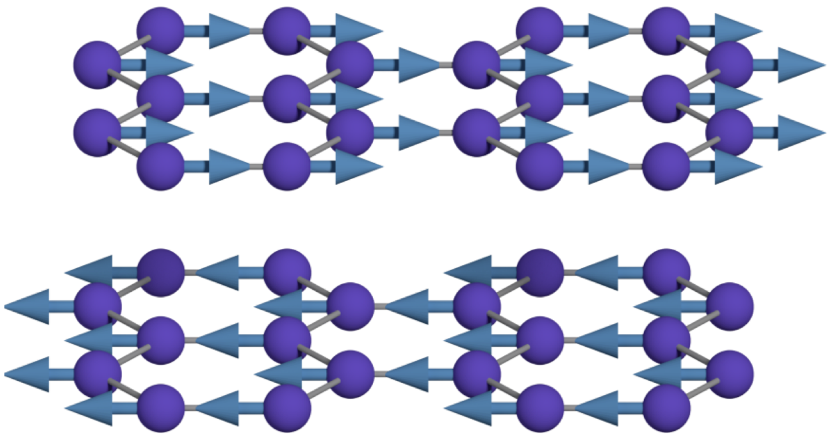
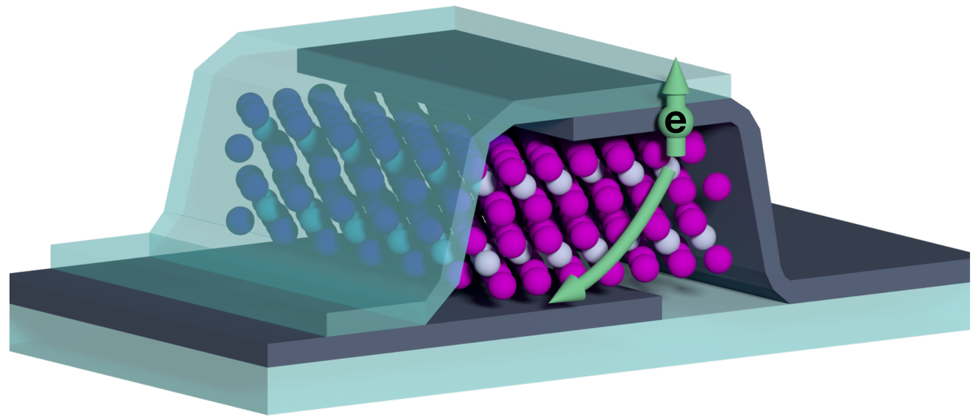
Magnetism in the Ultrathin Chromium Trihalides





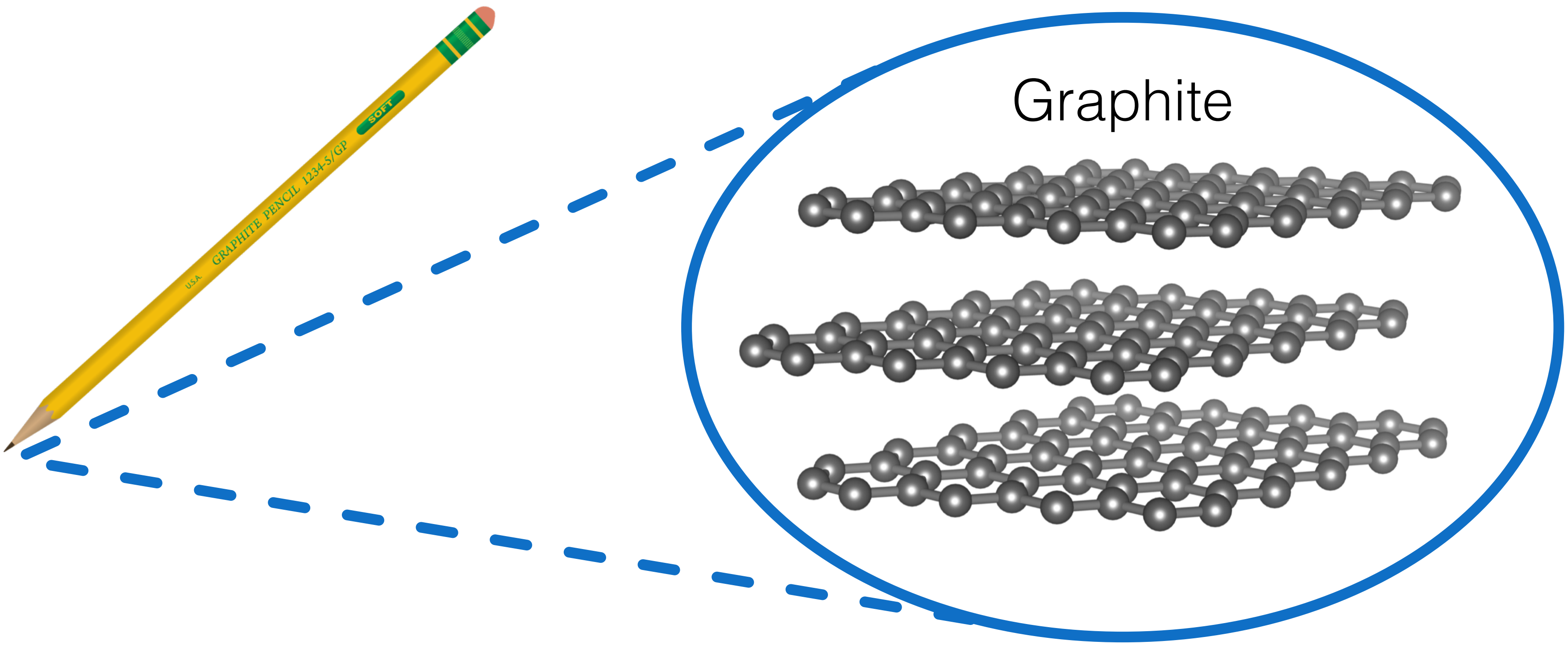
Dahlia Klein

Jarillo-Herrero Group

Outline

- Introduction to 2D magnets
- CrI_3: Detection & control of magnetism
- $CrCl_3$: Connecting magnetism & structure
- Outlook

2D van der Waals Materials



Strong bonds within each layer

Weak van der Waals bonds between layers

2D van der Waals Materials

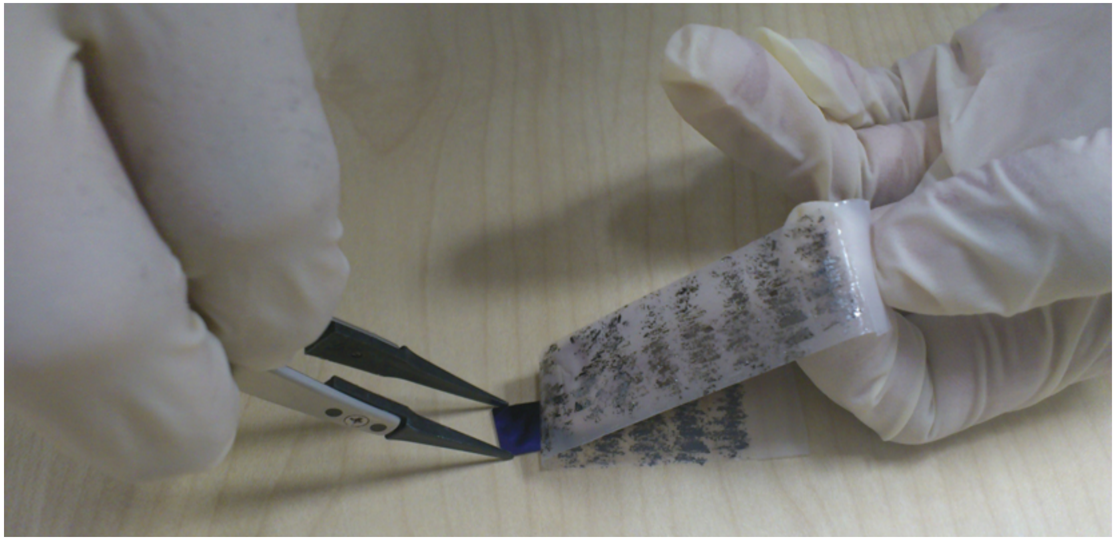
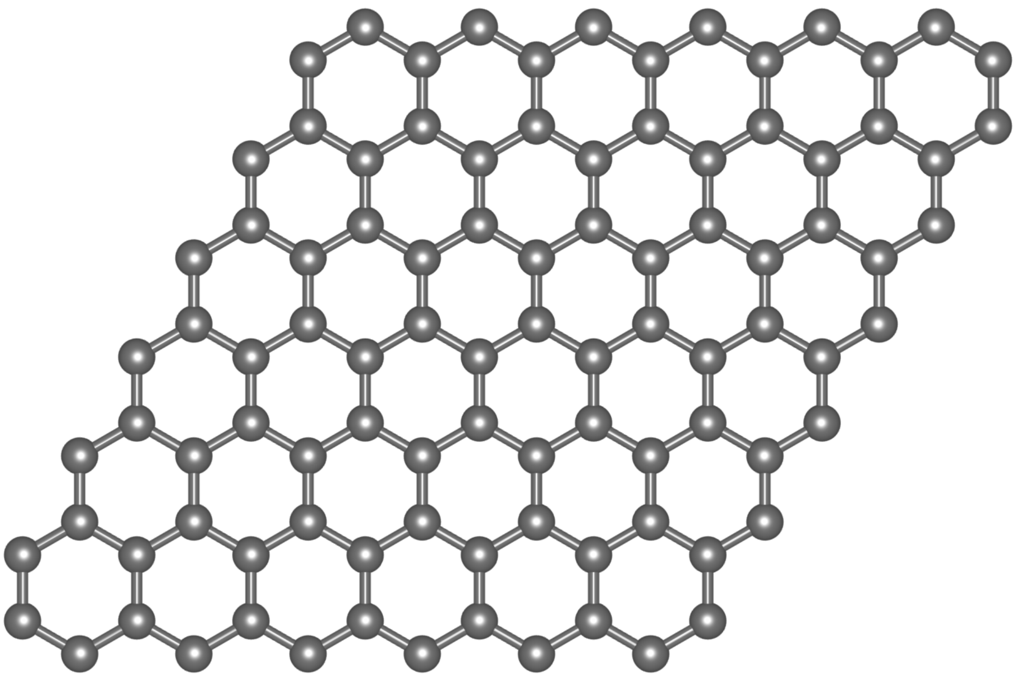


