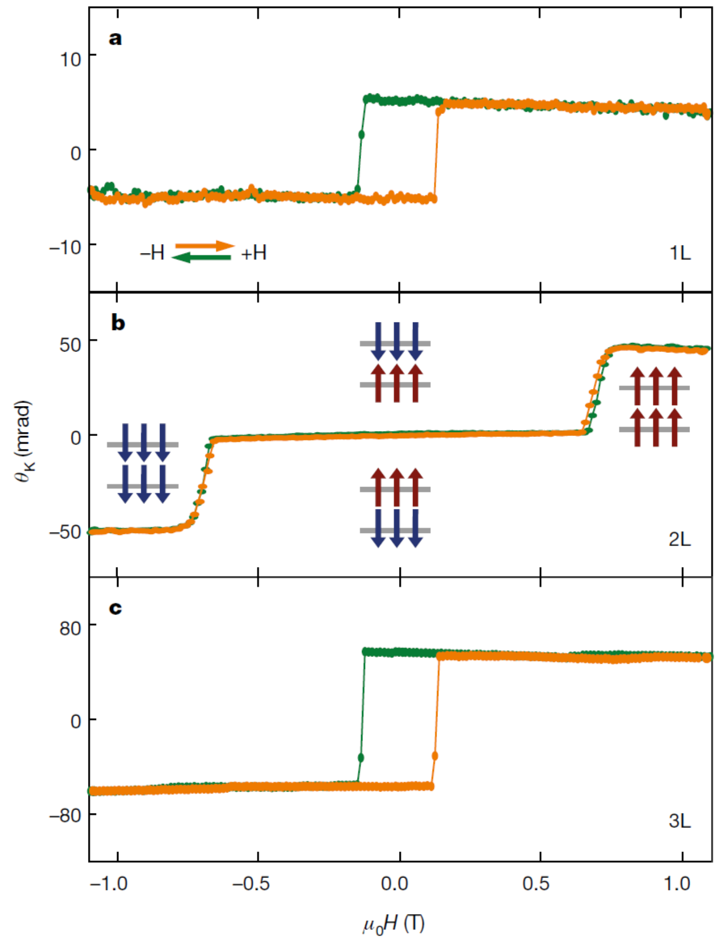
Magneto-optical Kerr effect to probe magnetism



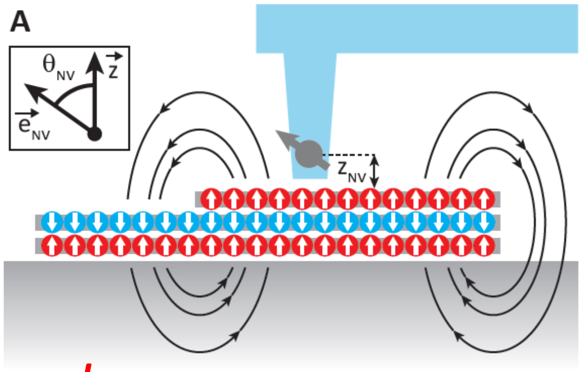


Hysteretic Kerr rotation angle as expected for ferromagnets

How to measure magnetization of 2D materials?
Scanning magnetometry of 2D magnets

Single-spin magnetometer:

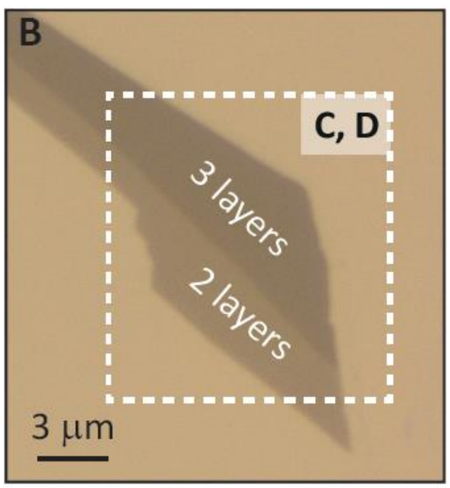
Maletinsky's group



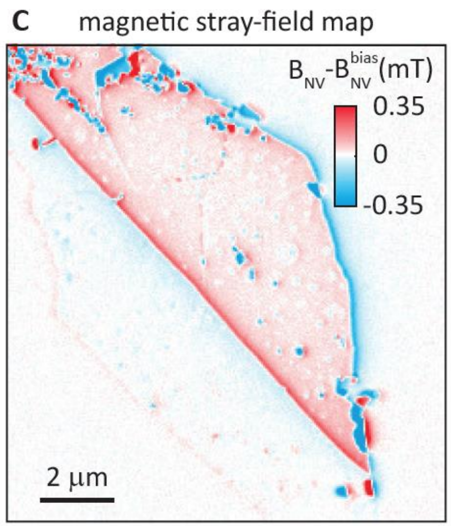
Individual NV-center on diamond tip

- *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*

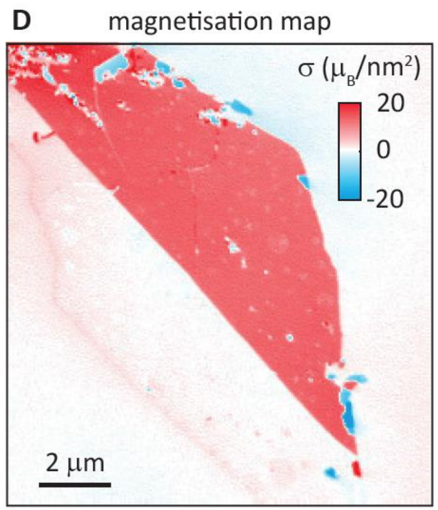
Example



2L and 3L CrI3 on same flake



Fringing field only on 2L

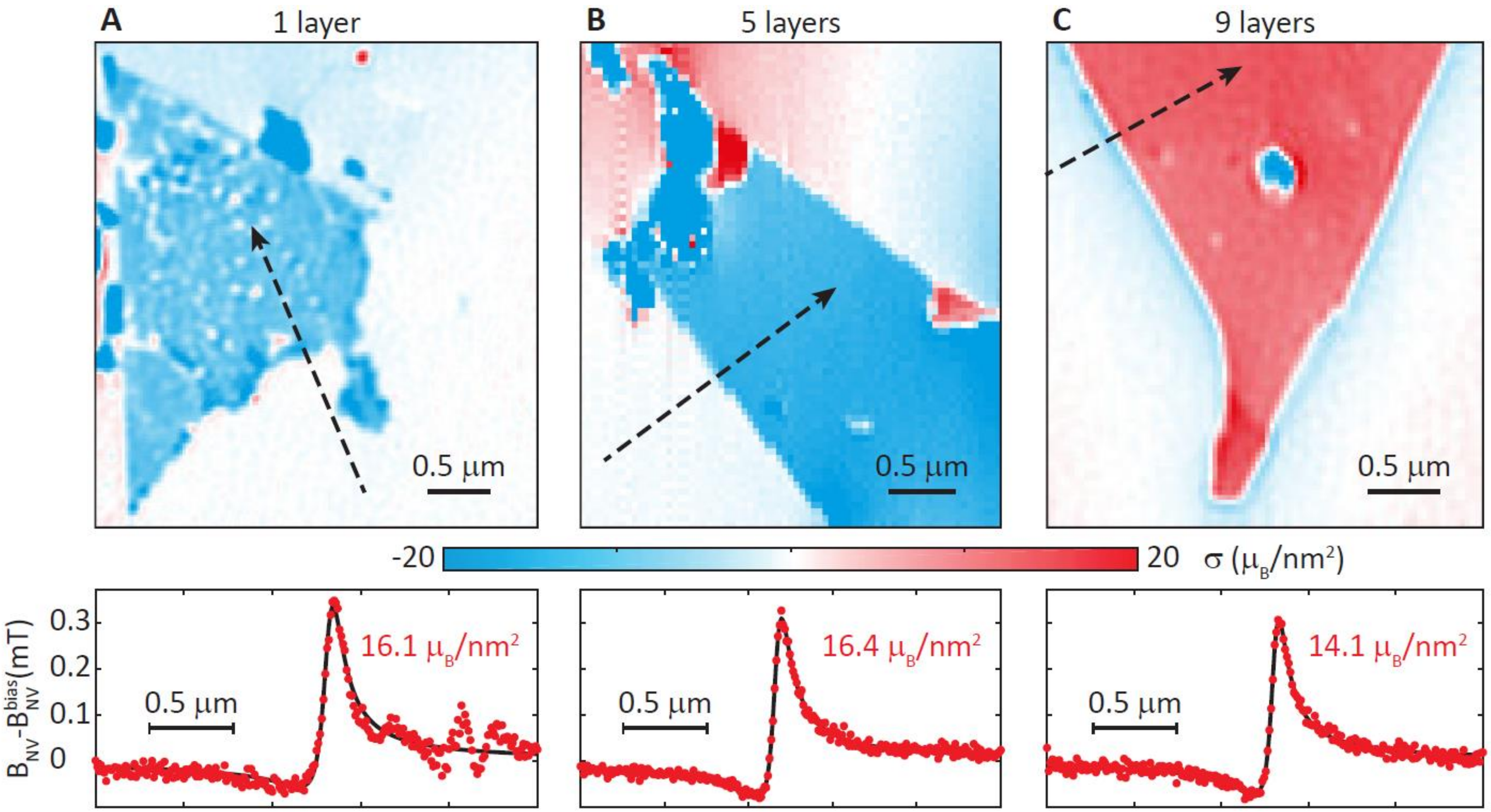


M(2L) = 0
M(3L) ~ 16 μ_B/nm^2

Direct observation of layered antiferromagnetism

In all even multilayers: M = 0

In all odd multilayers: M ~ 16 μ_B/nm^2

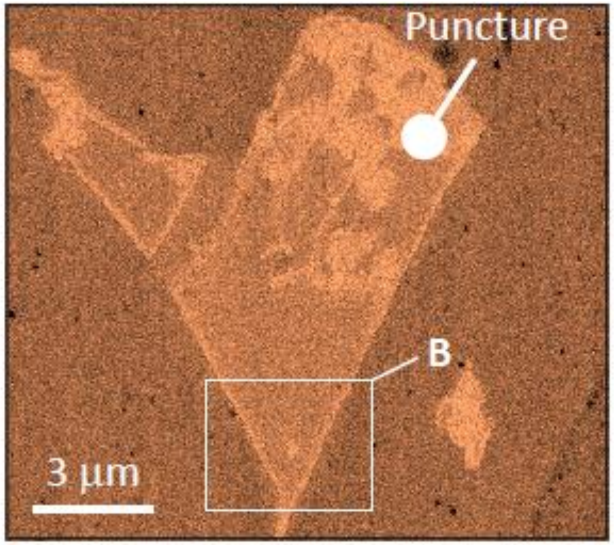


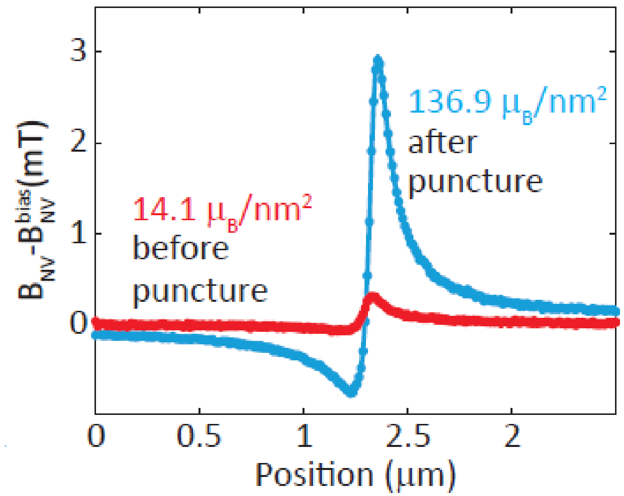
L.Thiel, Z. Wang, AM, P. Maletinsky et al Science 2019

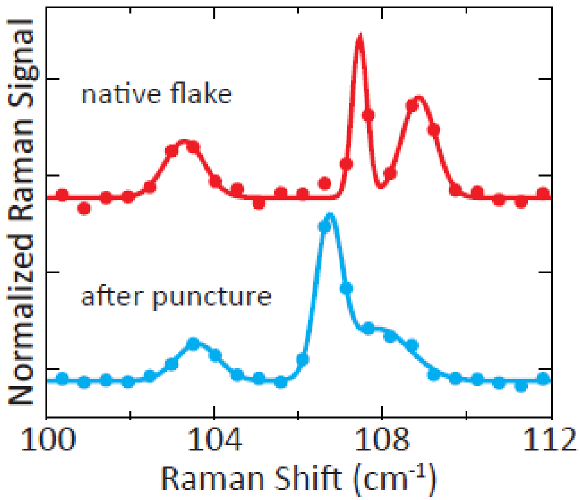
Sign of exchange coupling depends on strain?