Photo: *American Scientist*

Mechanical Exfoliation

Graphene



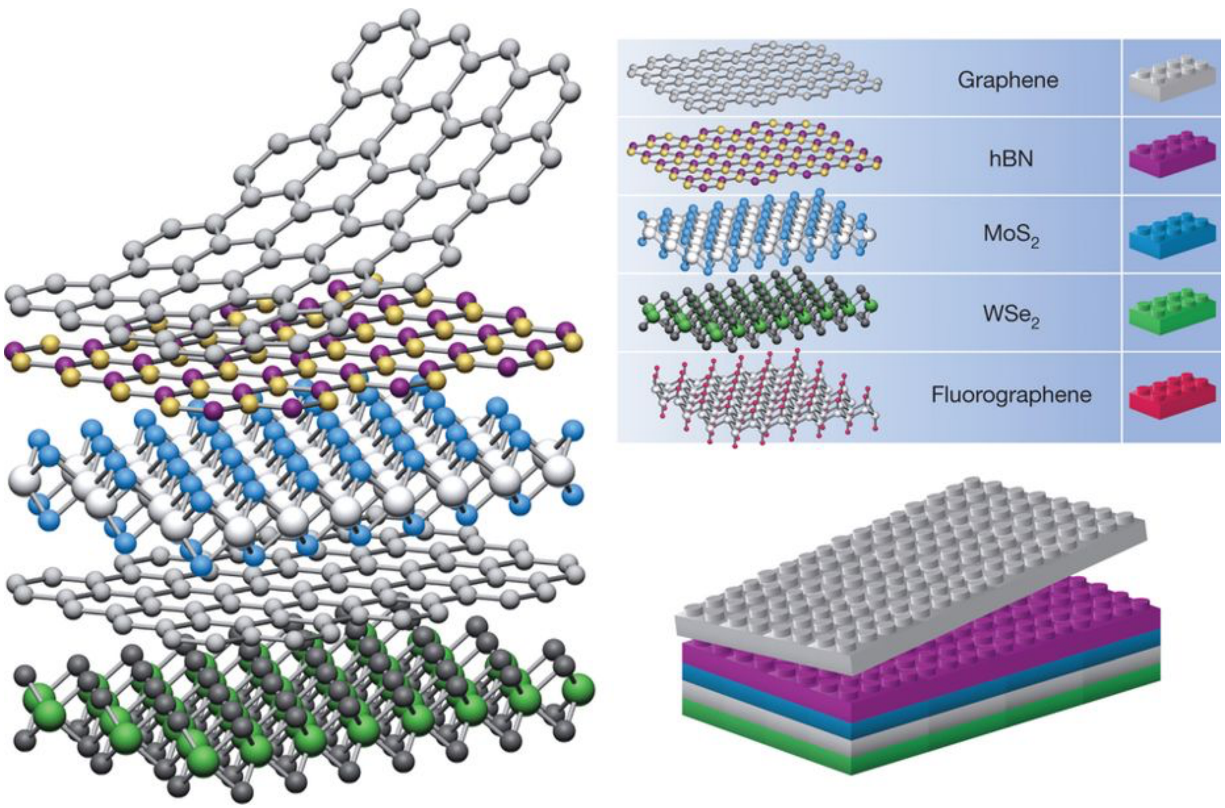
Single atomic layer of graphite

2004: First isolated

2010: Nobel Prize in Physics

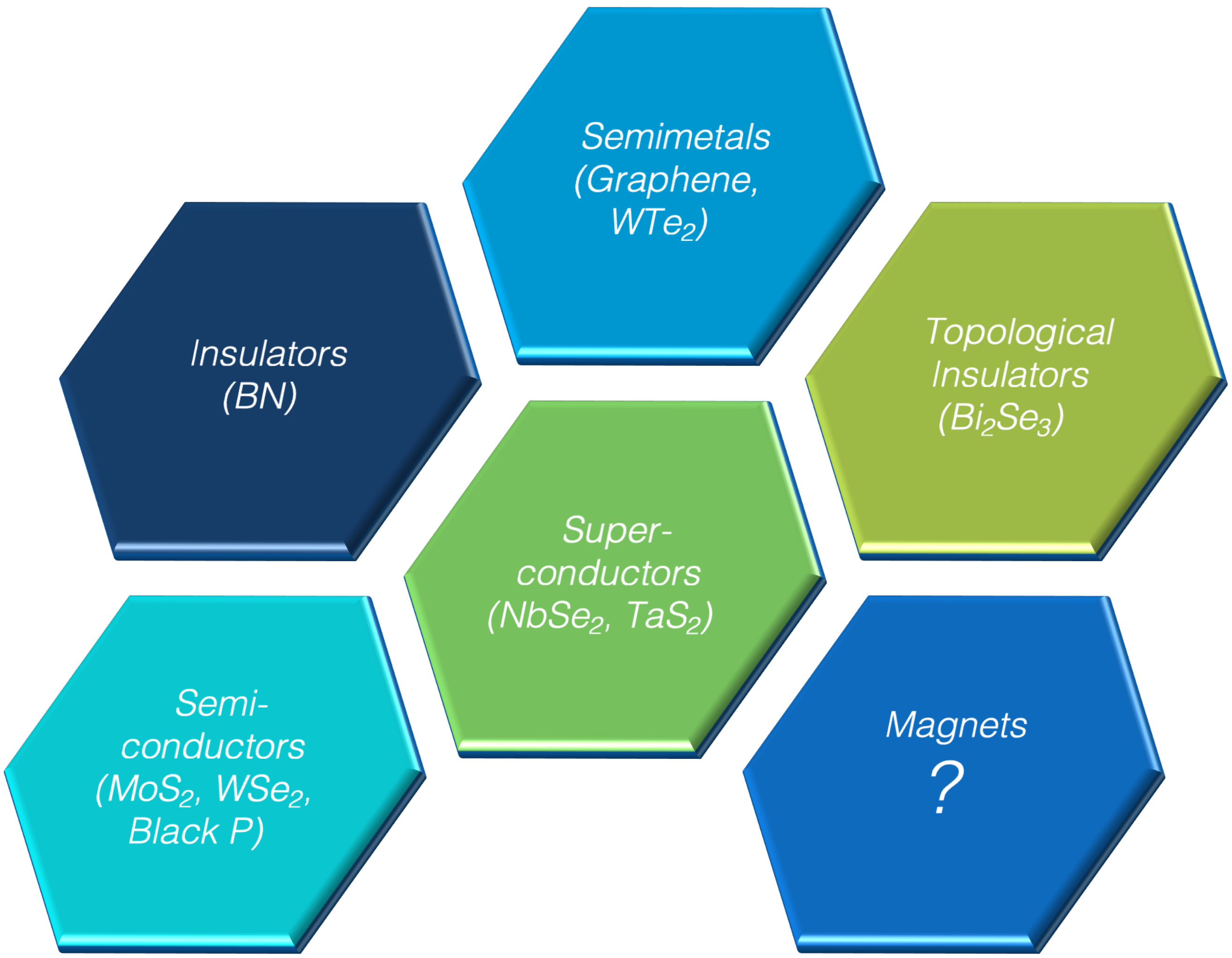
Beyond Graphene

Many 2D materials cleavable to few-layer limit



Geim & Grigorieva, *Nature* (2013)

Family of 2D Materials



2D Magnets

Insulators/semiconductors:

- CrX_3 (X = Cl, Br, I)
- $CrXTe_3$ (X = Si, Ge)
- MPS_3 (M = Fe, Mn, Ni)
- α-$RuCl_3$

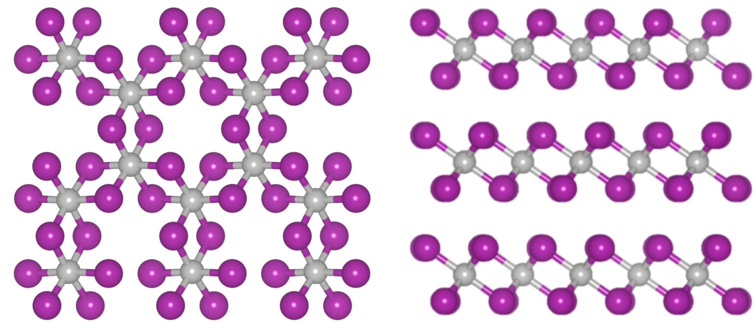
Conductors:

- Fe_3GeTe_2
- MSe_2 (M = Cr, Mn, V)

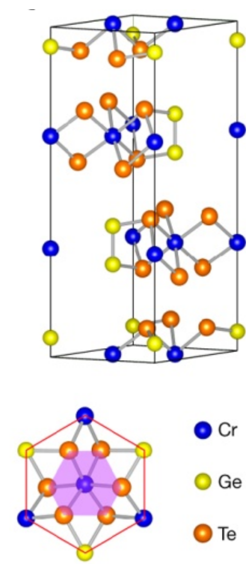
Topological insulators:

- $MnBi_2Te_4$

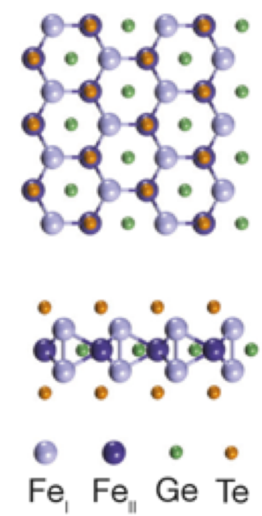
Other candidates…



CrI_3
Huang *et al.*, *Nature* (2017)



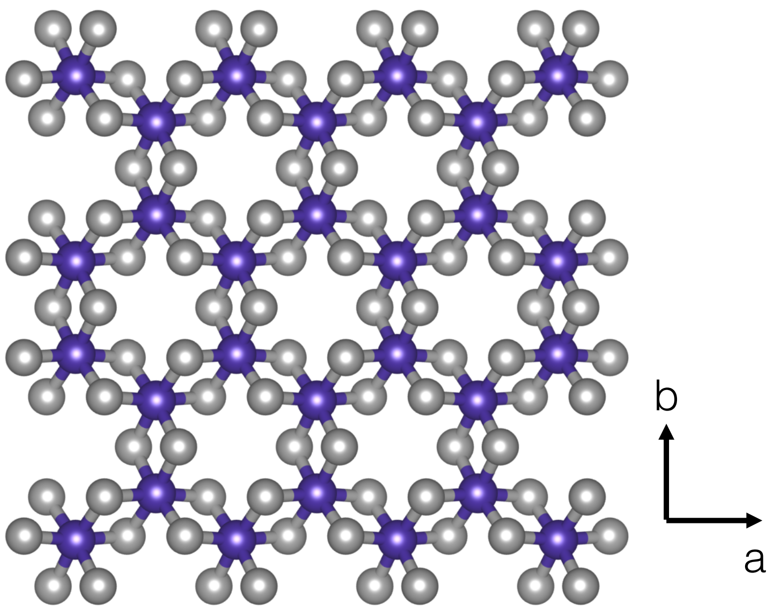
$CrGeTe_3$
Gong *et al.*, *Nature* (2017)

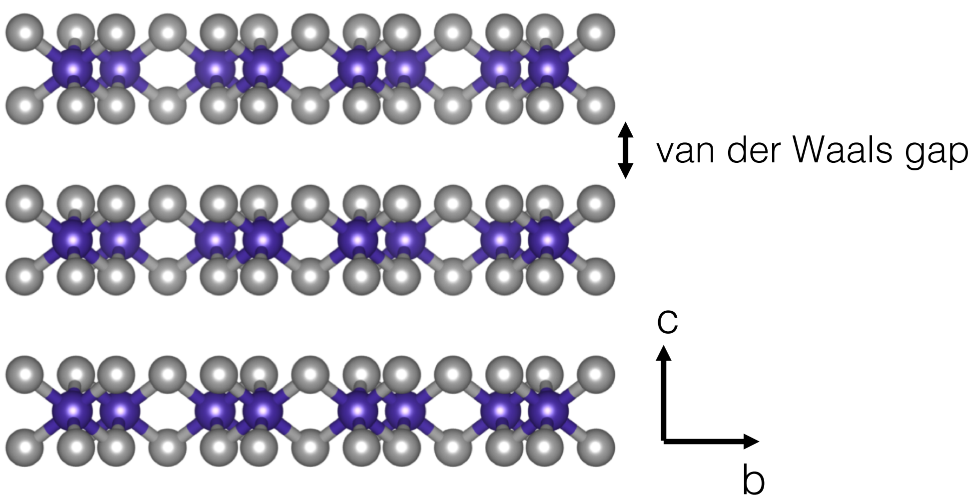


Fe_3GeTe_2
Deng *et al.*, *Nature* (2018)

CrX_3 Crystal Structure

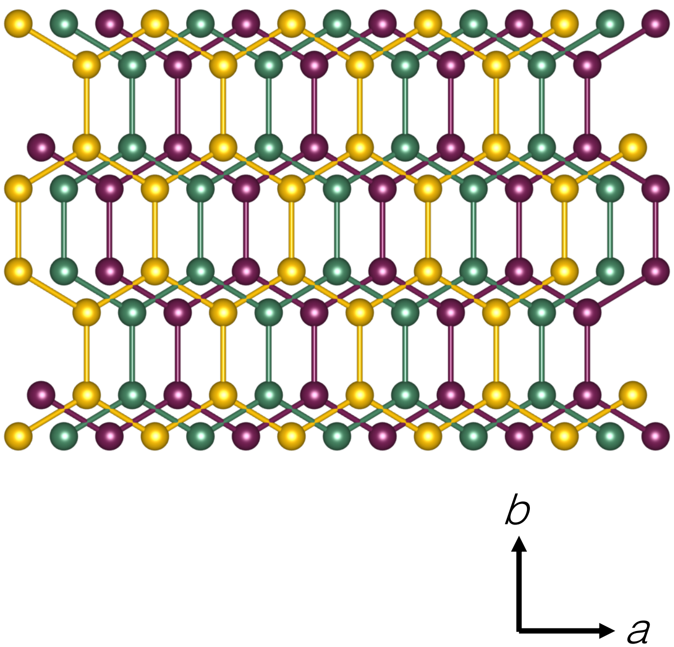
Cr^{3+} honeycomb structure surrounded by X^{-} octahedra





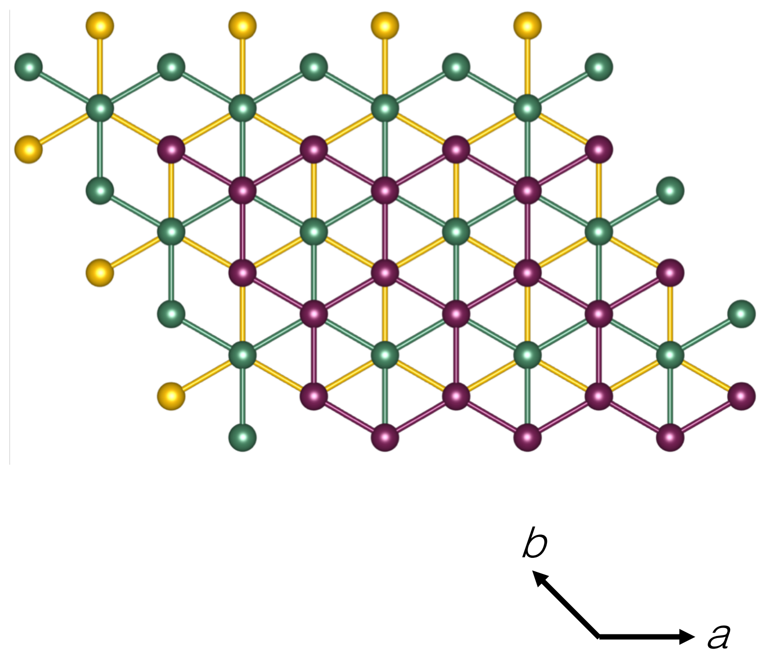
Stacking Phase Transition

*C*2/*m*
Monoclinic



Cool below T_S

$R\bar{3}$
Rhombohedral

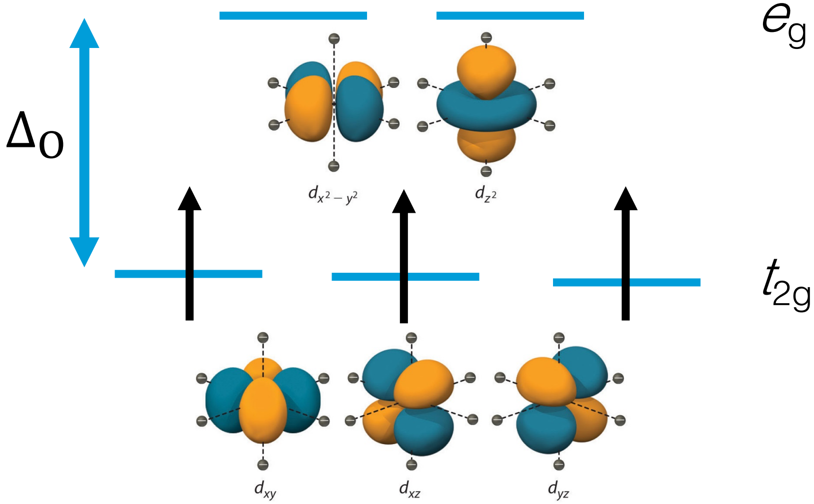


T_S = 240 K ($CrCl_3$), 420 K ($CrBr_3$), 210 K (CrI_3)