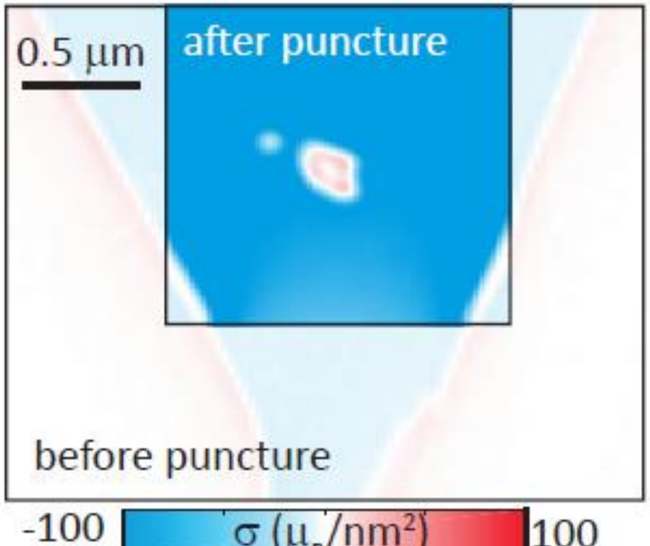
Why bulk is FM and multilayers are AFM?

Magnetic state may depend on structure



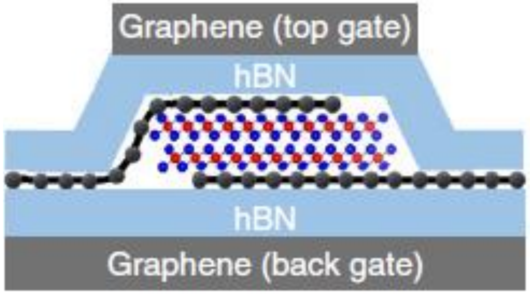




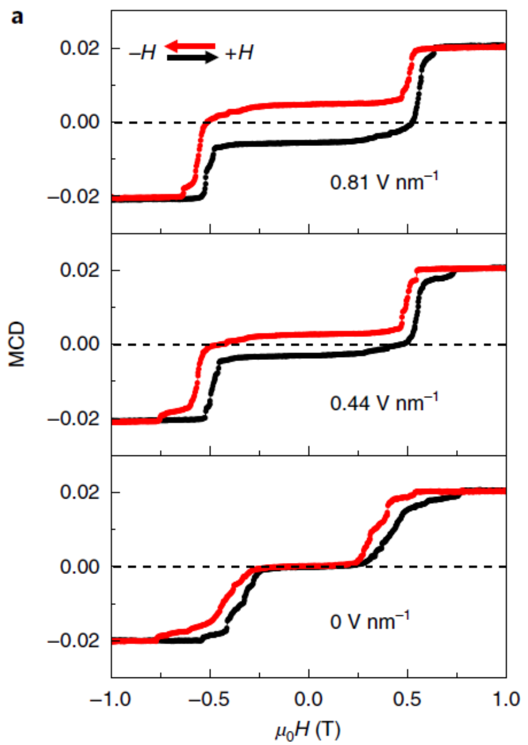


L.Thiel, Z. Wang, AM, P. Maletinsky Science 2019

Kerr-effects in double gated CrI_3 bilayer devices

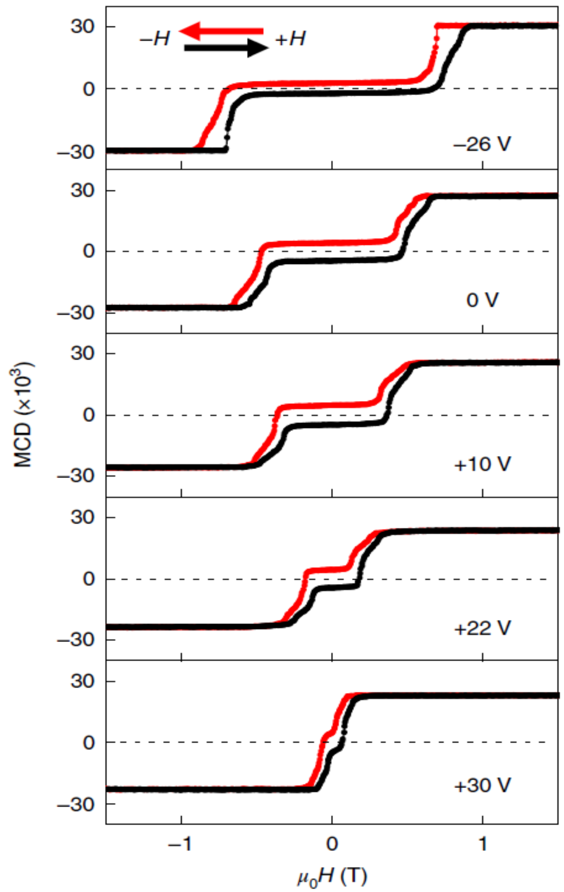


Opposite polarity =
E-field



Magnetoelectric effect

Same polarity =
n accumulation



Electron accumulation:
Turns AFM into FM

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

...But...

1) In which states does the charge go?

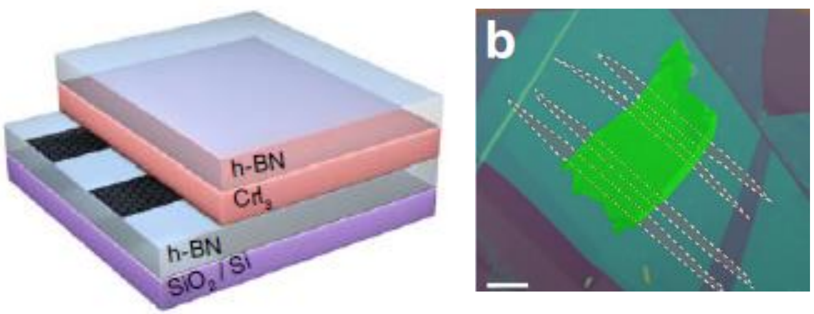
CrI_3 = semiconductor

E_F is in the gap

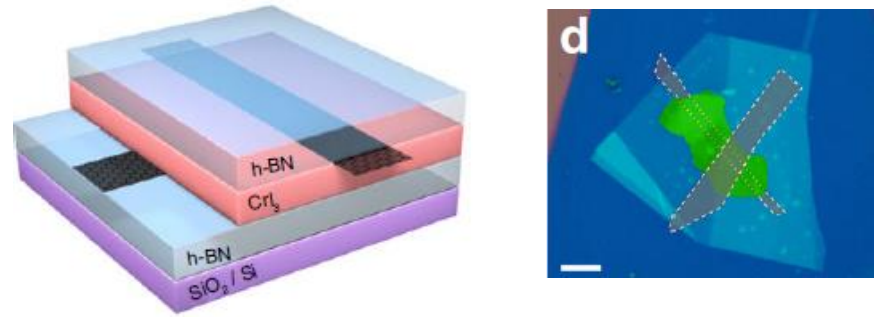
2) How much charge is accumulated?

Devices for transport measurements

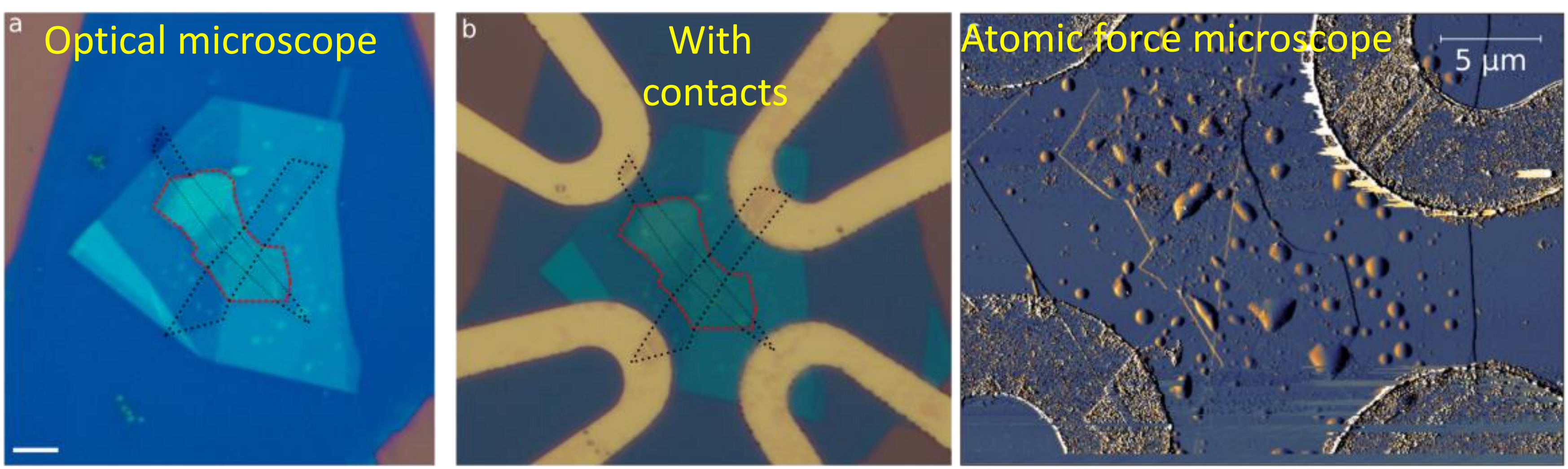
In-plane transport =
field-effect transistor



Thin CrI_3 as tunnel barrier
between graphene contacts

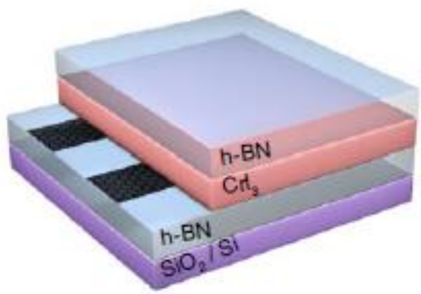


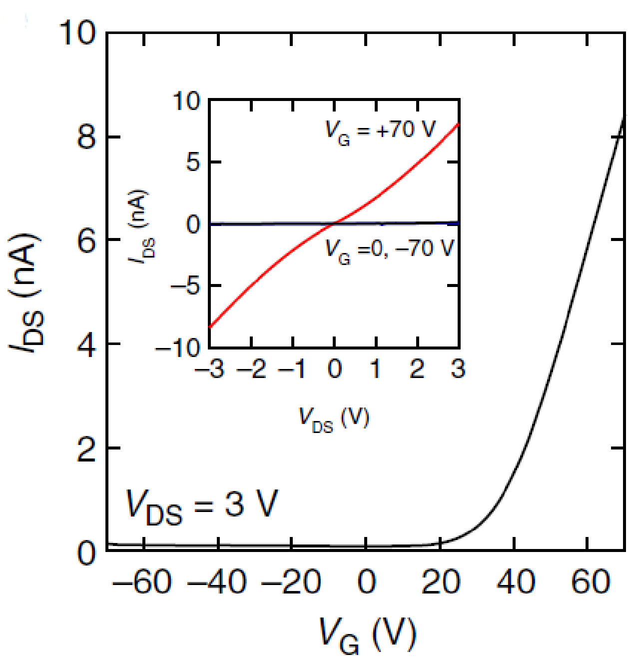
Example of tunnel barrier device



In-plane and vertical transport

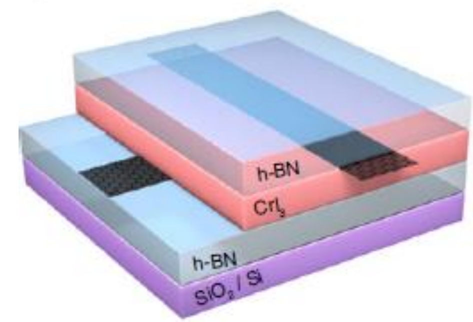
In-plane transport =
field-effect transistor

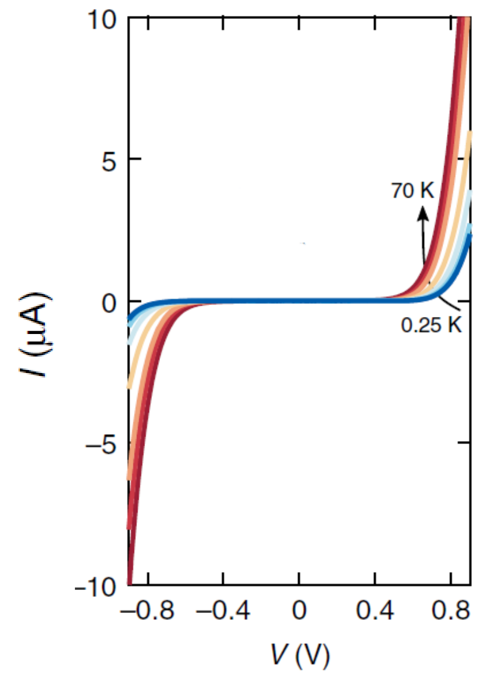


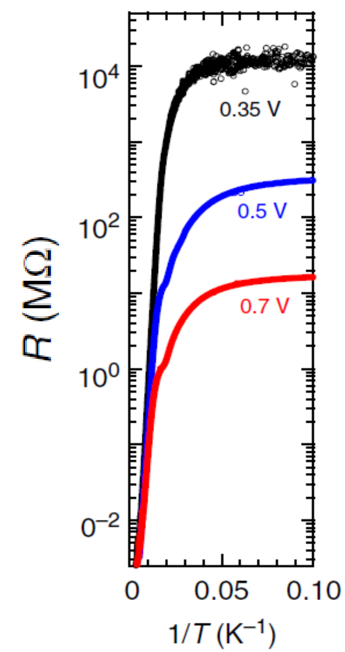


Below 150 K: too insulating

Vertical transport =
tunnel barrier





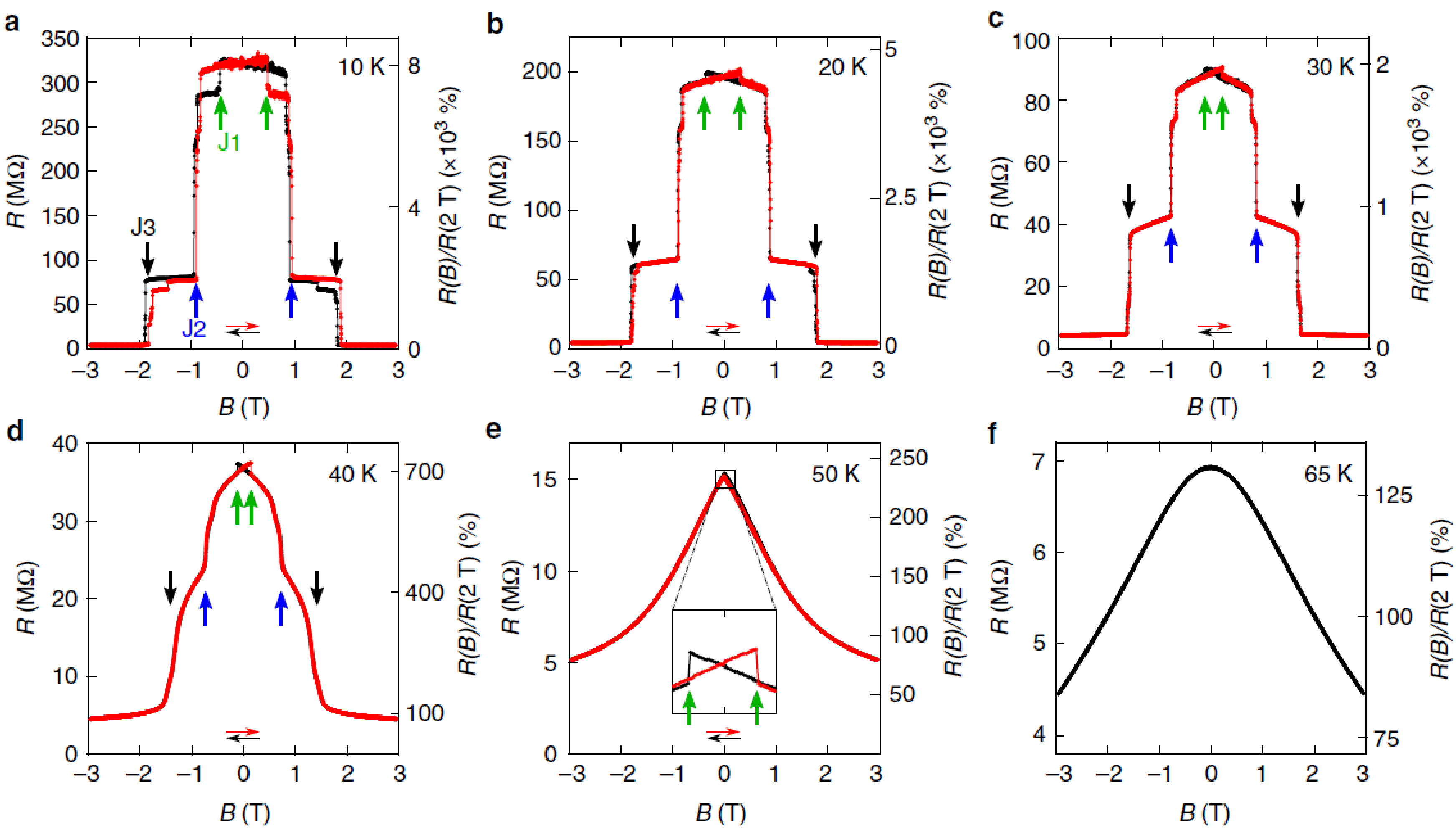


Works down to the lowest T

Tunneling Magnetoresistance

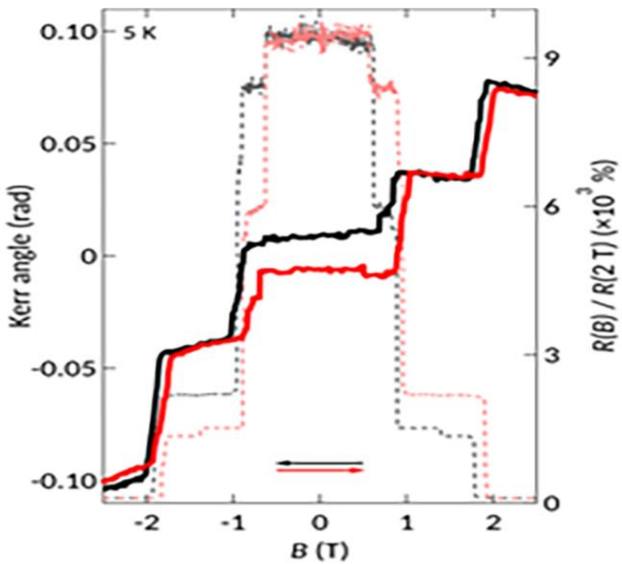
New phenomenon:

10'000 % magnetoresistance due to magnetic states of the tunnel barrier

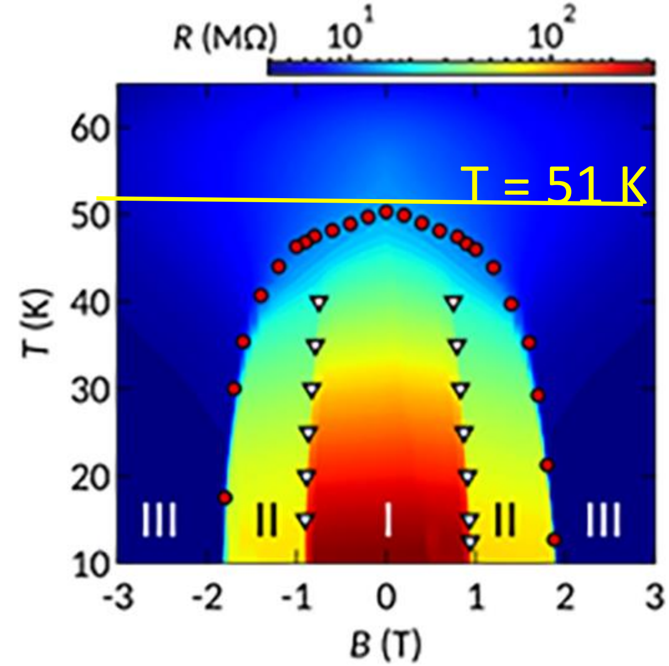


Different Magnetic States in Atomically Thin CrI_3

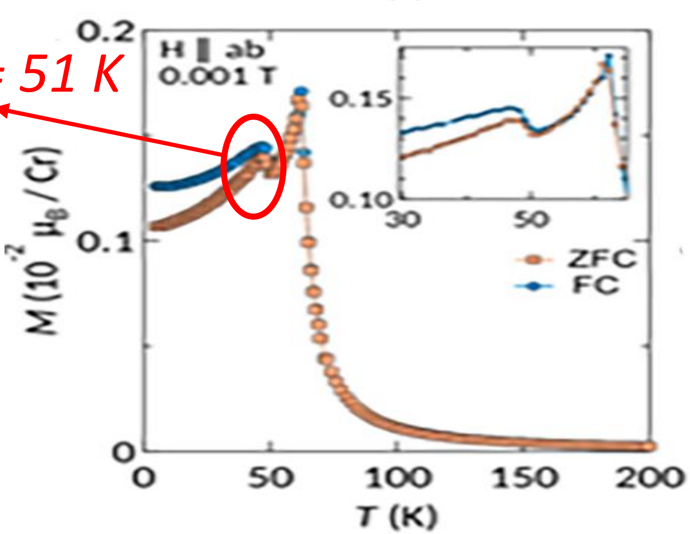
Steps also visible in Kerr effect
(with A. Imamoglu, M. Kroner @ETH)



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



T_c = 51 K



Questions:

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

Z. Wang et al Nat Comms 9, 2516 (2018)

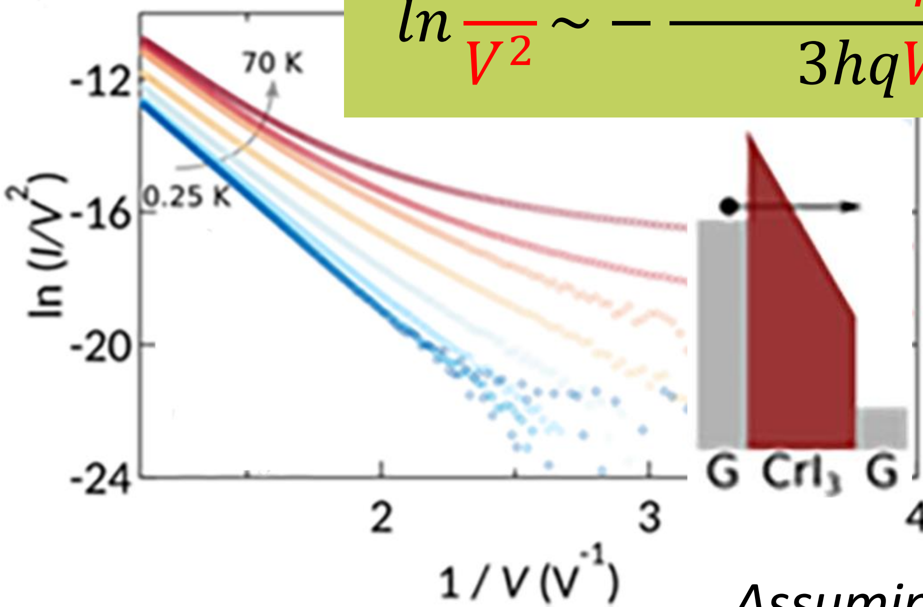
Similar results on MR

Science 360, 1214 (2018) Xu's group

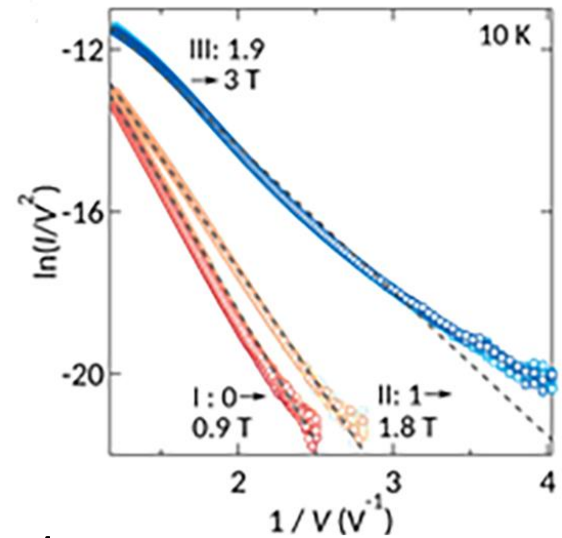
360, 1218 (2018) Jarillo-Herrero's group

Tunneling: Fowler-Nordheim regime

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



Barrier height depends
on magnetic state

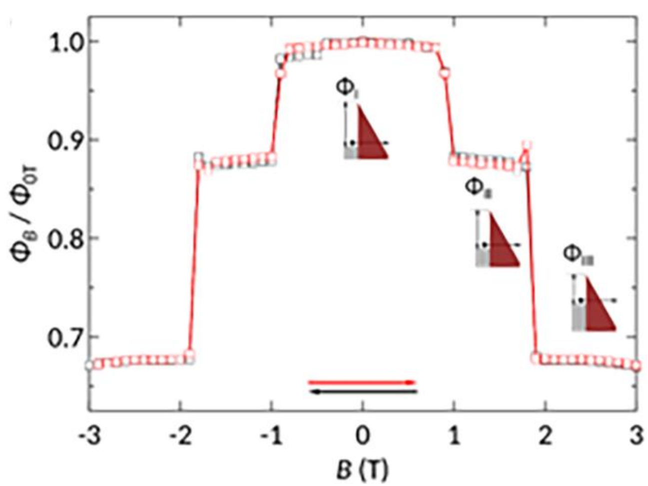


Assuming m* = free-electron mass

Barrier height:

B = 0 ~ 250 meV

B = 2T ~ 170 meV



Change in barrier height: 50 – 100 meV

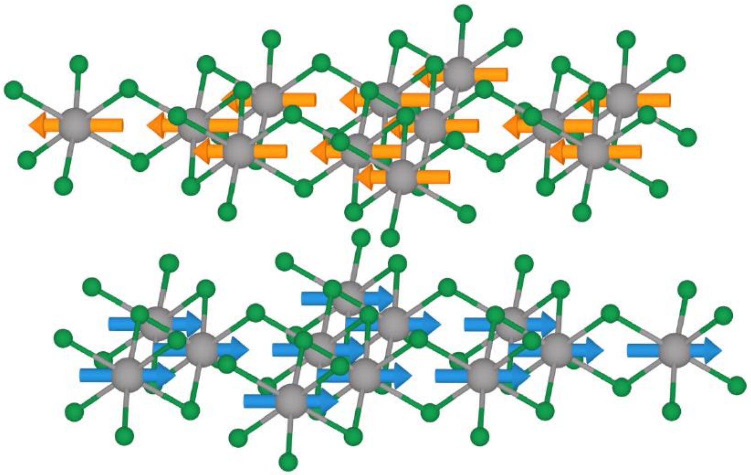
But exchange integrals 2-3 meV…

???