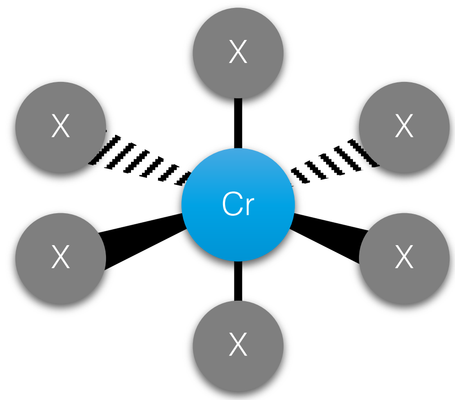
Magnetic Order

Octahedral Crystal Field

Cr 3d orbitals



Principles of General Chemistry
Averill & Eldredge



$Cr^{3+} \rightarrow 3d^3$

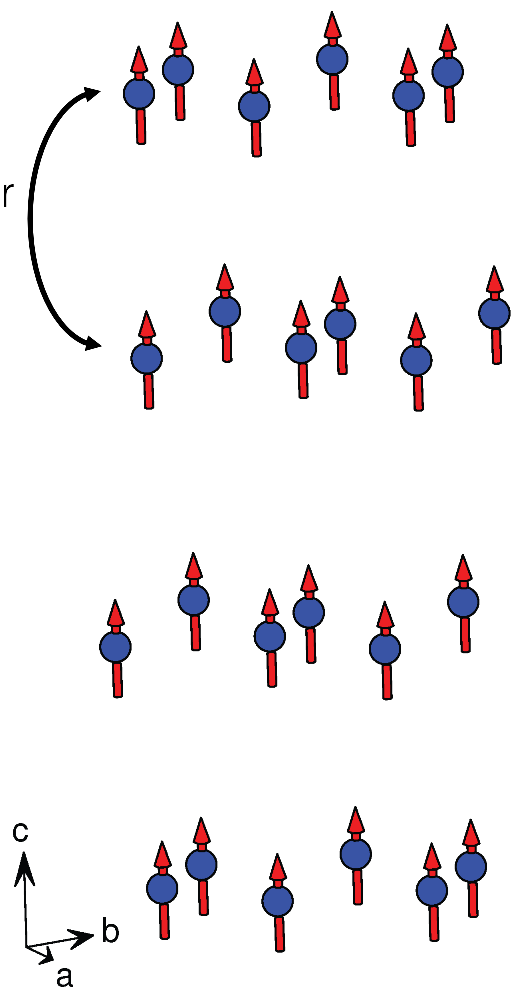
Consistent with saturation moment $3\mu_B$/Cr

Magnetic Order

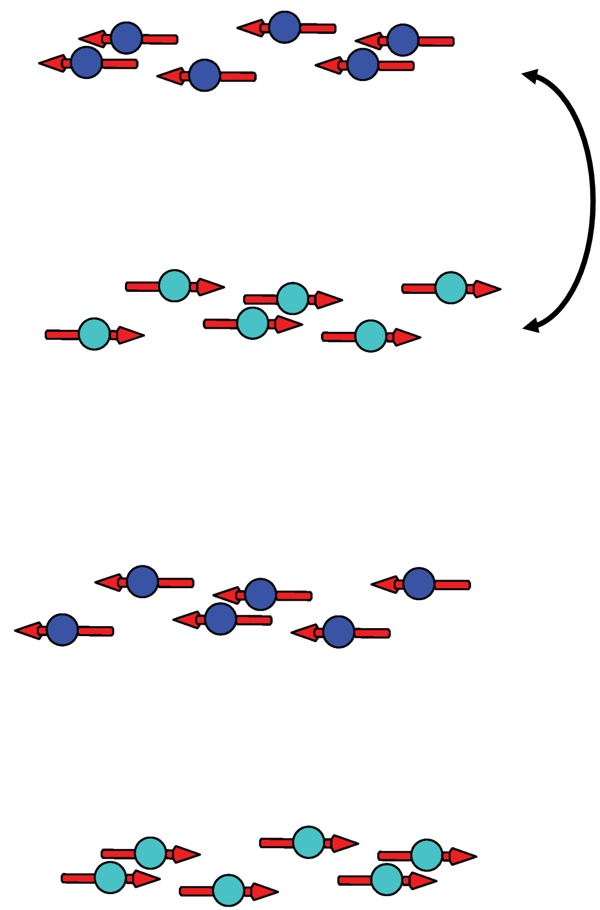
CrI_3, $CrBr_3$
Out-of-plane FM

$CrCl_3$
In-plane AFM

FM interlayer coupling



AFM interlayer coupling

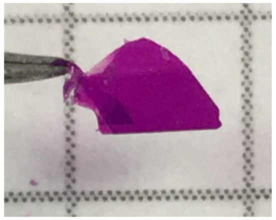


McGuire, *Crystals* (2017)

From Bulk to Monolayer Magnets

Bulk Crystal Growth

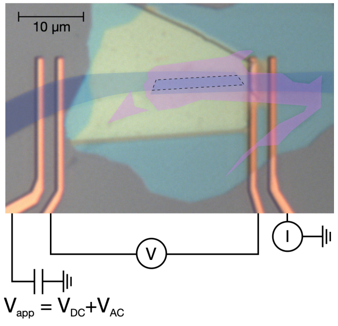
CrI_3



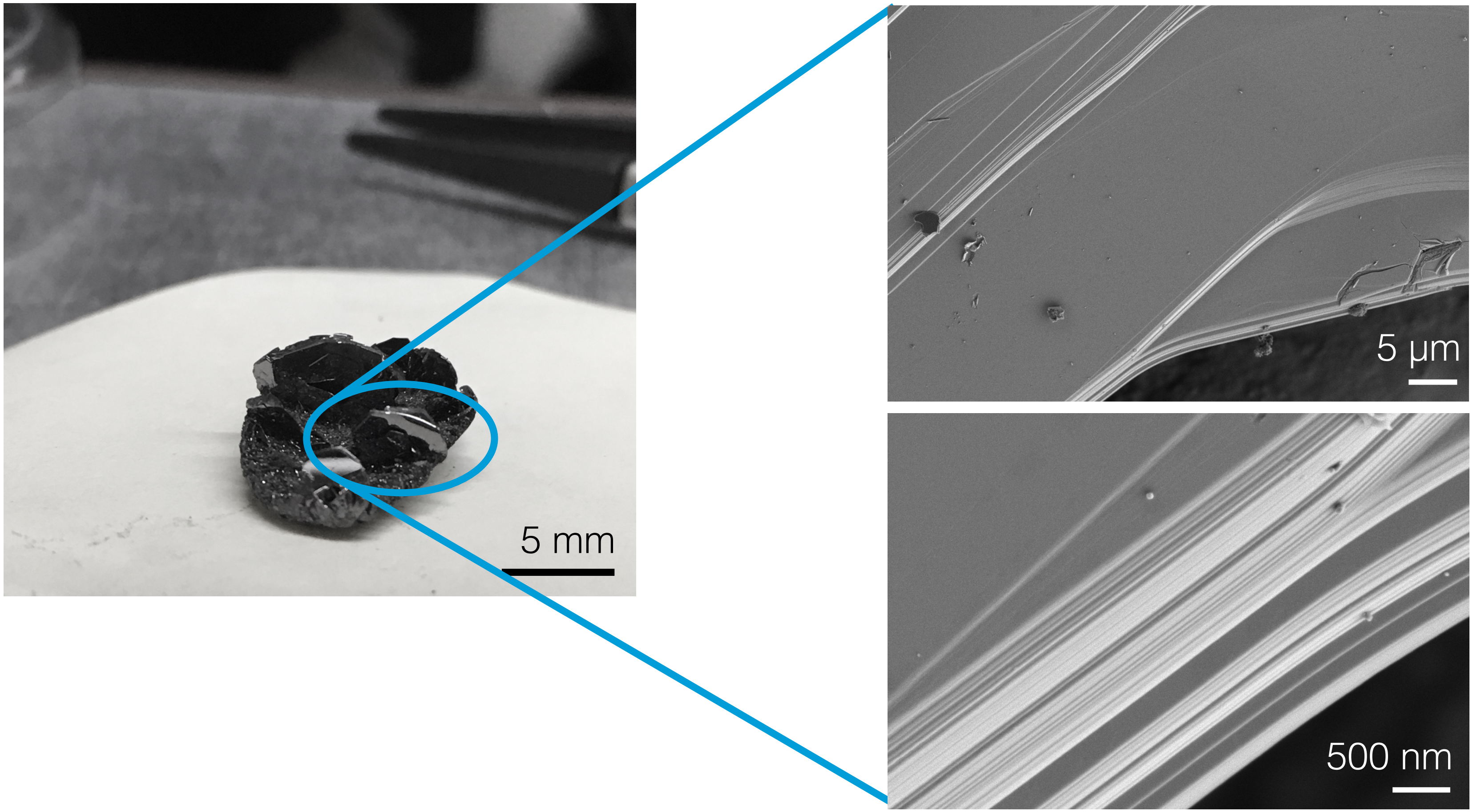
$CrCl_3$

Exfoliation

Measurement

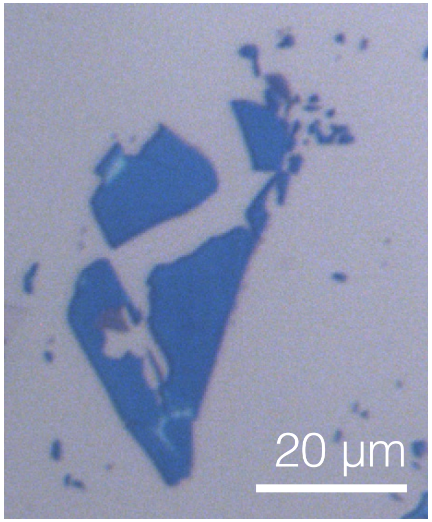


Growth of CrI_3



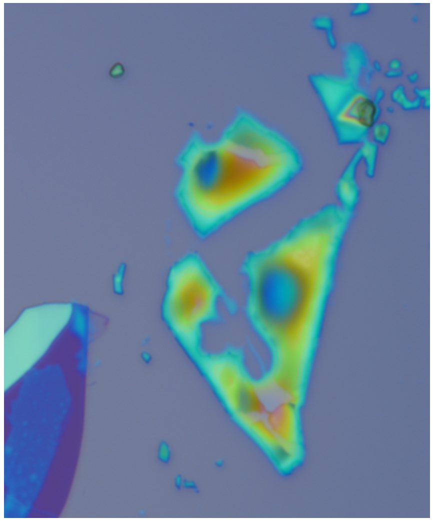
SEM

Mechanical Exfoliation



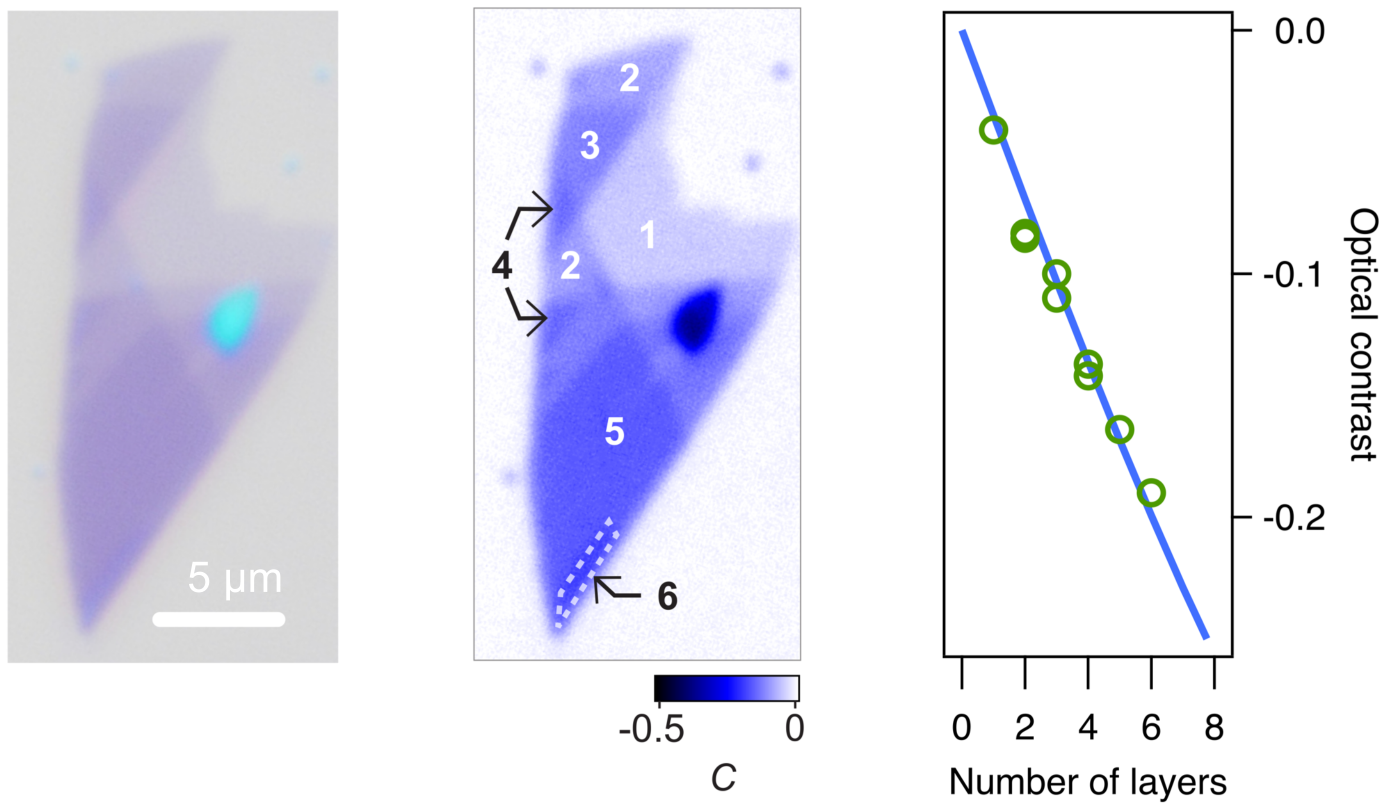
~20 nm thick

Few minutes
in air



Inert atmosphere required
to prevent hydration

Mechanical Exfoliation



✓ Exfoliate and identify flakes down to monolayer

? Magnetic order in few-layer CrI_3?