$$H = \sum J_{ij} \boldsymbol{S}_i \cdot \boldsymbol{S}_j - D\,({S_z}^2)$$

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

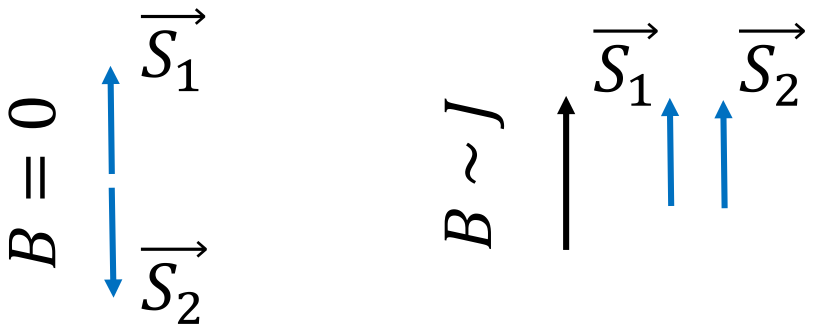
Energy scales and magnetic states of an antiferromagnet

Exchange = J ; $E = J\overrightarrow{S_1} \cdot \overrightarrow{S_1}$ Anisotropy = K ; $E = -K{S_z}^2$

Zeeman = μB ; $E = -\mu\vec{B} \cdot \vec{S}$

Bulk

Strong anisotropy = Large K

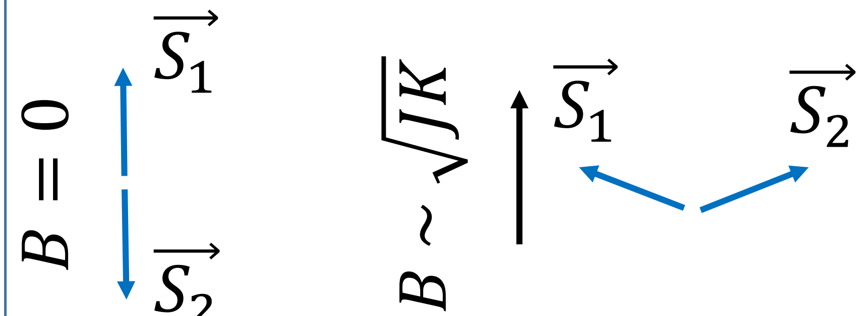


Energy balance:

$$\Delta E \sim -\ \mu B + J$$

Spin-flip transition

Weak anisotropy = Small K

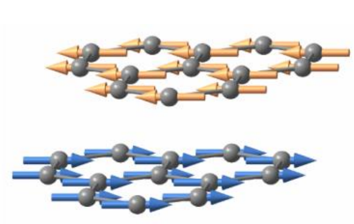


Energy balance:

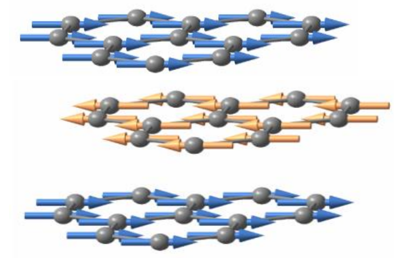
$$\Delta E \sim -\frac{\mu B}{J}\mu B + K$$

Spin-flop transition

Even-odd effect in weakly anisotropic AFM multilayers

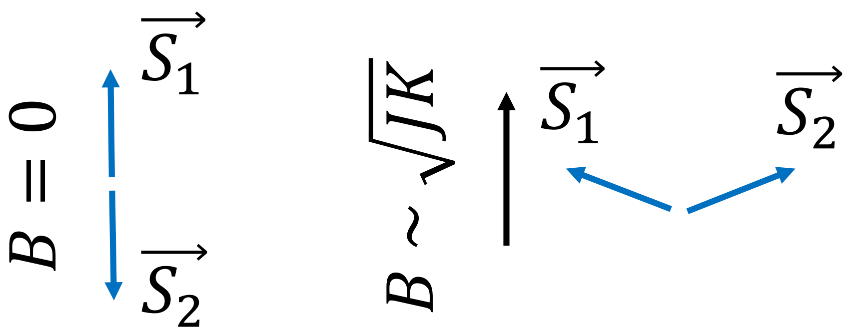


$CrCl_3$ = *layered antiferromagnet with weakly anisotropic easy plane*



K=0

Even-N



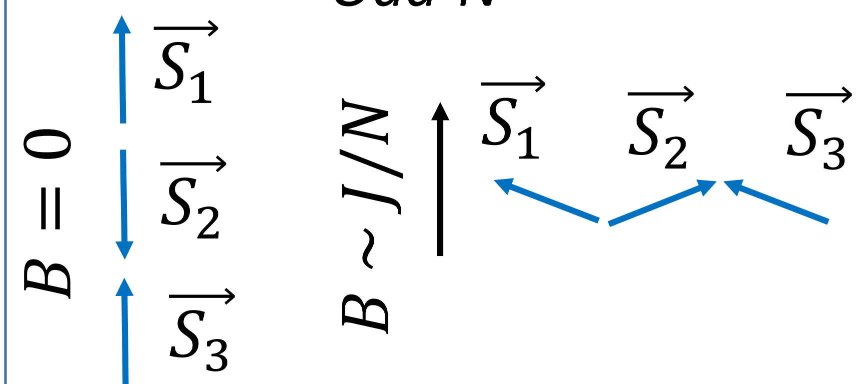
Just like in the bulk

Energy balance:

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

Spin-flop transition at B ~ 0

Odd-N



Net magnetization for odd N

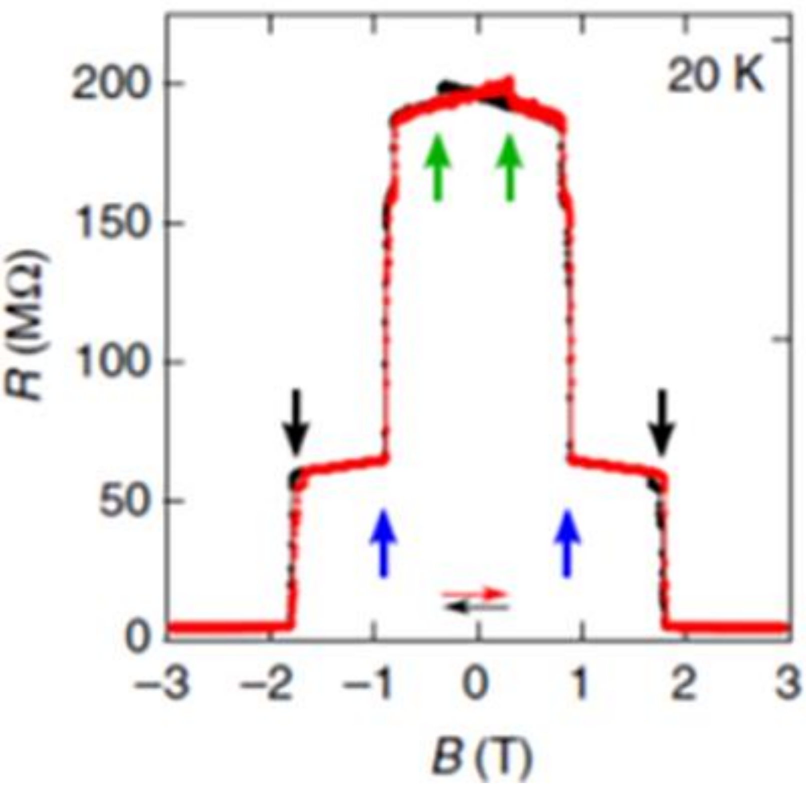
Energy balance:

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

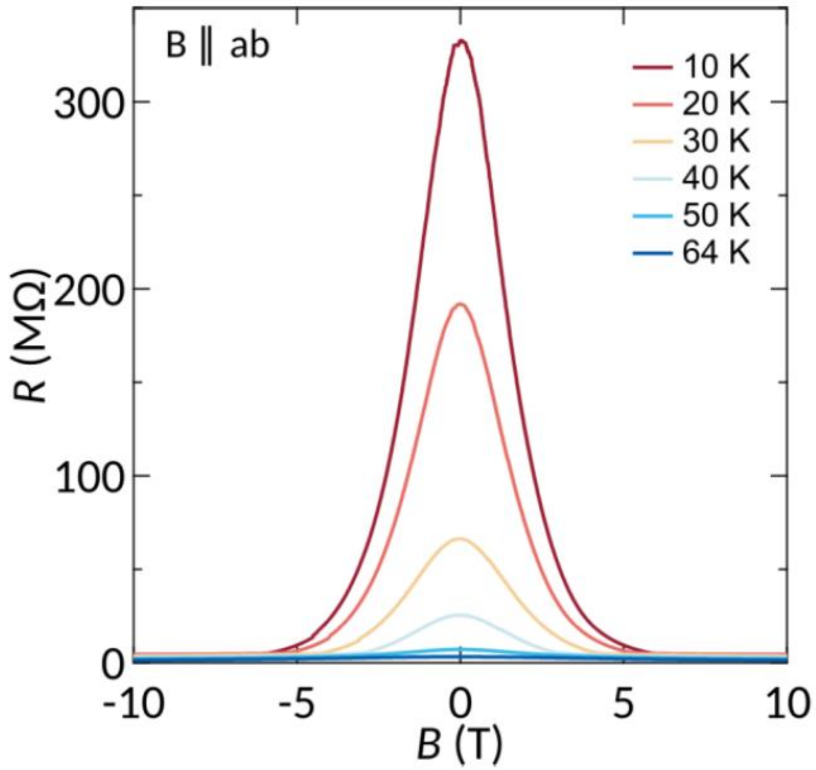
Spin-flop transition at B ~ J/N

Compare with CrI_3

Perpendicular field



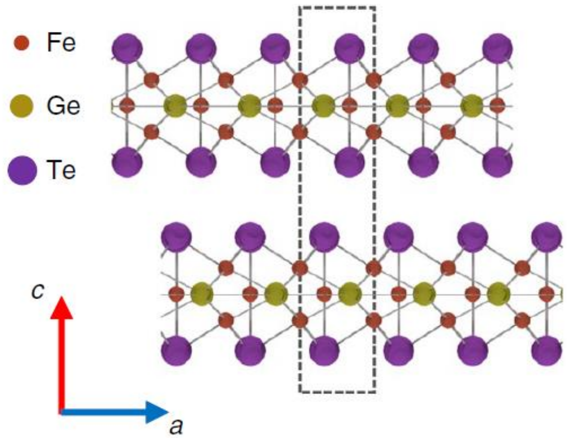
In-plane field

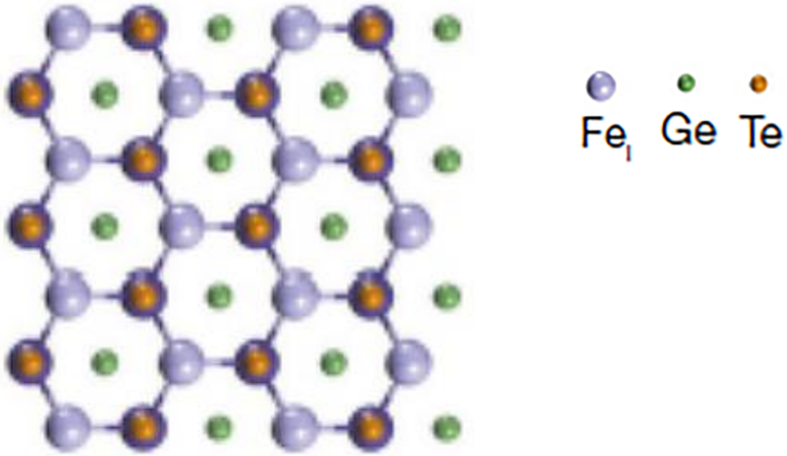


Strong uniaxial anisotropy in CrI_3

Spin alignment occurs different in in-plane and perpendicular field

Fe_3GeTe_2: a van der Waals ferromagnetic metal





Gate-tunable room-temperature ferromagnetism in two-dimensional Fe_3GeTe_2

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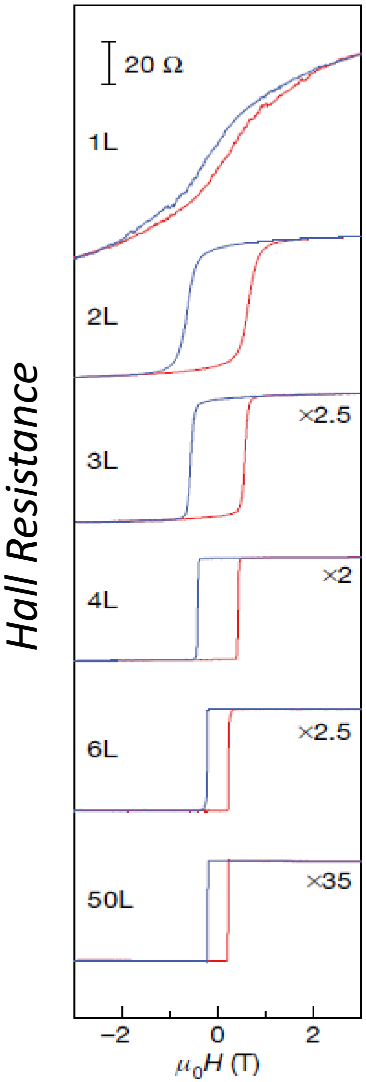
Yuanbo Zhang's group @Fudan

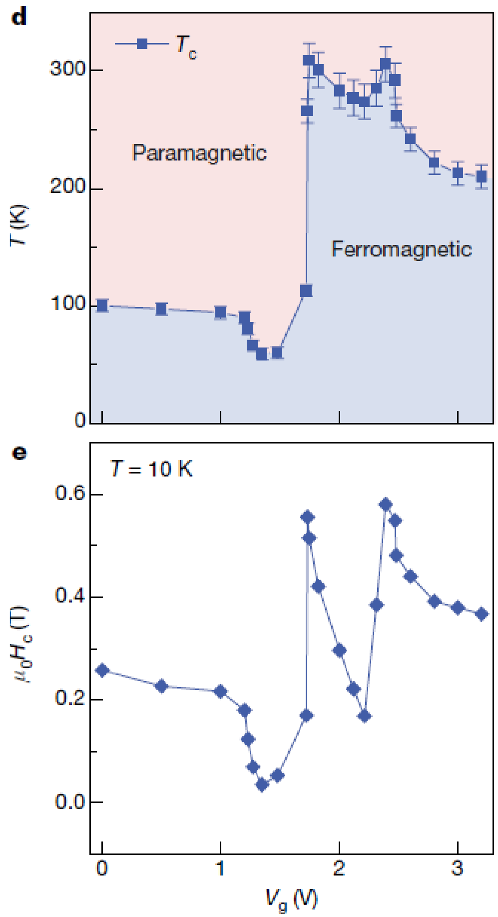
Thickness evolution

(ML T_c ~ 20 K)



Gate-driven

Li intercalation

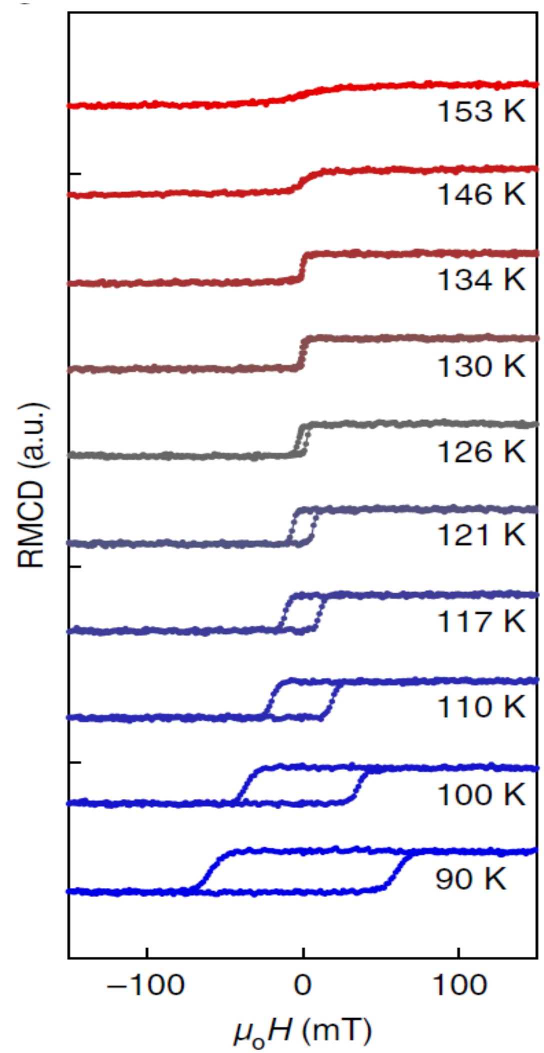


Two-dimensional itinerant ferromagnetism in atomically thin Fe_3GeTe_2

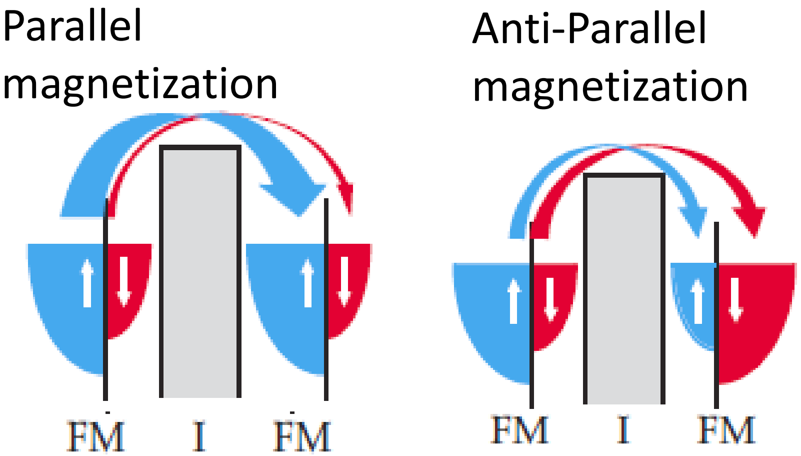
NATURE MATERIALS | VOL 17 | SEPTEMBER 2018 | 778–782 |

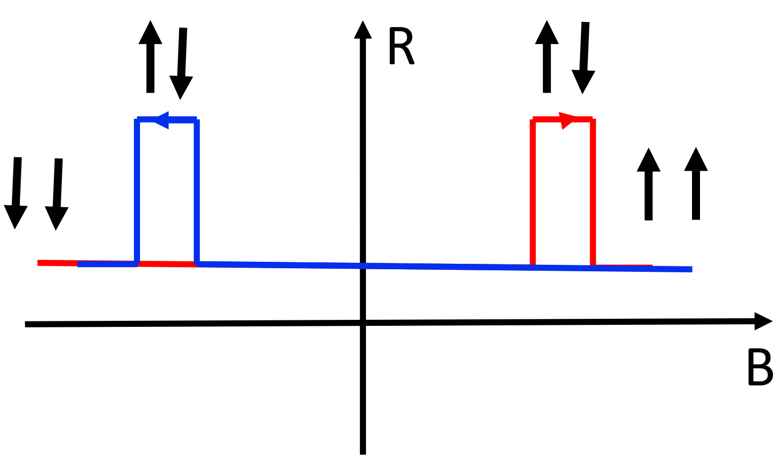
Xiadong Xu's group @Seattle

MOKE: ML T_c ~ 130 K



Tunneling Spin Valves





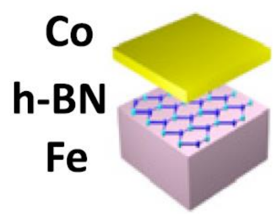
$$TMR = \frac{R_{AP} - R_P}{R_{AP}} = \frac{2P_1P_2}{1 - P_1P_2}$$

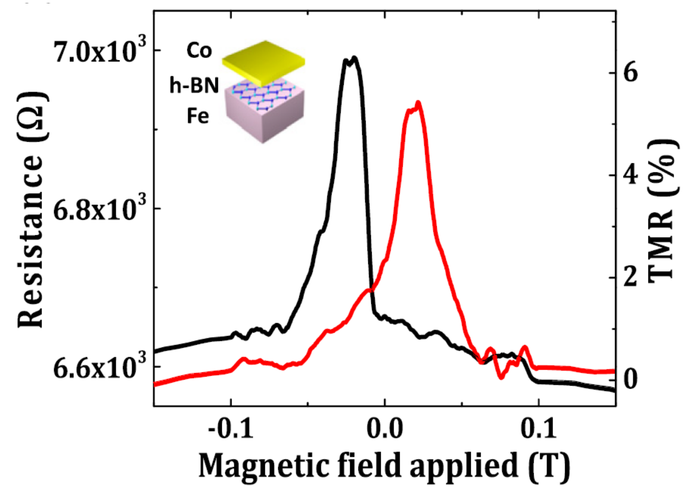
Conventional ferromagnetic metal films with hBN tunnel barrier

Magnetic tunnel junctions with monolayer hexagonal boron nitride tunnel barriers

M. Piquemal-Banci,[1] R. Galceran,[1] S. Caneva,[2] M.-B. 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)



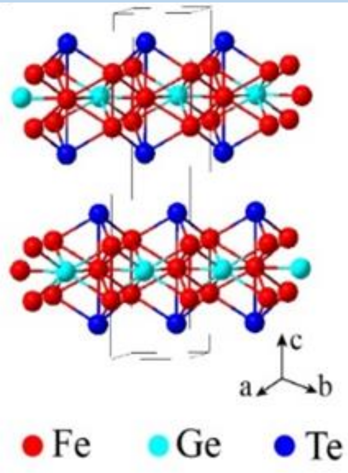


Ideal behavior difficult to achieve

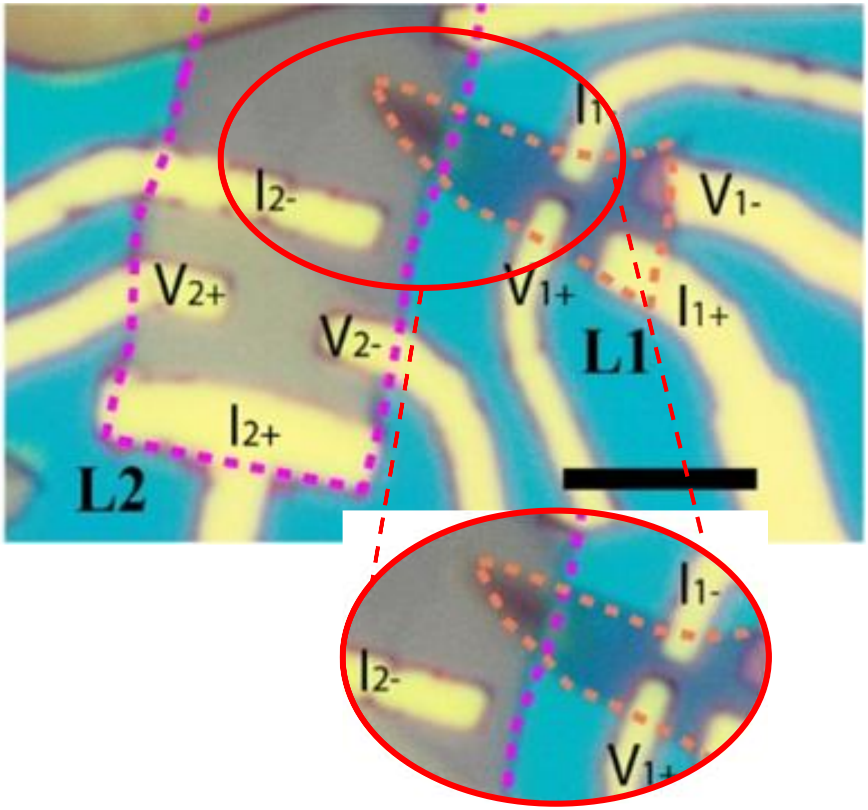
- Magnetization switching
- Tunnel barrier quality
- etc.