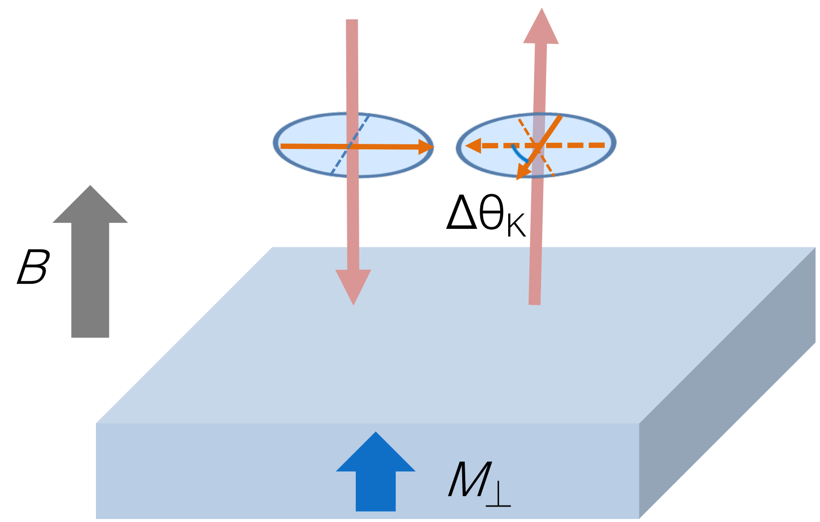
Huang *et al.*, *Nature* (2017)

Magneto-Optical Kerr Effect (MOKE)

Measure polarization rotation $\Delta\theta_K$ of reflected light

Sensitive probe of perpendicular sample magnetization $M_\perp$

Vary applied magnetic field B

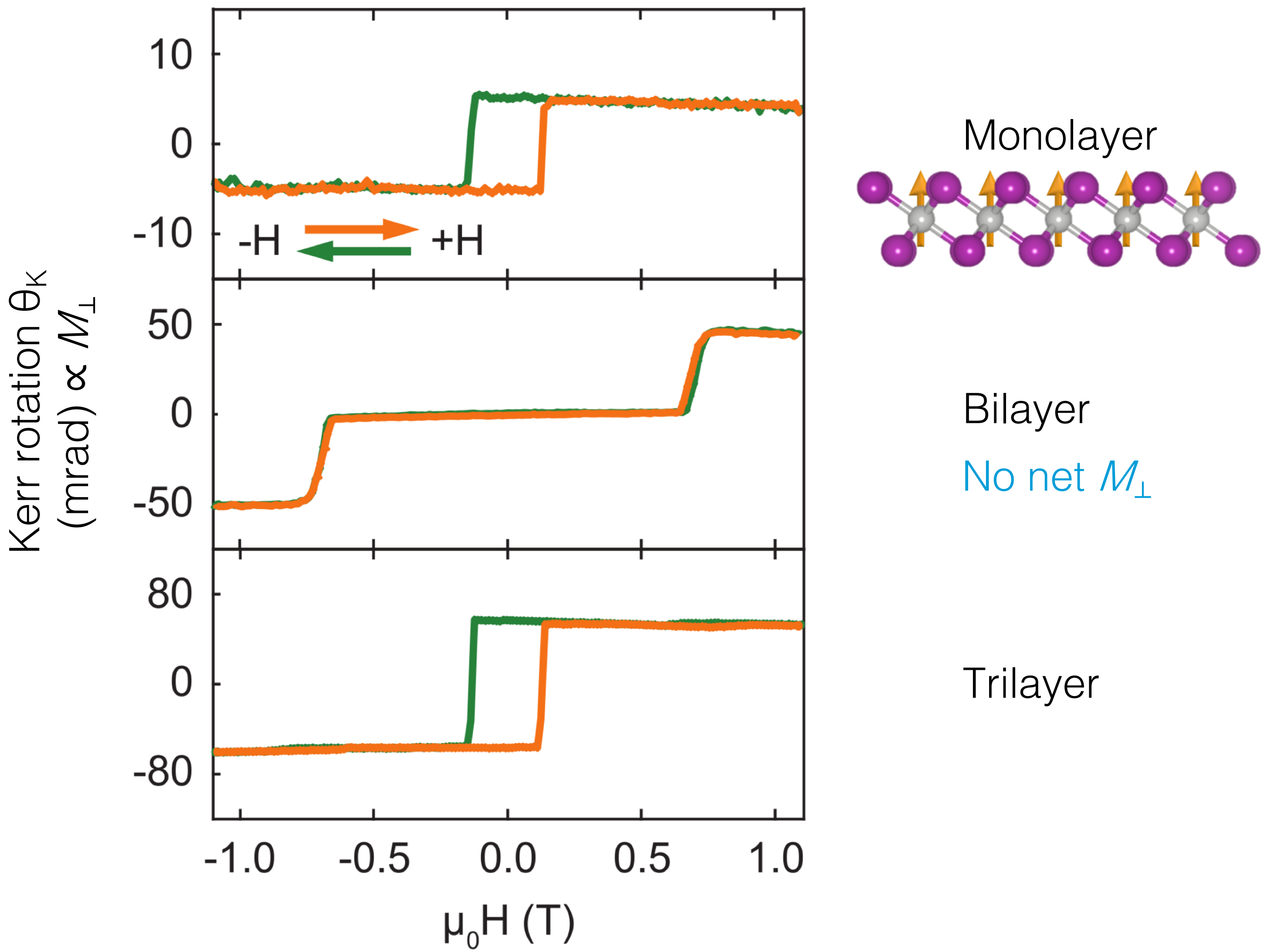


$$\Delta\theta_K \propto M_\perp$$

Collaboration with Xiaodong Xu

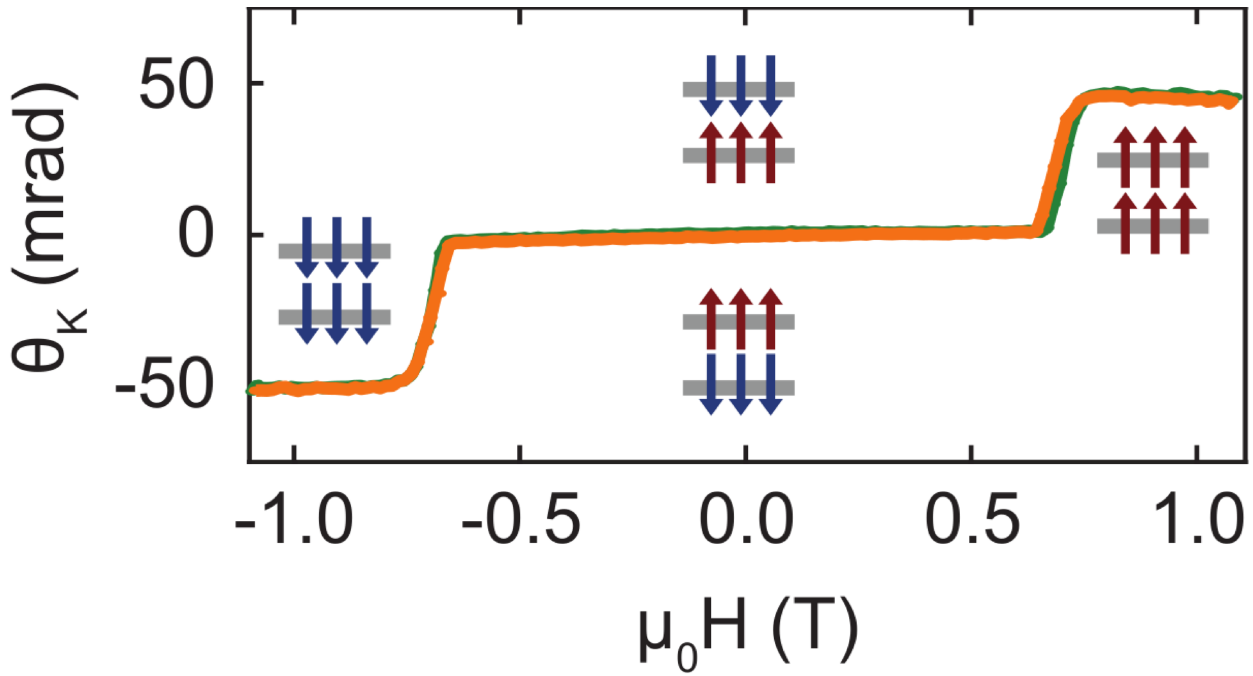
UNIVERSITY of WASHINGTON

Layer-Dependent Magnetism in CrI_3



Huang *et al.*, *Nature* (2017)

Ultrathin CrI_3: Layered AFM



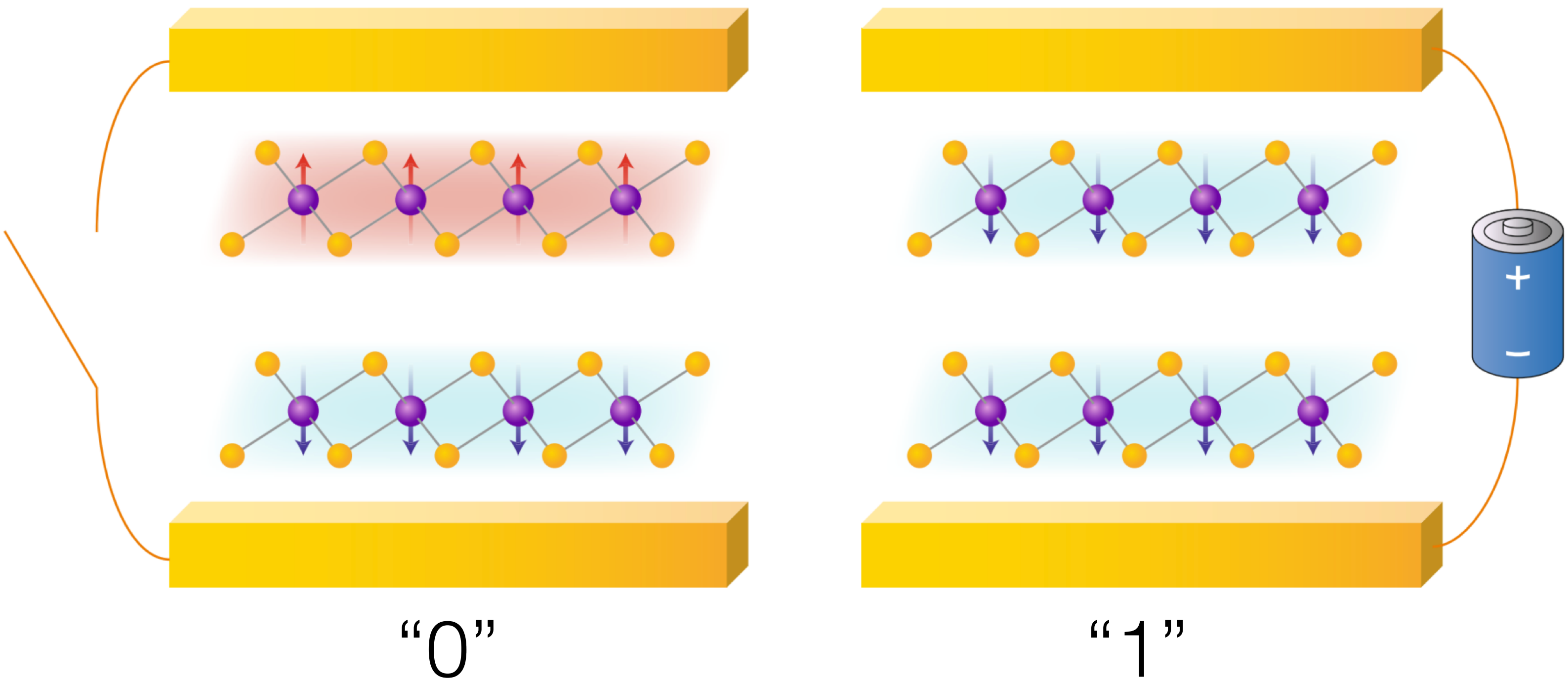
Can we electrically control this magnetic transition?

Huang *et al.*, *Nature* (2017)

Goal: Electrical Control of 2L CrI_3

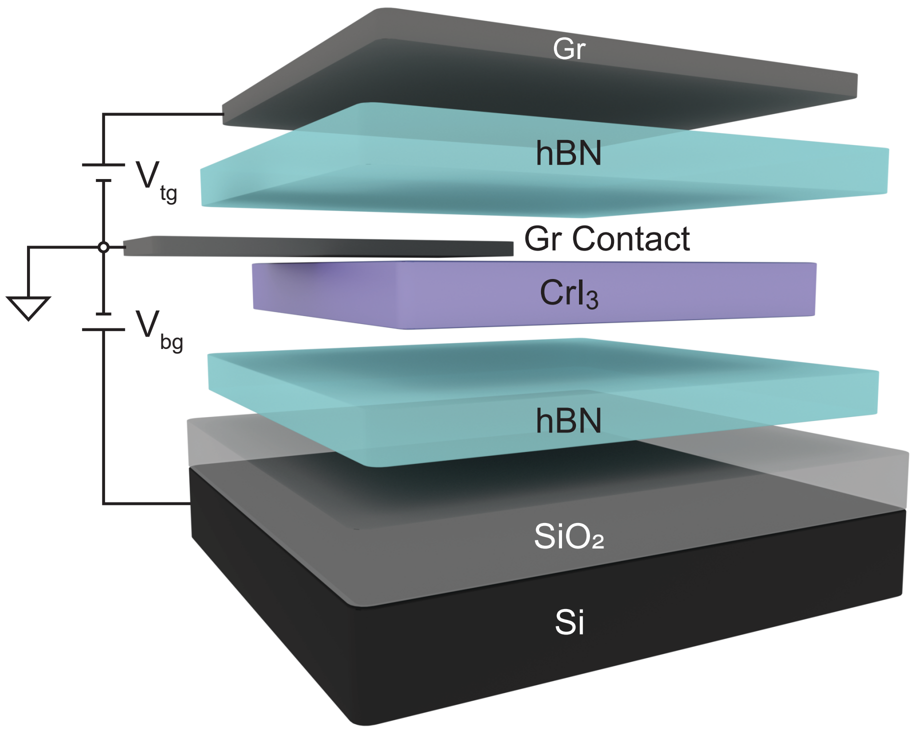
Applications for magnetic memory need current/voltage control

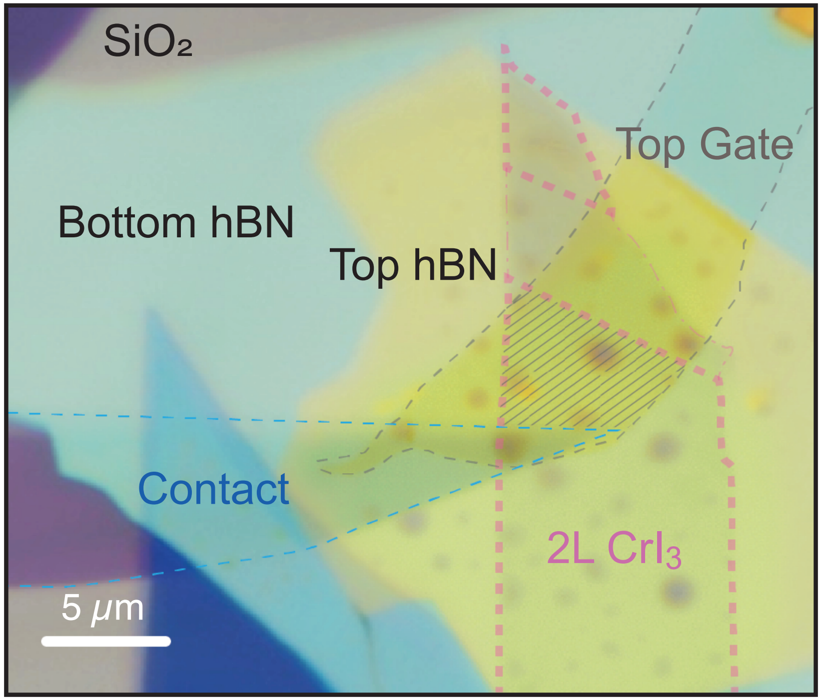
Want to reversibly drive between AFM & FM states



Burch *et al.*, *Nat. Nanotechnol.* (2018)

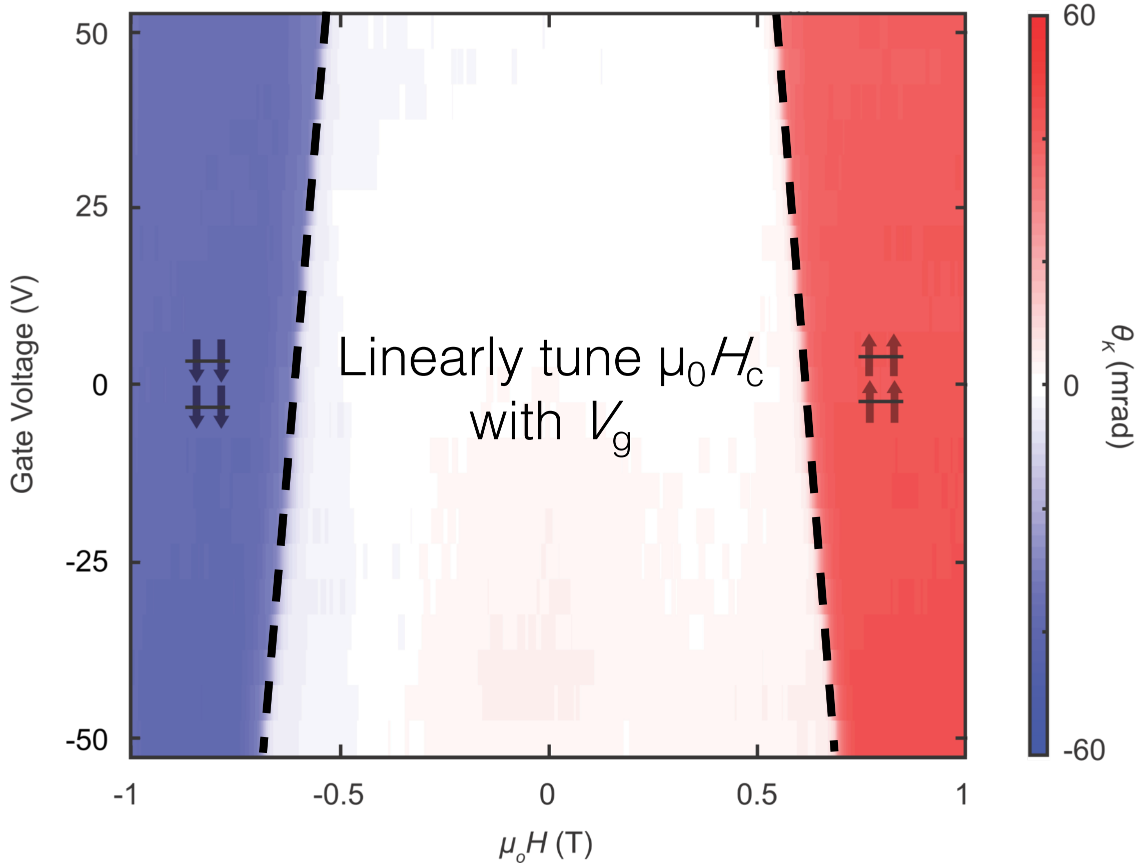
Gated 2L CrI_3





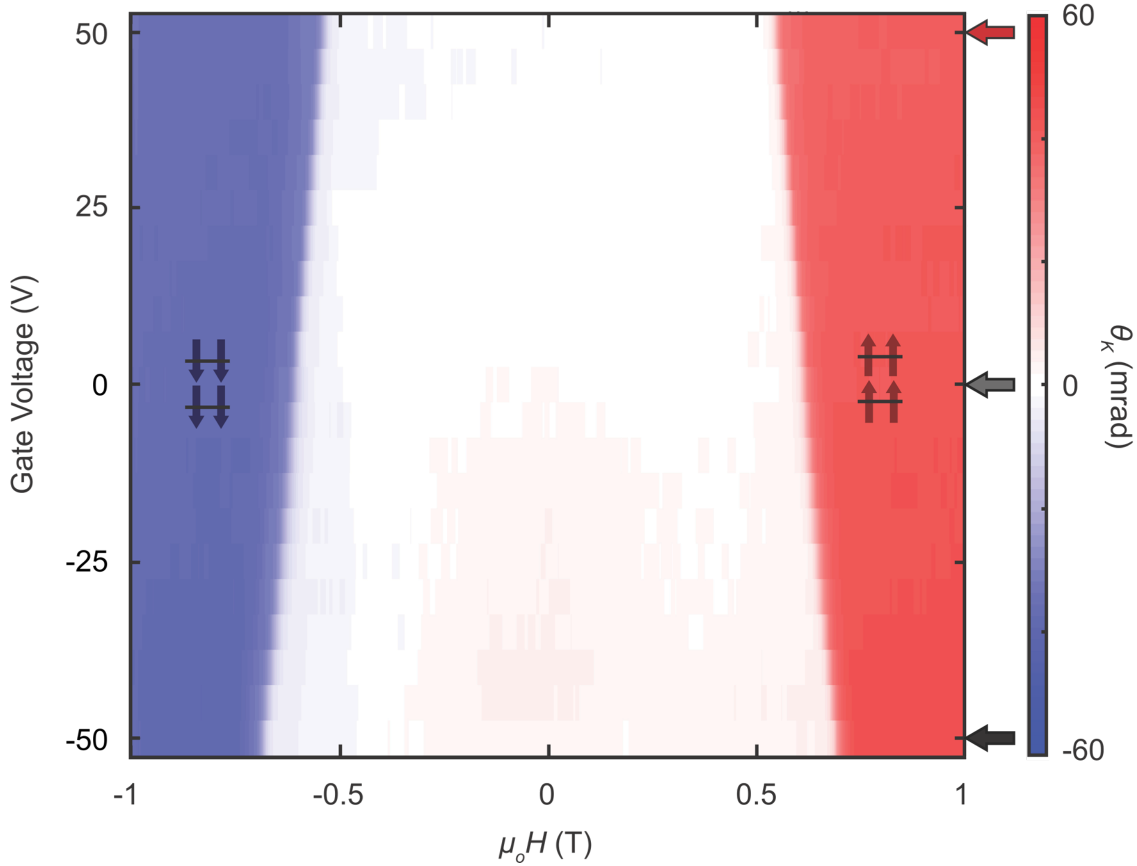
Huang *et al.*, *Nat. Nanotechnol.* (2018)

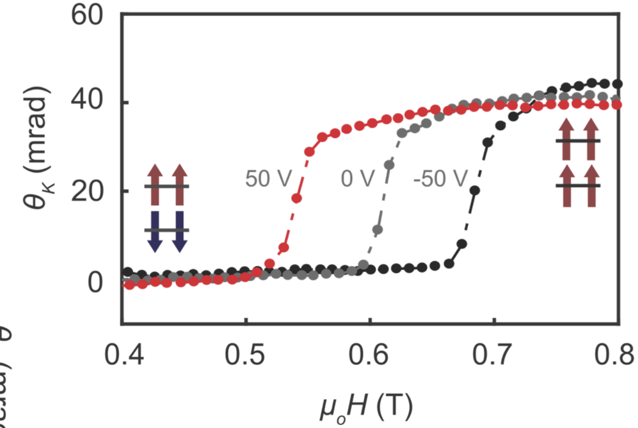
Gated 2L CrI_3



Huang *et al.*, *Nat. Nanotechnol.* (2018)

Gated 2L CrI_3

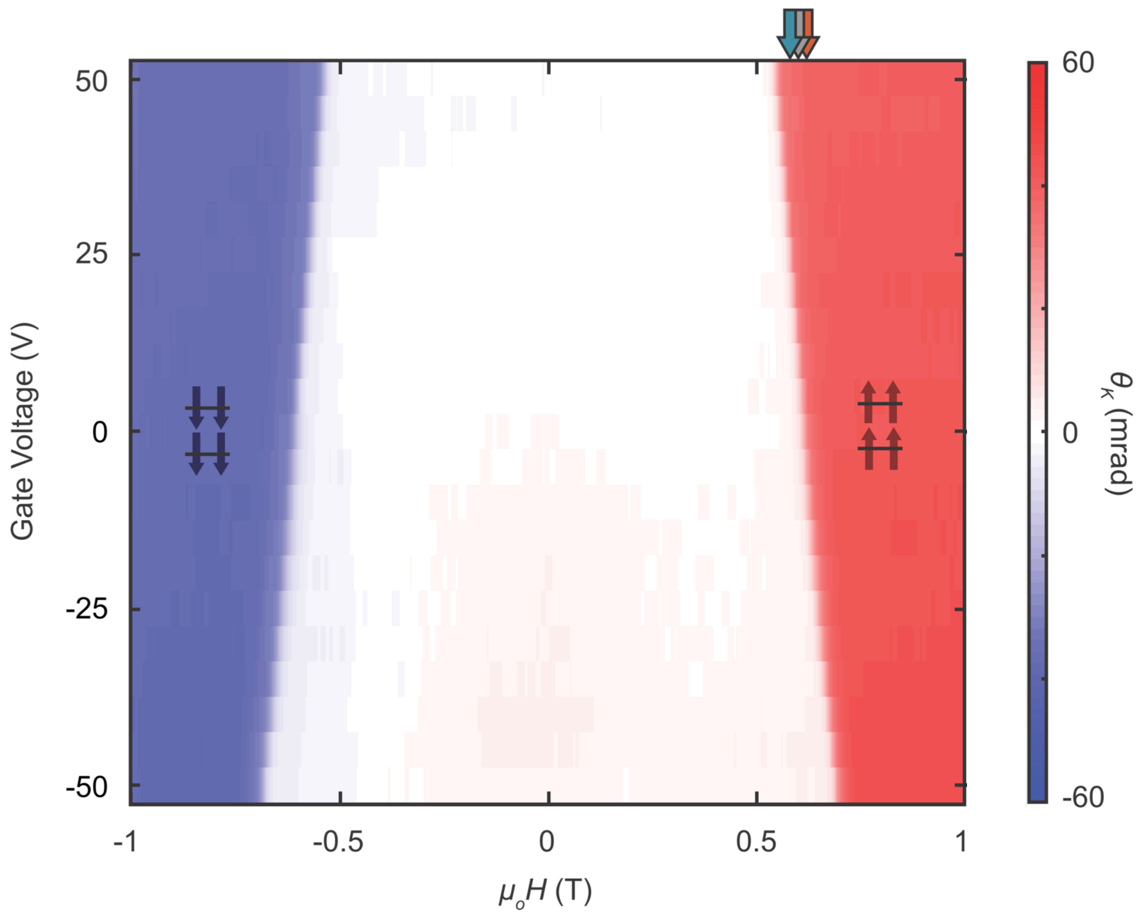




Horizontal linecuts:
Tune $\mu_0 H_c$ by ±0.2 T

Huang *et al.*, *Nat. Nanotechnol.* (2018)