Van der Waals Magnetic tunnel junction

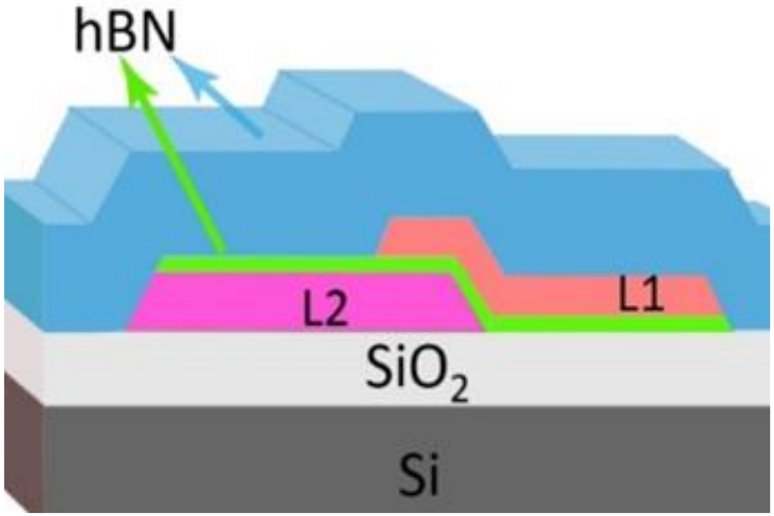
Fe_3GeTe_2 / hBN / Fe_3GeTe_2



Fe_3GeTe_2: *ferromagnetic for $T < T_c = 220$ K*



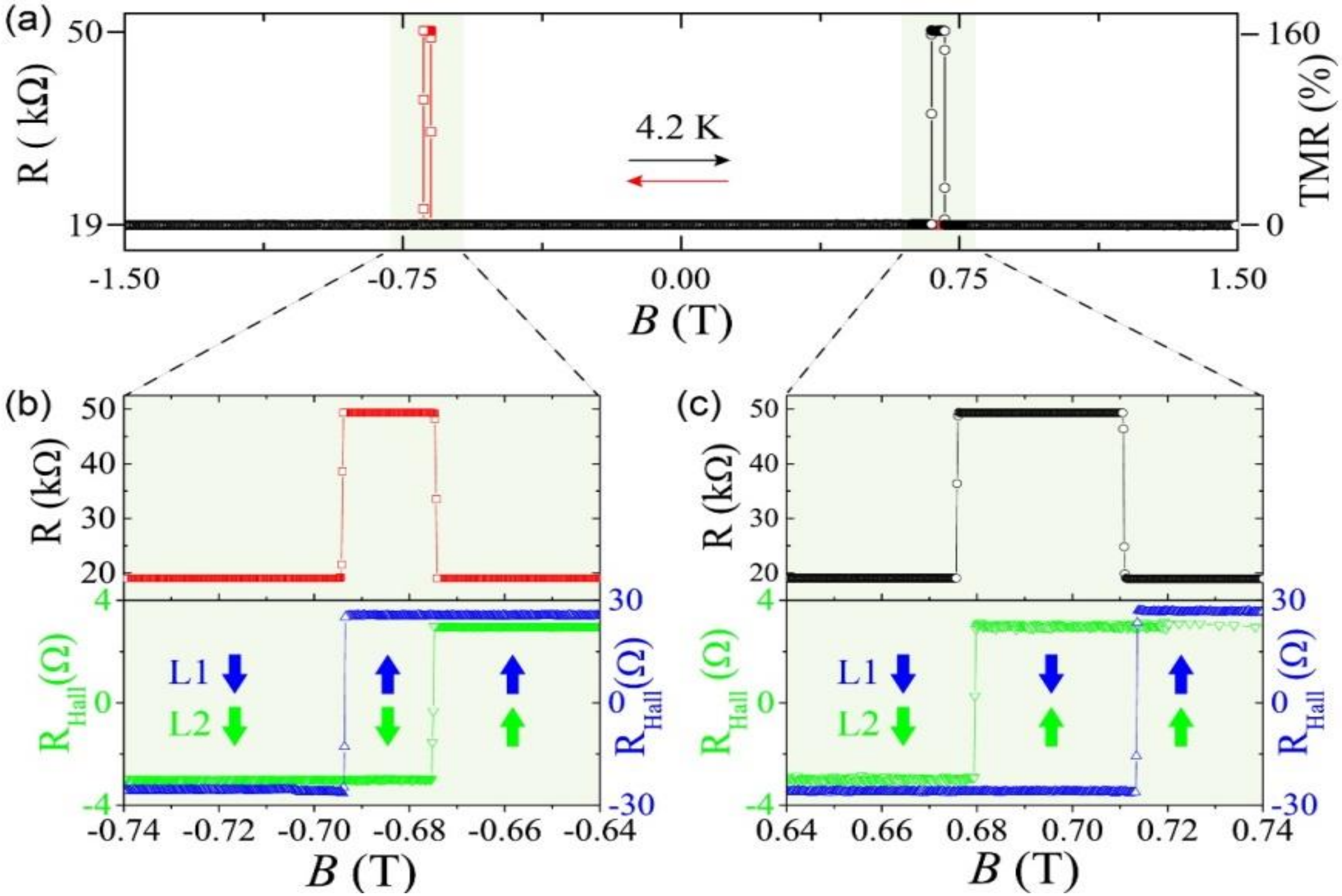
Van der Waals Heterostructure = *Tunneling spin valve*



Measure TMR + anomalous Hall effect

$$R_{Hall} = R_H H + R_A M$$

Fe_2GeTe_3 / hBN /Fe_2GeTe_3 = Ideal TMR behavior



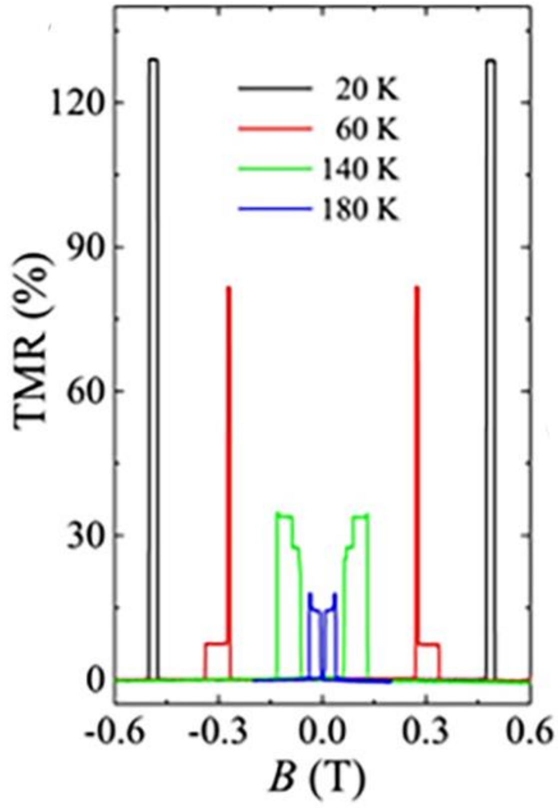
TMR = 160 %

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

Z. Wang, AM et al Nano Letters 2018

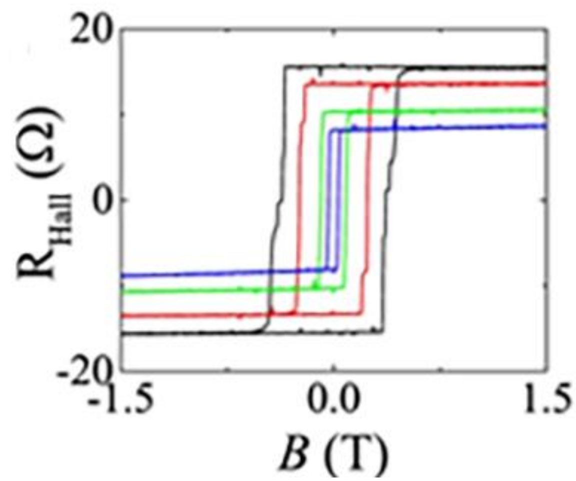
TMR & anomalous Hall conductivity = same T dependence

Tunneling Magneto-Resistance

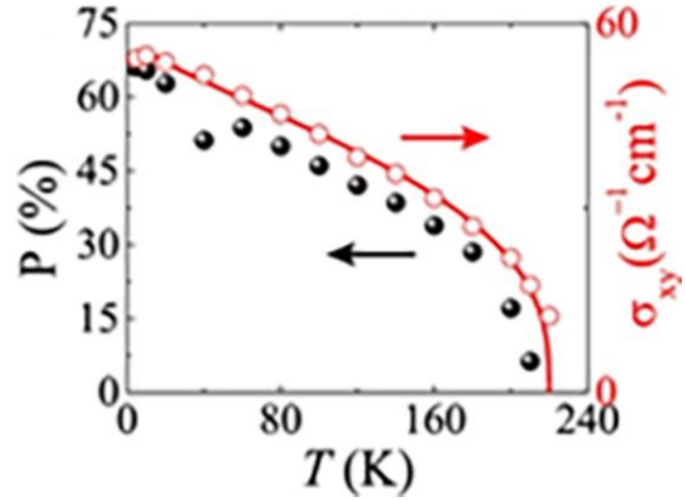


Anomalous Hall effect

$R_{Hall} = R_H H + R_A M$



Compare temperature dependence



Spin polarization at the surface proportional to bulk magnetization

$Co_{1/3}NbS_2$ a helical magnet with 48 nm pitch

Topological transitions:
states with different spin winding number

Controlling the Topological Sector of Magnetic Solitons in Exfoliated $Cr_{1/3}NbS_2$ 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)

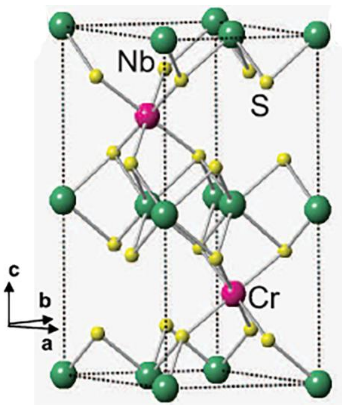
Chiral Magnetic Soliton Lattice on a Chiral Helimagnet PRL **108**, 107202 (2012)

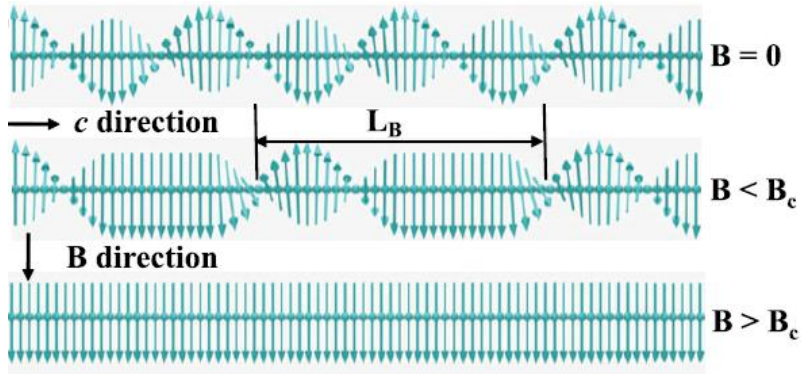
Y. Togawa,[1,2] T. Koyama,[3] K. Takayanagi,[1] S. Mori,[2,3] Y. Kousaka,[4] J. Akimitsu,[4] S. Nishihara,[5] K. Inoue,[5,6] A. S. Ovchinnikov,[7] and J. Kishine[8]

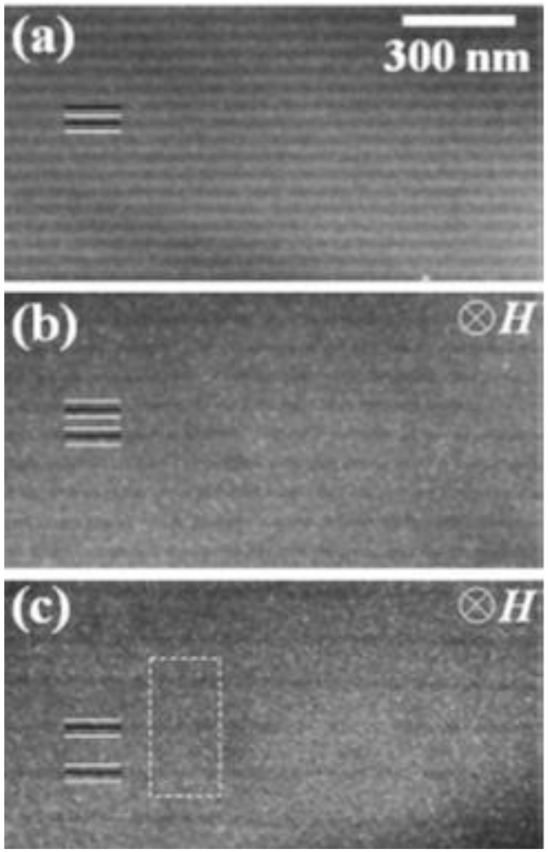
Interlayer Magnetoresistance due to Chiral Soliton Lattice Formation in Hexagonal Chiral Magnet $CrNb_3S_6$ PRL **111**, 197204 (2013)

Y. Togawa,[1,2,*] Y. Kousaka,[3] S. Nishihara,[4] K. Inoue,[4,5] J. Akimitsu,[3] A. S. Ovchinnikov,[6] and J. Kishine[7]

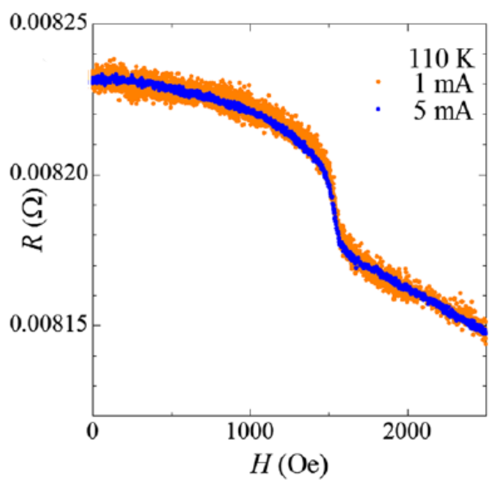
Direct observation by Lorentz microscopy







Magnetic structures coupled to transport: *aligning spins lowers resistance*



Spin structure of the anisotropic helimagnet $Cr_{1/3}NbS_2$ in a magnetic field

Benjamin J. Chapman,[1] Alexander C. Bornstein,[1] Nirmal J. Ghimire,[2,3] David Mandrus,[2,3,4] and Minhyea Lee[1]