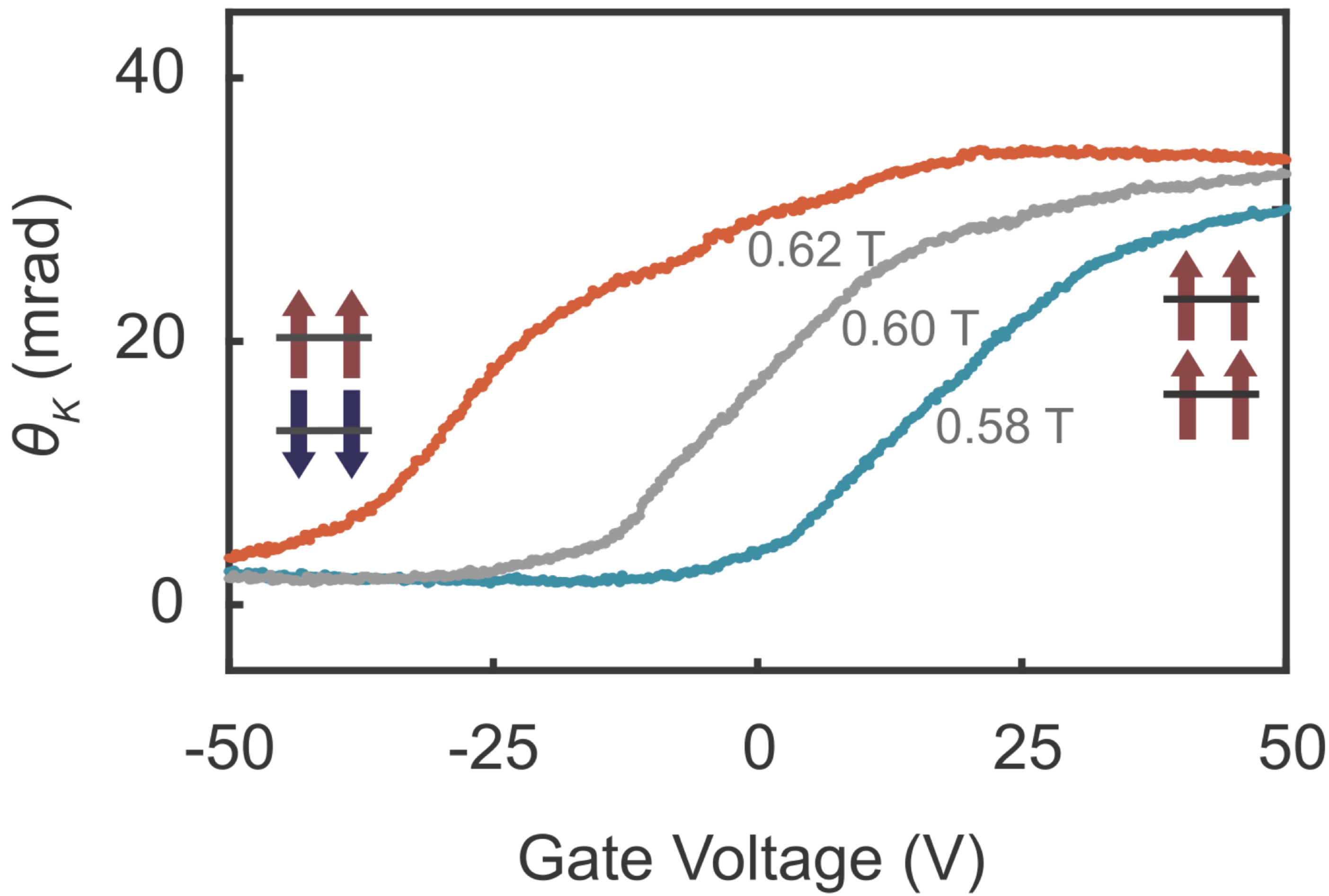
Gated 2L CrI_3



Vertical linecuts:
Fix field near $\mu_0 H_c$

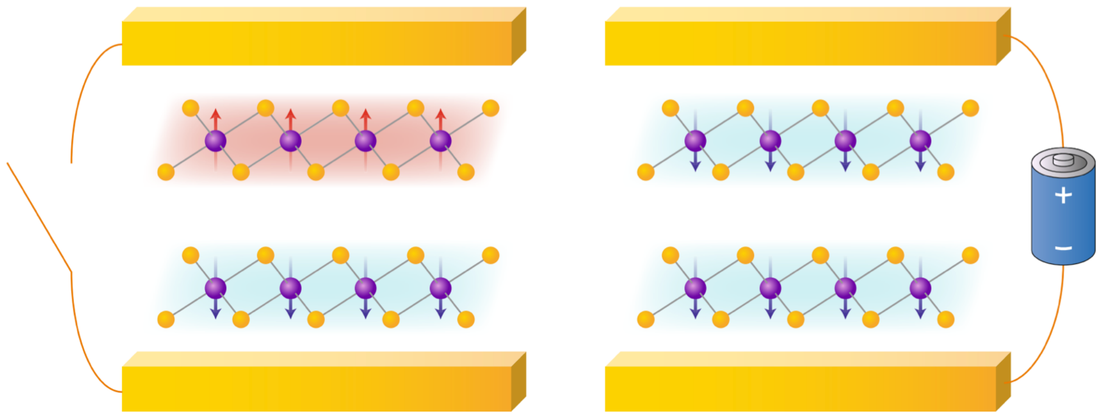
Huang *et al.*, *Nat. Nanotechnol.* (2018)

Gate Control of AFM-FM Transition



Huang *et al.*, *Nat. Nanotechnol.* (2018)

2D Magnetism for Applications

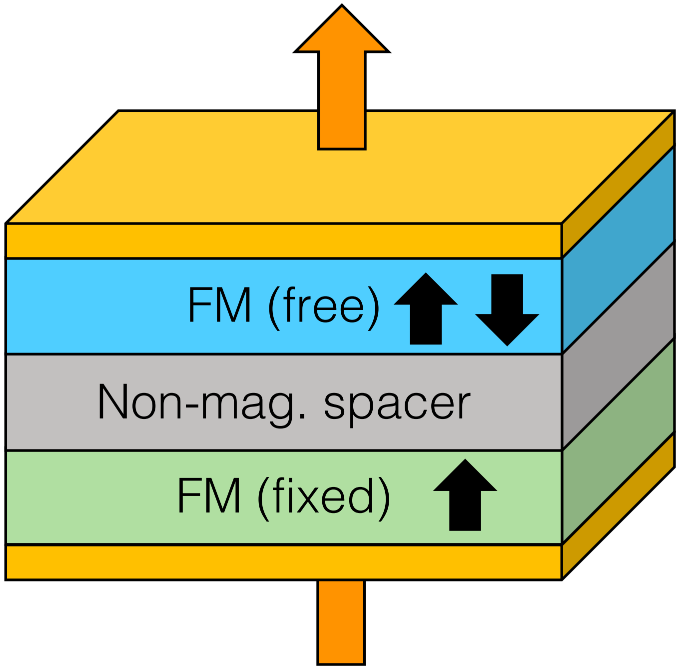


✓ Electrical control of 2D magnetism

? Electrical readout of 2D magnetism?

Approach: tunnel through magnet

Transport with Magnetic Layers

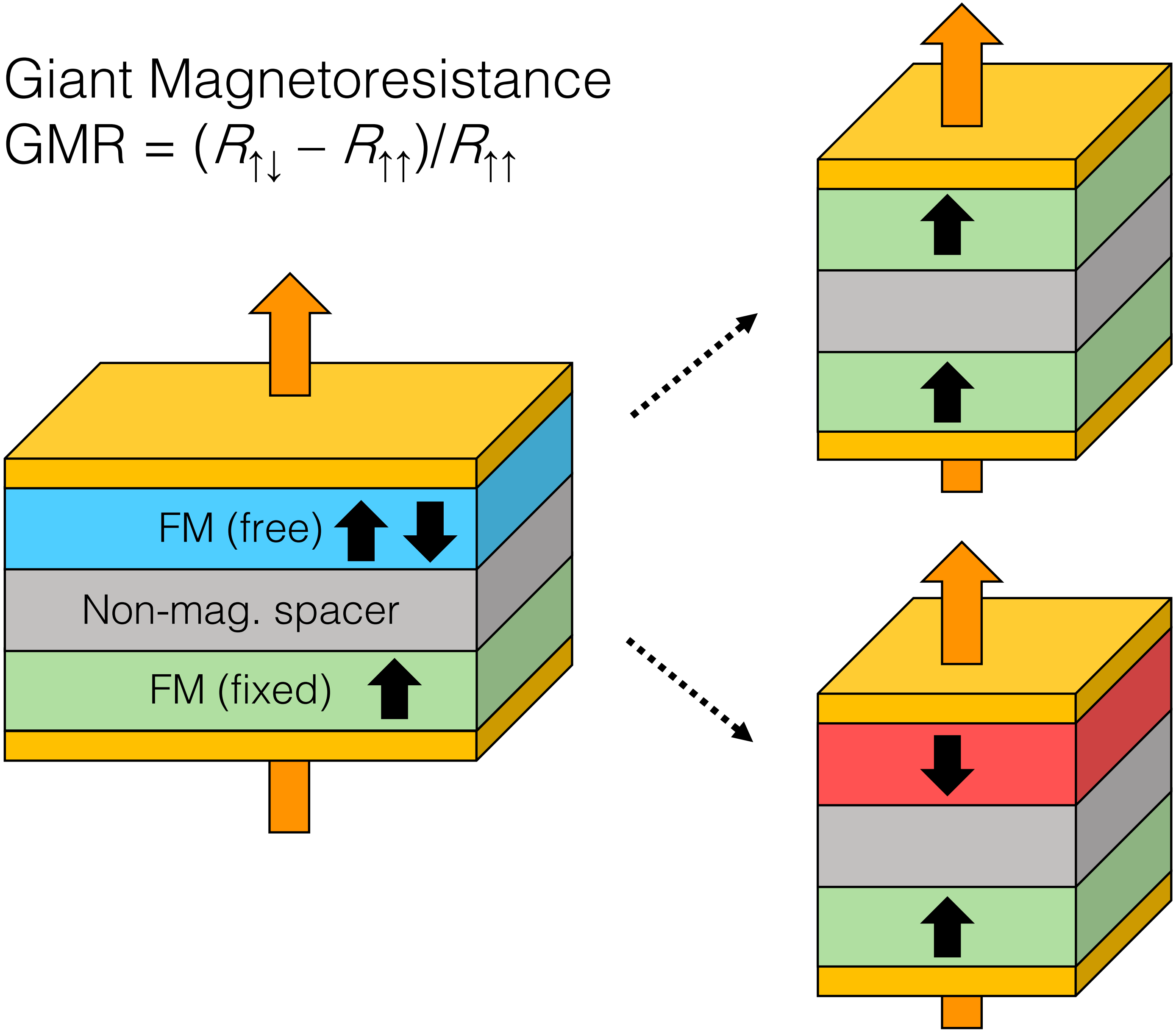


Resistance depends on relative magnetization of 2 FM layers

Transport with Magnetic Layers

Giant Magnetoresistance

GMR = $(R_{\uparrow\downarrow} - R_{\uparrow\uparrow})/R_{\uparrow\uparrow}$



$R_{\uparrow\uparrow}$ low

$R_{\uparrow\downarrow}$ high

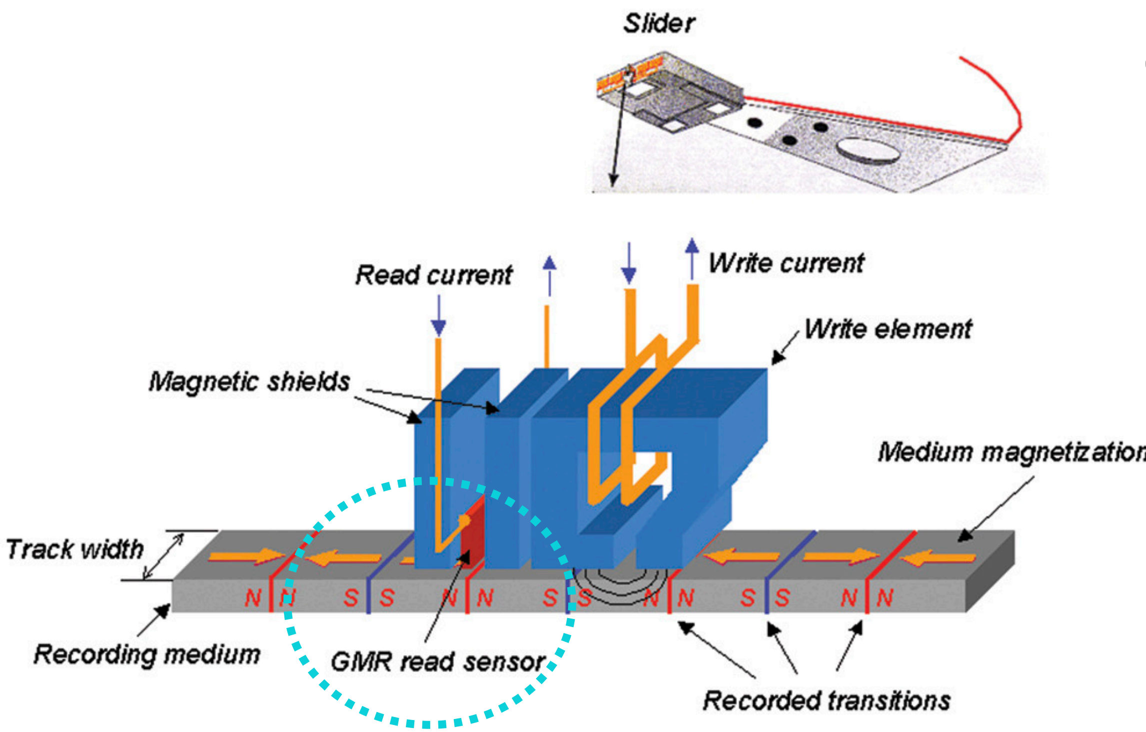
Giant Magnetoresistance

Giant Magnetoresistance

GMR $= (R_{\uparrow\downarrow} - R_{\uparrow\uparrow})/R_{\uparrow\uparrow}$

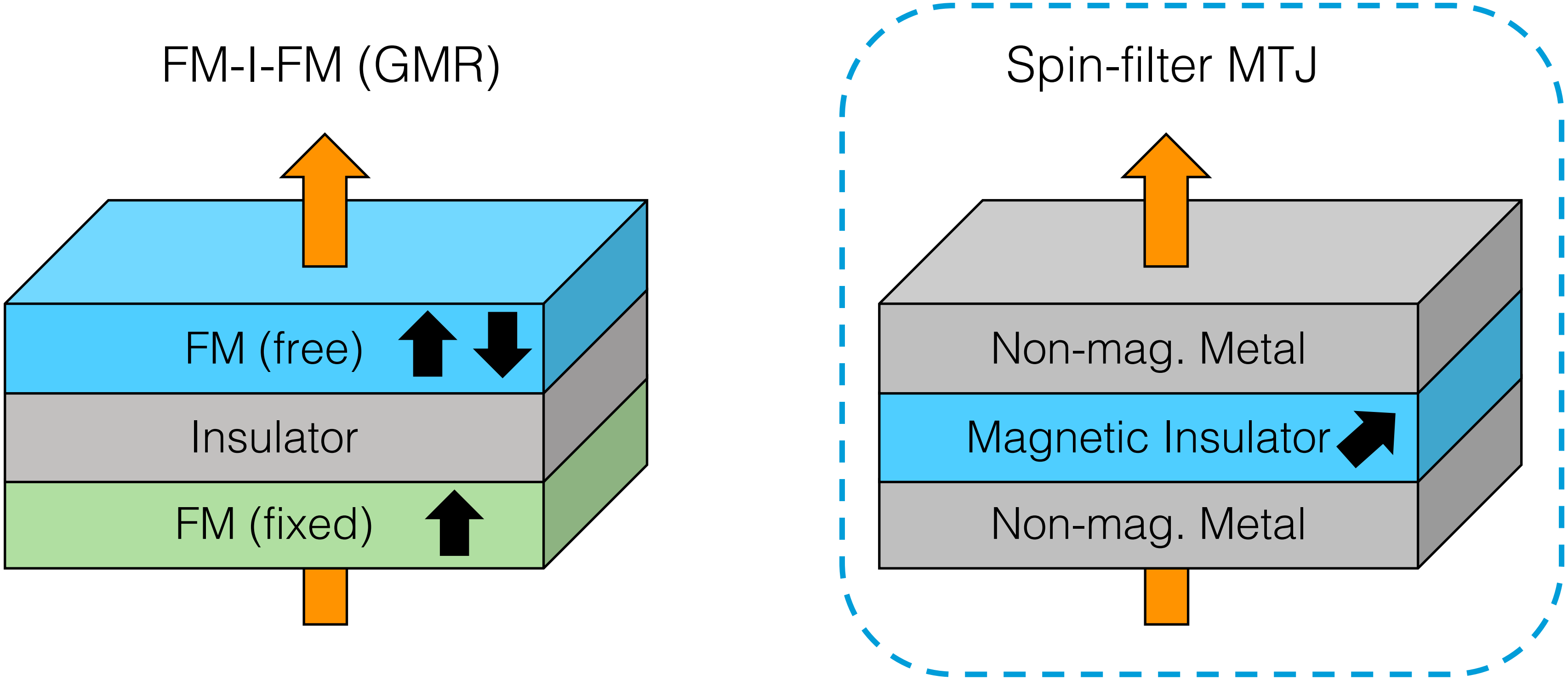
2007 Nobel Prize 

GMR-based read head of hard disk drive



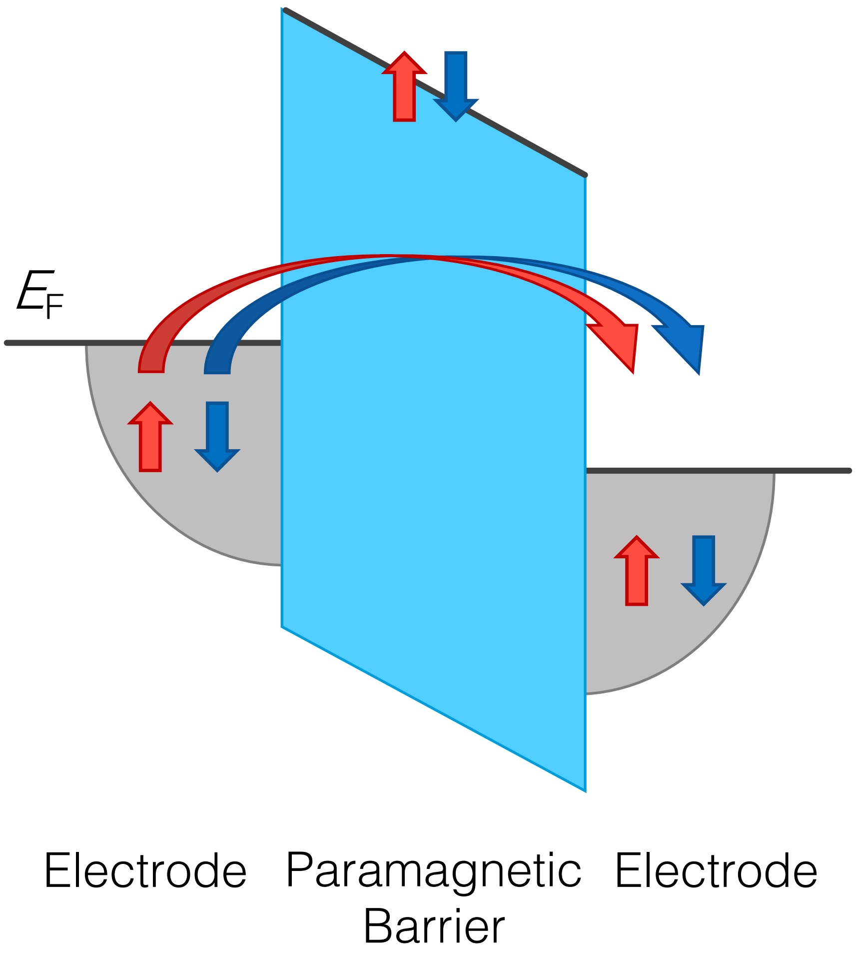
Materials Today (2003)

Magnetic Tunnel Junctions



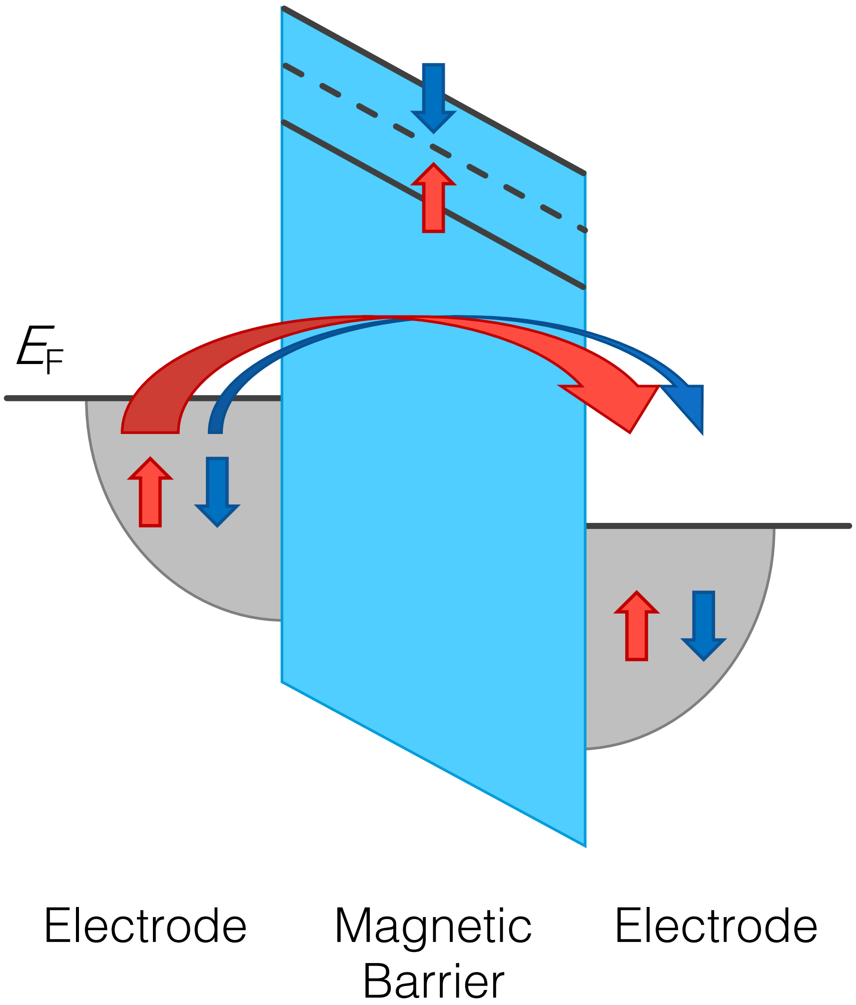
Same principle: Tunneling *R* depends on *M*

Spin-Filter Effect



Paramagnet:
No spin polarization above T_C or T_N

Spin-Filter Effect

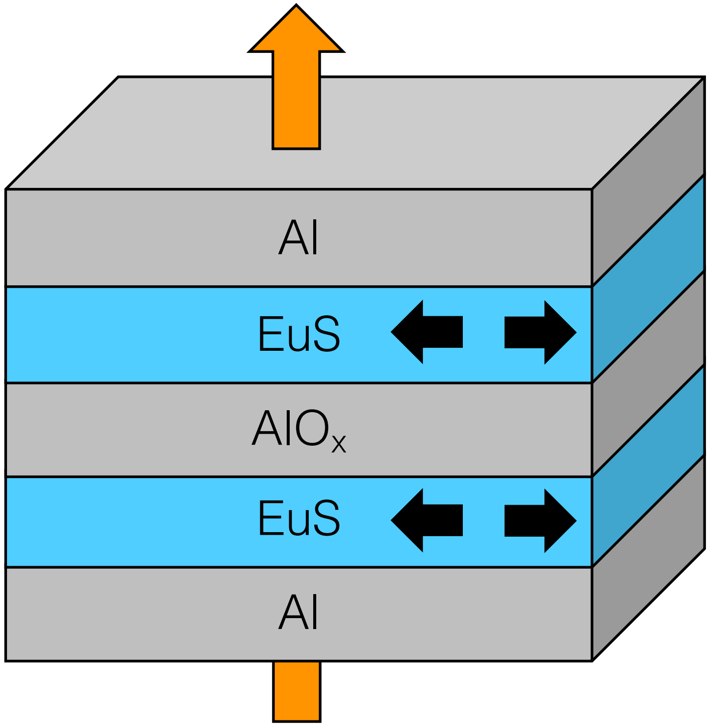


Ferromagnet:
Barrier height depends on electron spin polarization

→ Spin-dependent tunneling probability

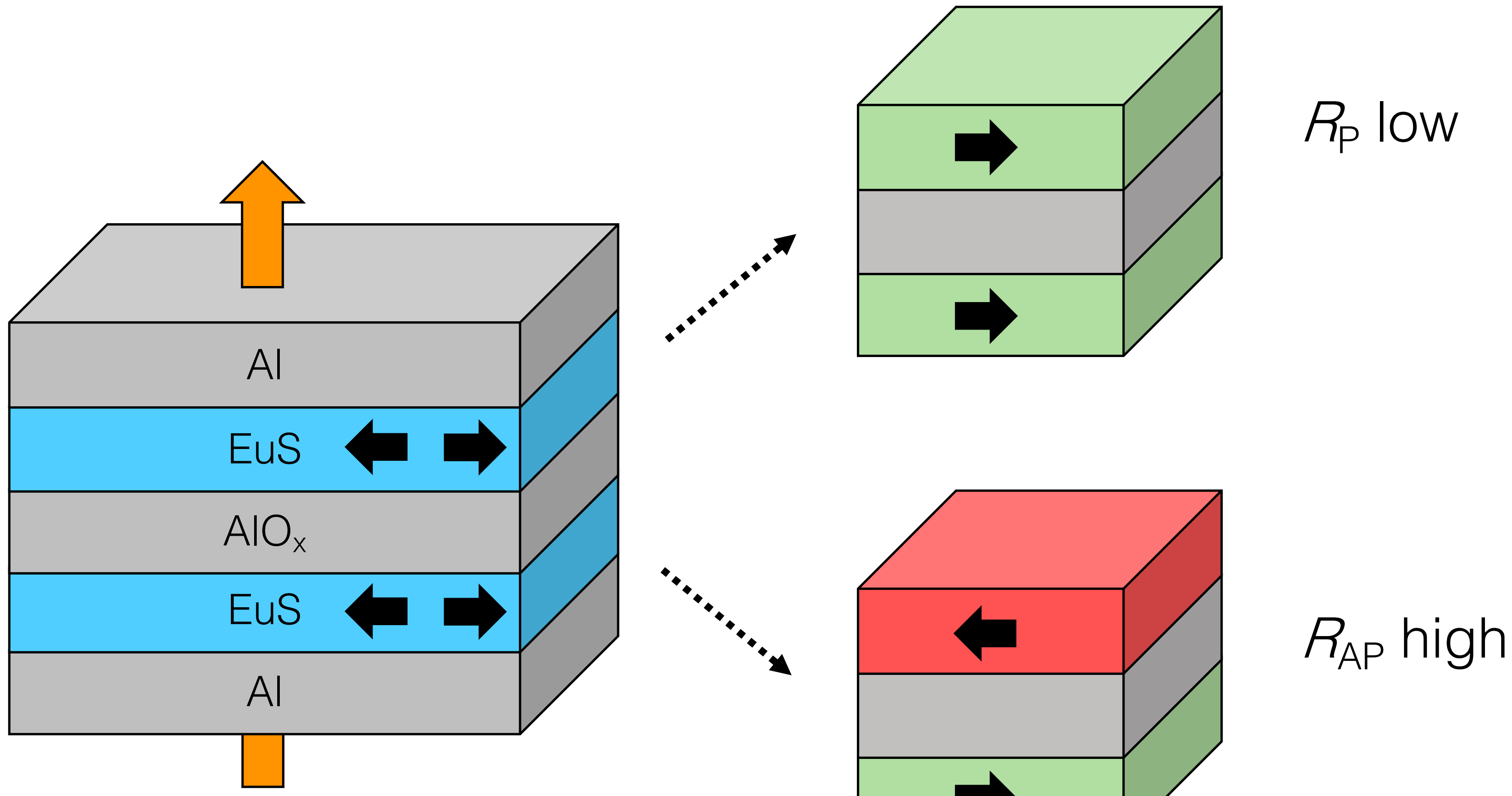
→ Spin-polarized current

Double Spin Filter



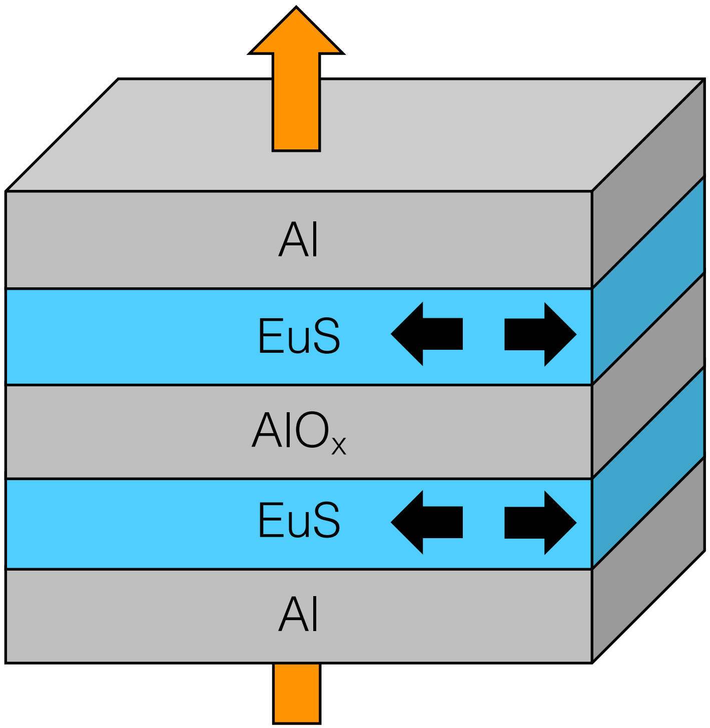
Resistance depends on relative magnetization of 2 FM layers