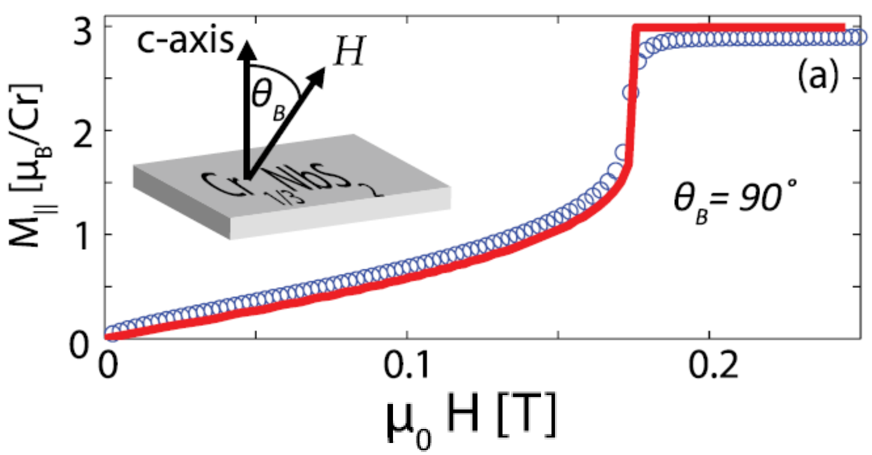
APPLIED PHYSICS LETTERS **105**, 072405 (2014)

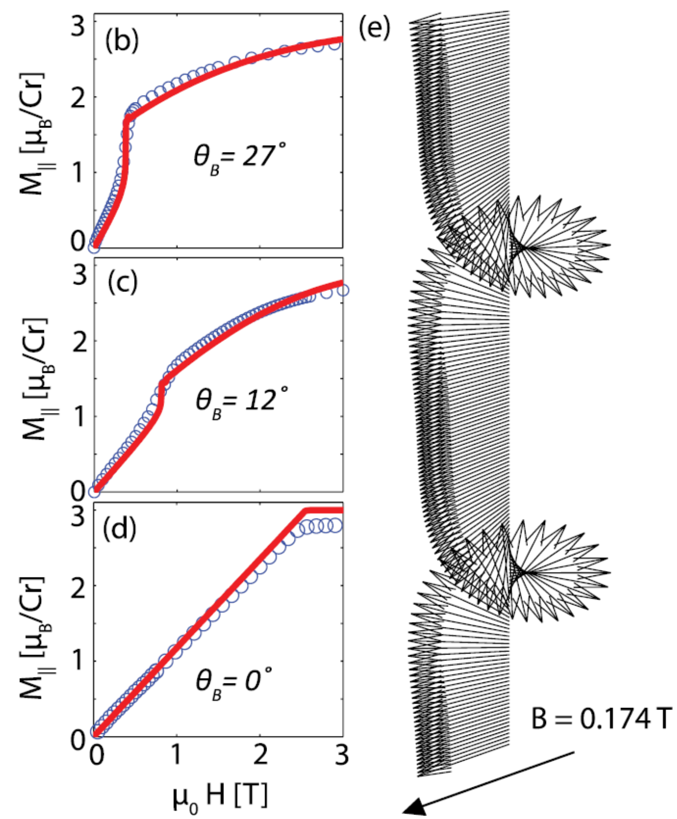
$$\mathcal{H} = \sum_i \left[-J\, \boldsymbol{s}_i \cdot \boldsymbol{s}_{i+1} - \boldsymbol{D} \cdot (\boldsymbol{s}_i \times \boldsymbol{s}_{i+1}) - \mu_B \boldsymbol{B} \cdot \boldsymbol{s}_i + A(\hat{z} \cdot \boldsymbol{s}_i)^2 \right]$$

Ferromag. exchange

Dzyaloshinskii Moriya

In-plane anisotropy



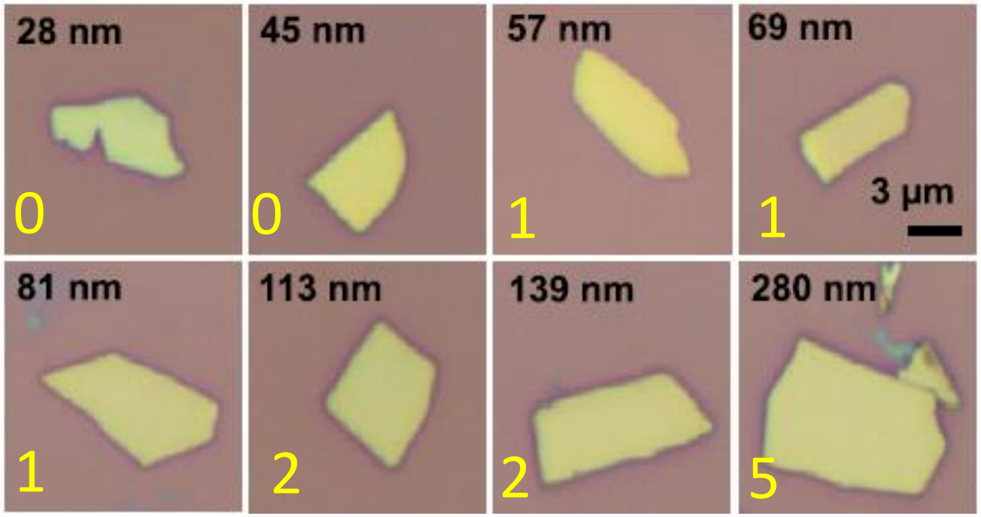


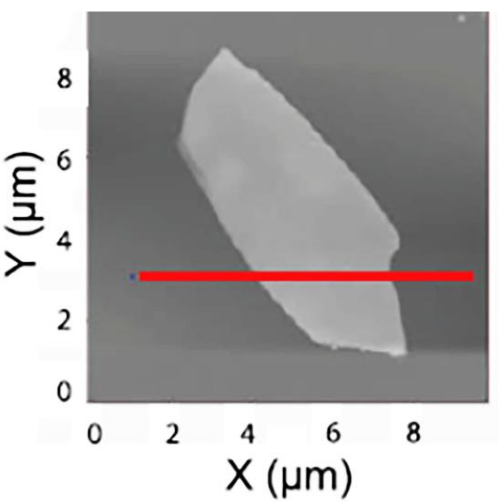
- *Bulk well-understood*
- *Model parameters can be extracted quantitatively*

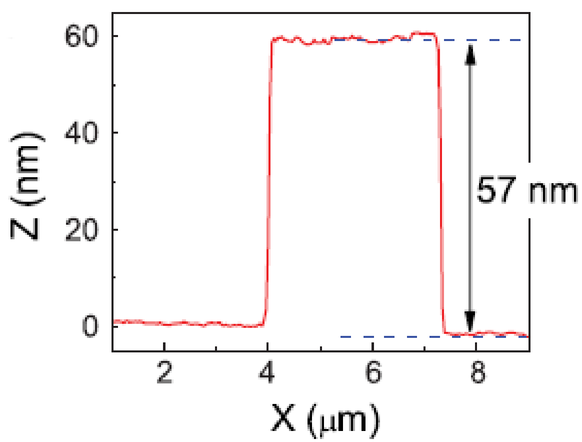
Varying thickness: shorter/longer than magnetic pitch

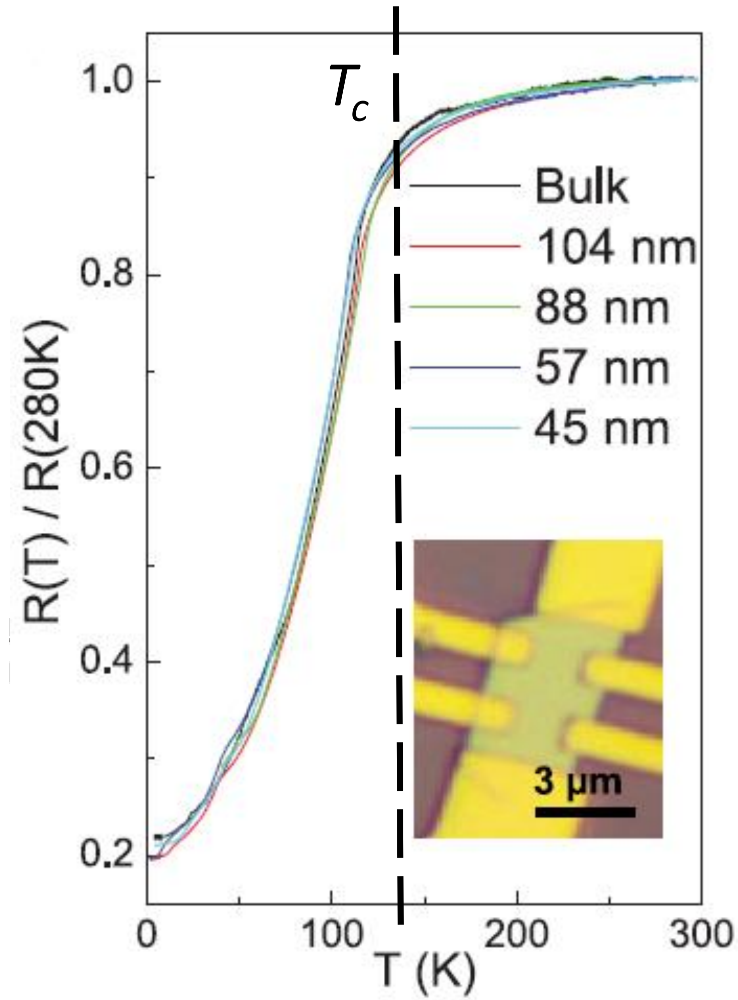
Thickness determines the spin winding number at B = 0 T;

It has no influence on the critical temperature



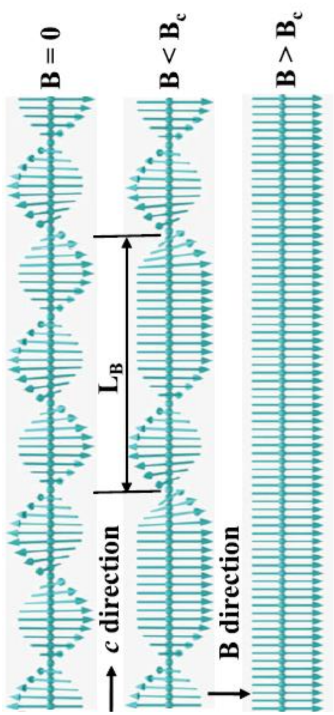


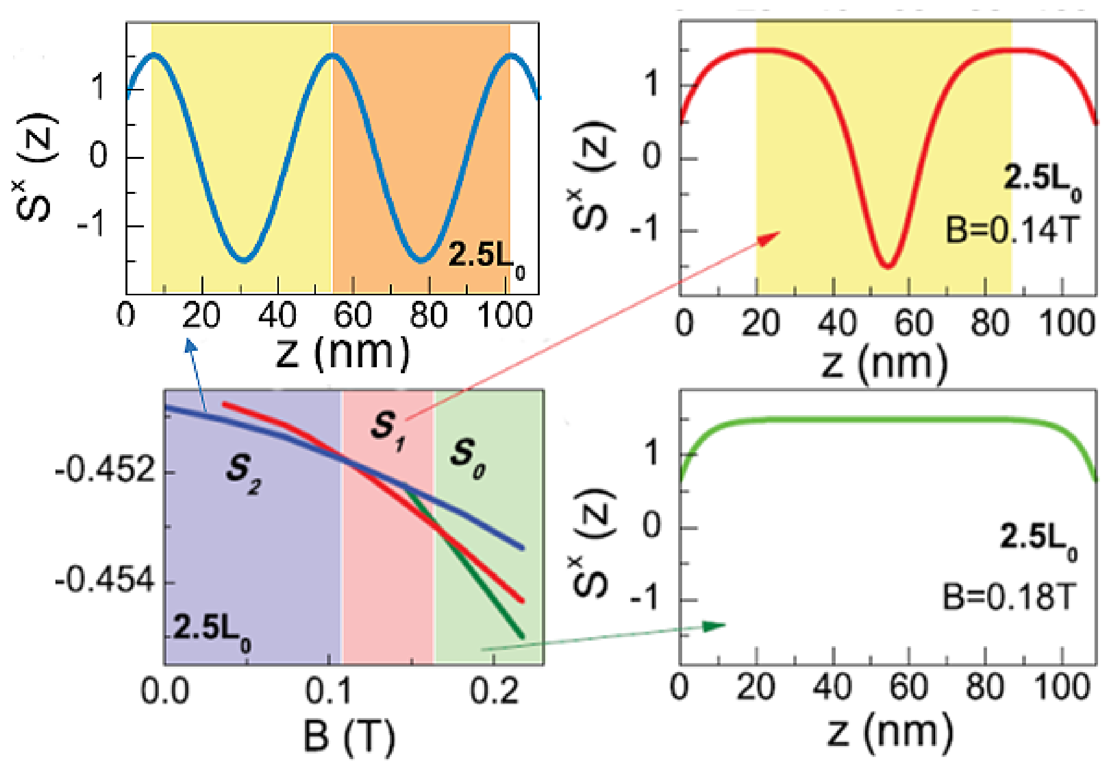




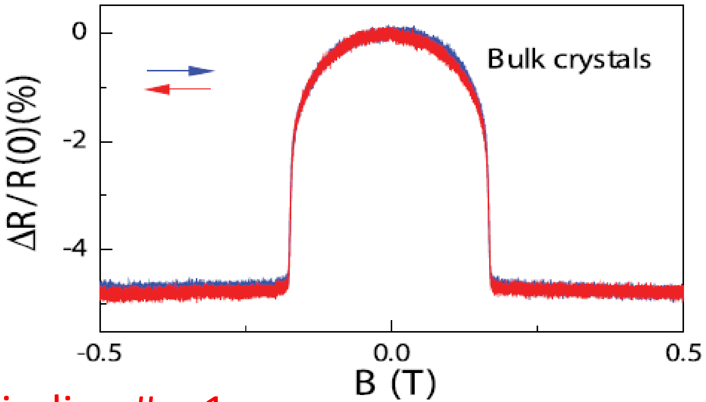
Ramping up magnetic field: first order transitions between different topological sectors

- *Ground state has different winding numbers in different B ranges*
- *1^{st}-order transitions between topological sectors change the spin configuration throughout the crystal thickness*
- *Hysteresis & abrupt magnetization jump -> resistance jumps*

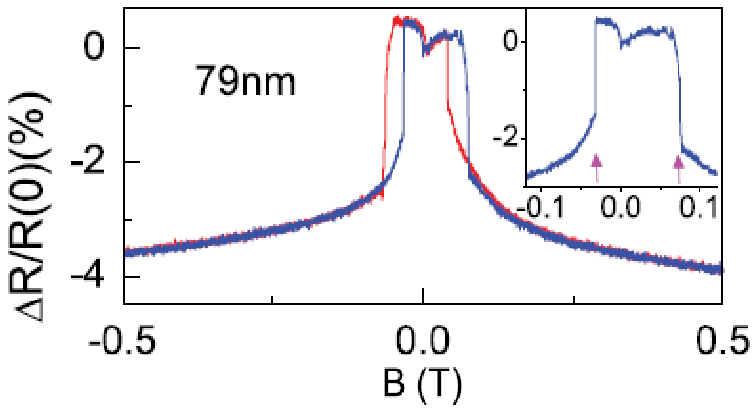




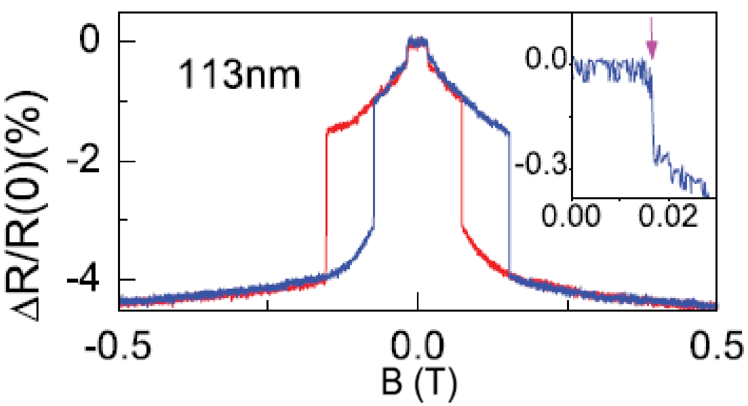
Compare MR of bulk and crystals with t > 48 nm



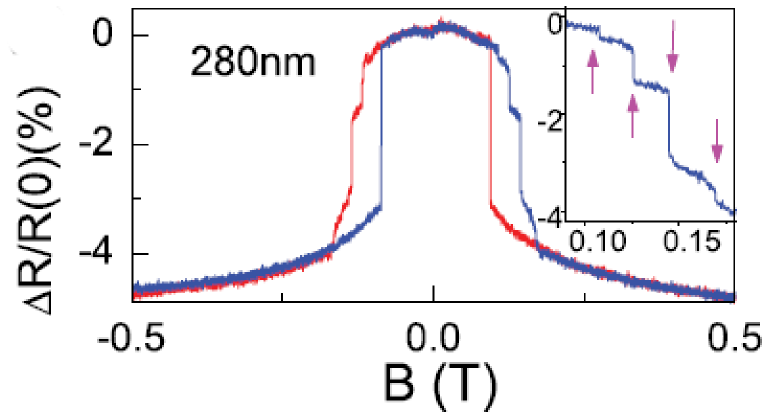
Winding # = 1



Winding # = 2

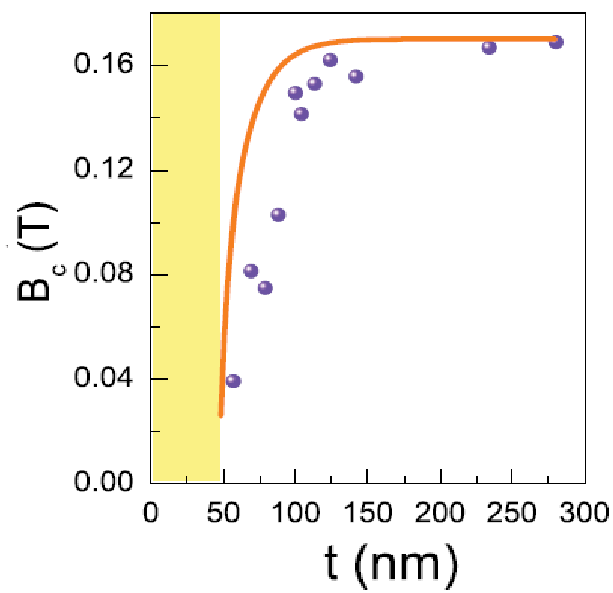


Winding # = 5



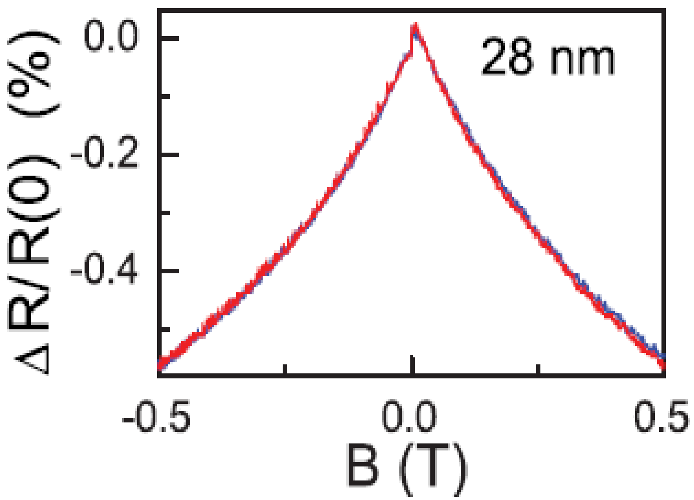
B value at which

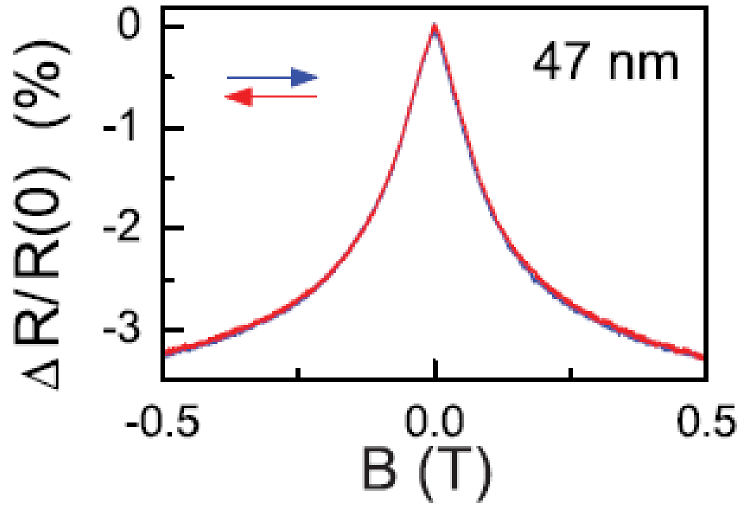
WN # 1 -> 0 transition occurs

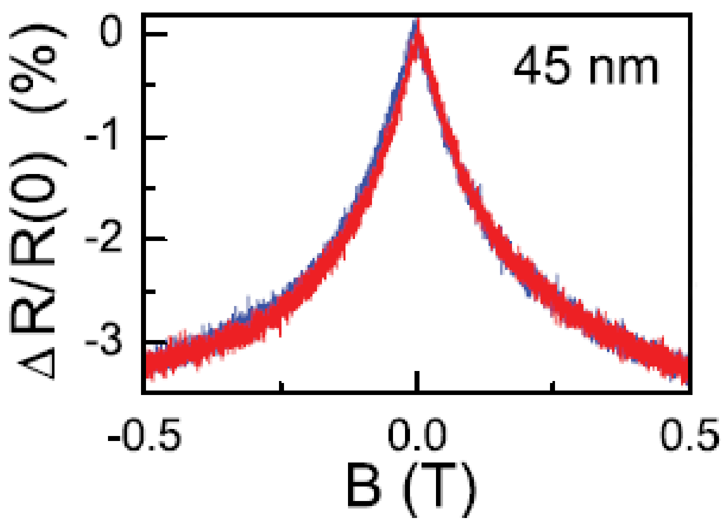


The magic of topology….

Drastic difference in the MR of $Cr_{1/3}NbS_2$



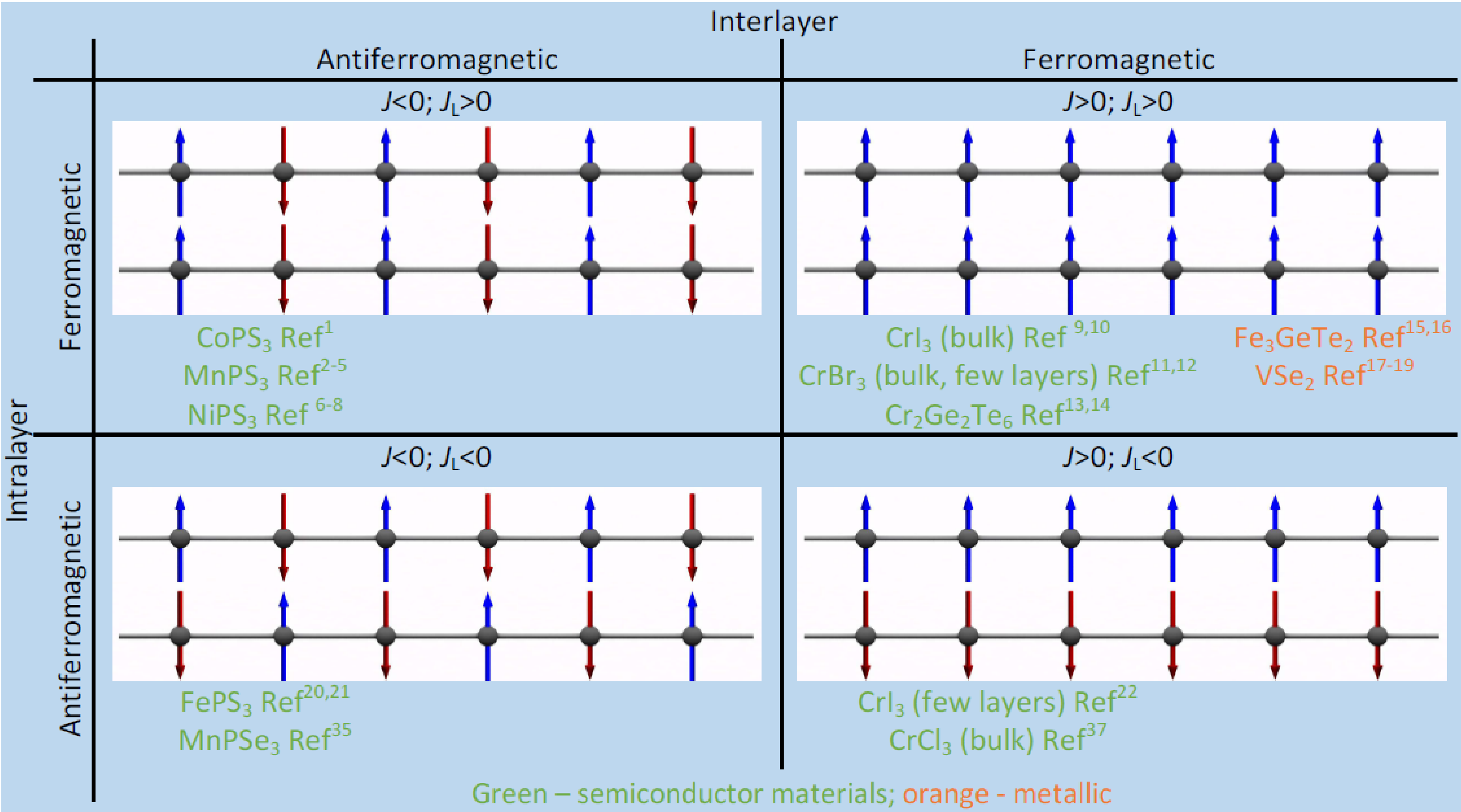




t > 48 nm -> hysteretic MR

t < 48 nm -> no hysteresis in MR

Conclusions



The game is on…