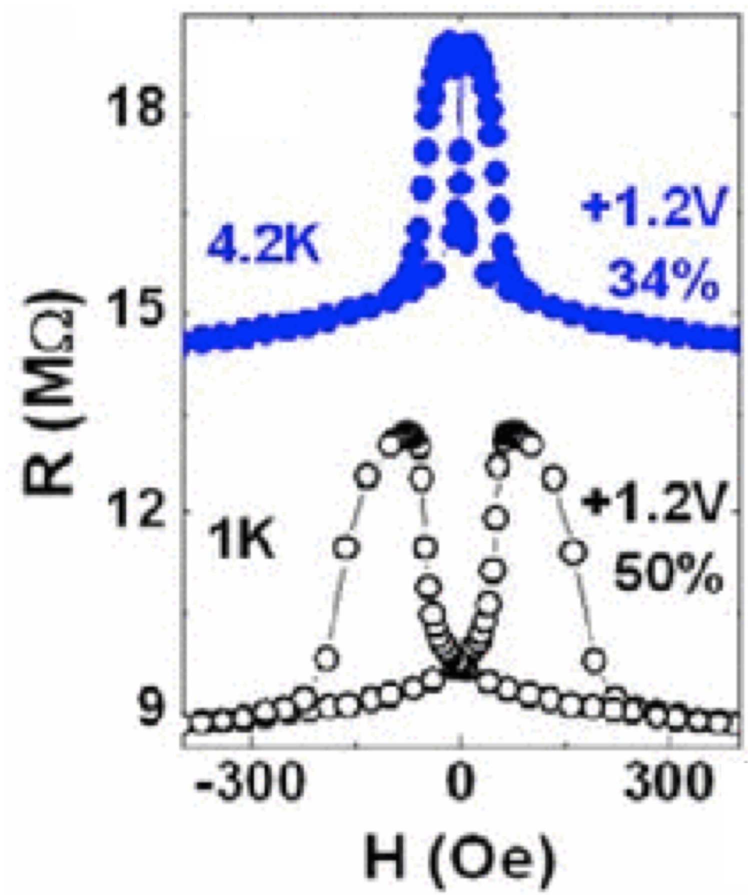
Double Spin Filter



Double Spin Filter

Moodera Group (MIT)

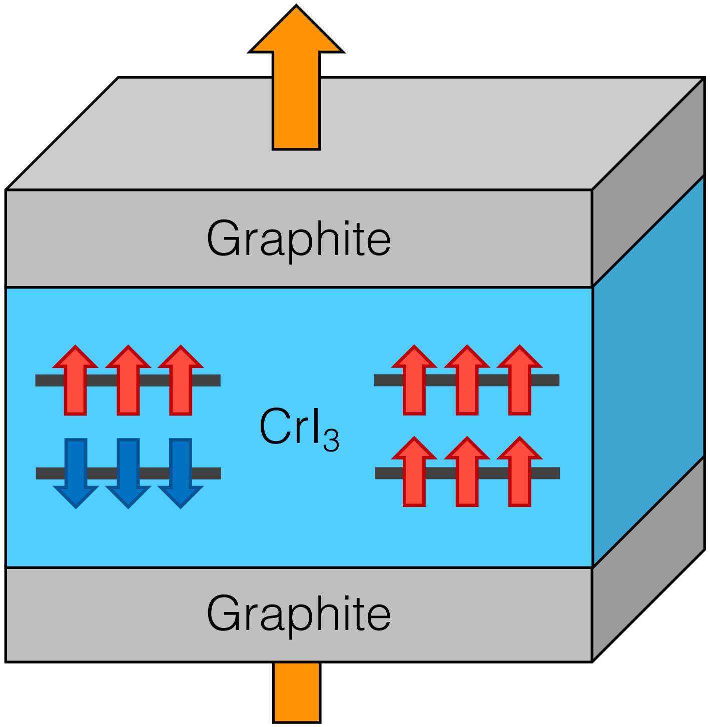




Miao *et al.*, *PRL* (2009)

van der Waals Spin-Filter MTJs

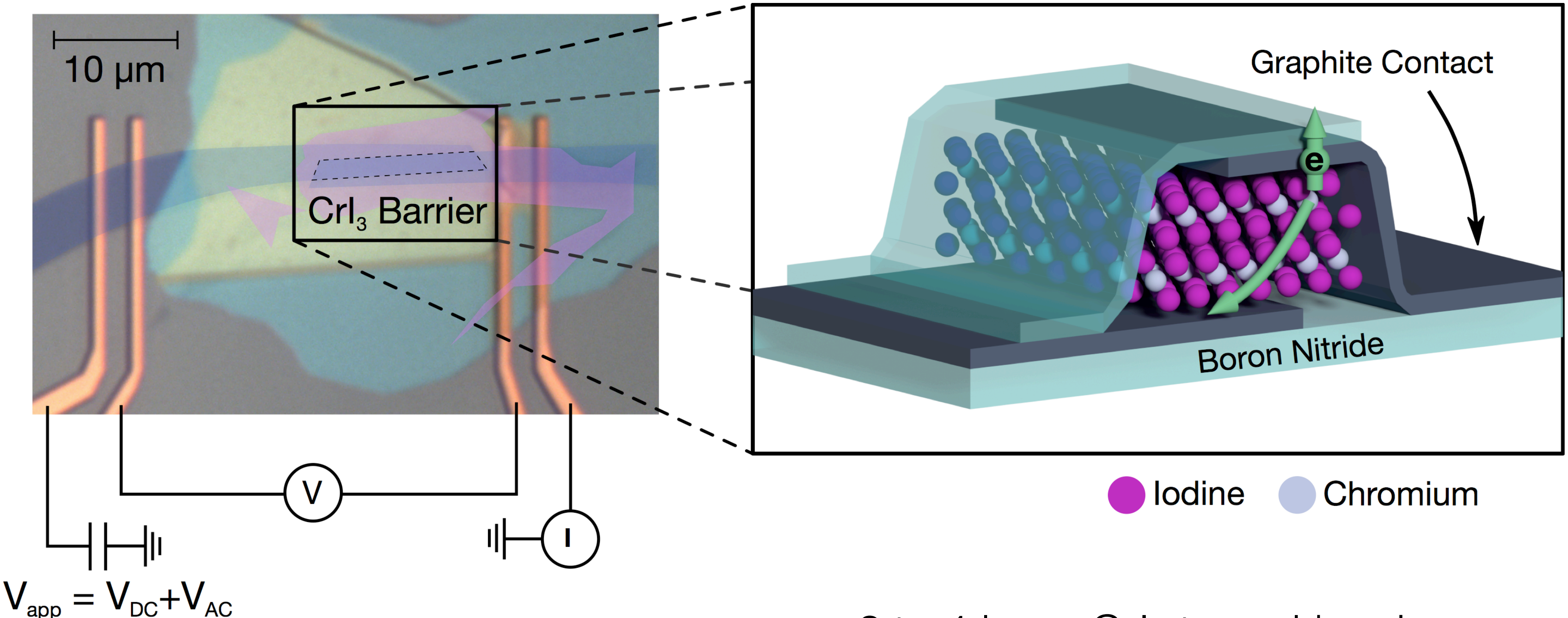
van der Waals heterostructures



2L CrI_3 acts as double spin filter

Tunnel through CrI_3 to electrically read out magnetic state (AFM vs. FM)

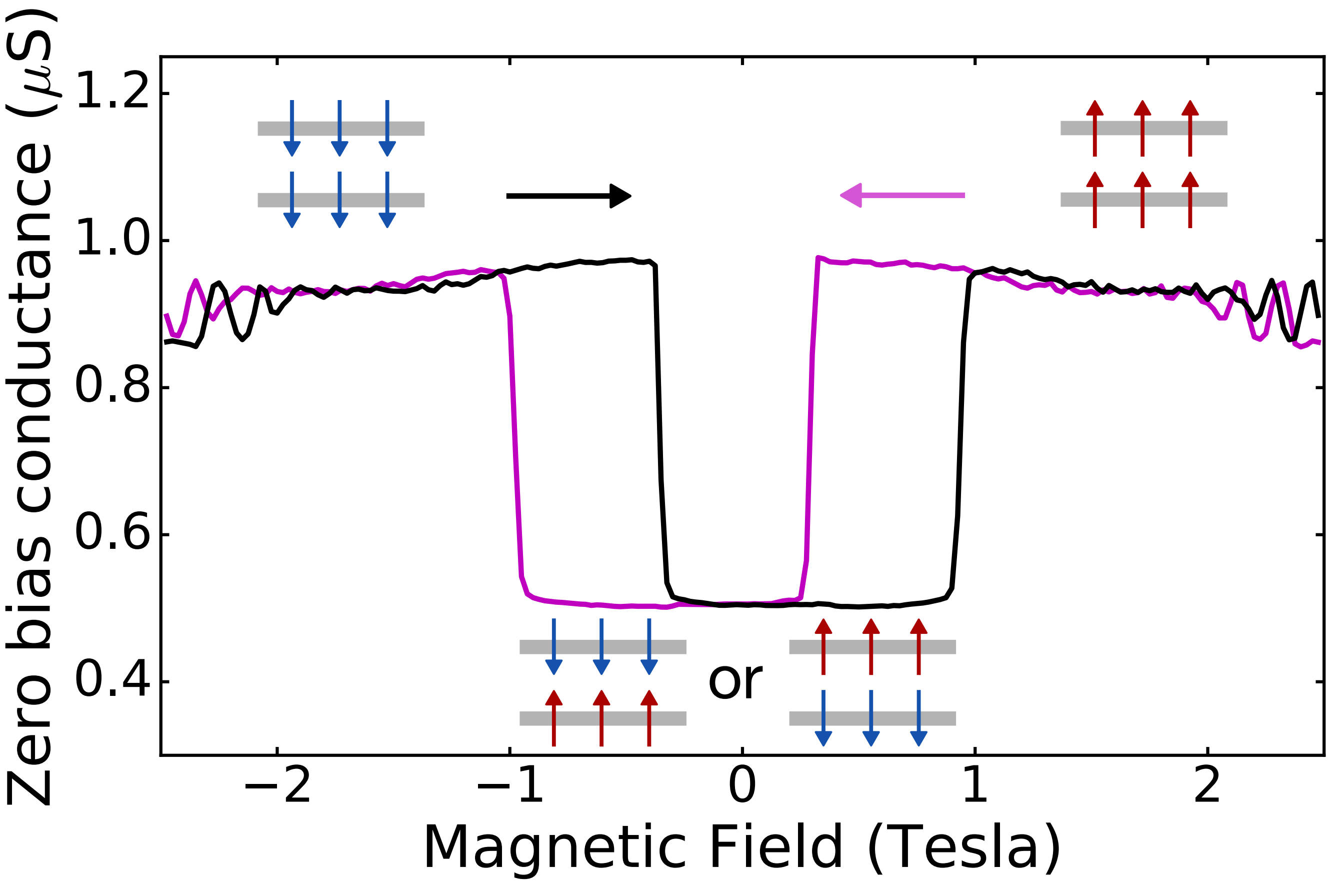
Device Structure



2 to 4 layer CrI_3 tunnel barrier

Klein *et al.*, *Science* (2018)

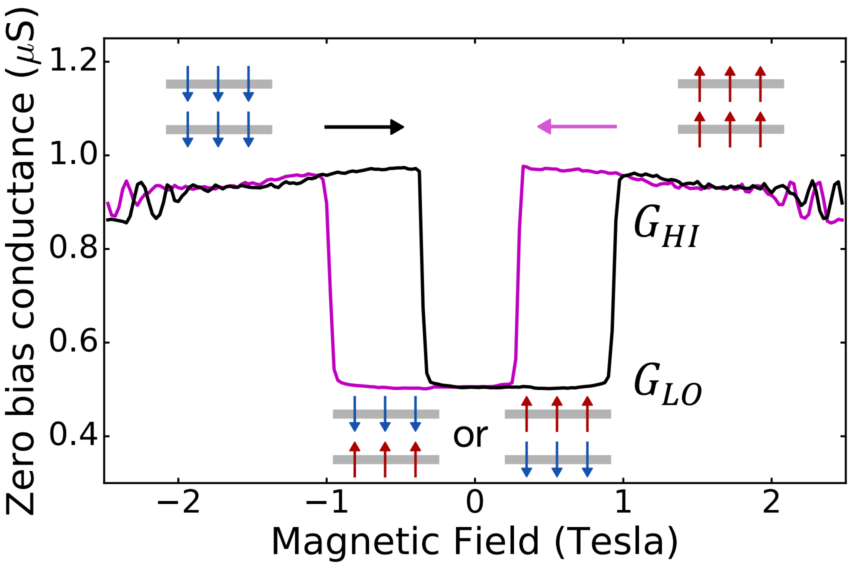
Bilayer CrI_3 Junction



Electrical detection of AFM-FM transition

Klein *et al.*, *Science* (2018)

Bilayer CrI_3 Junction



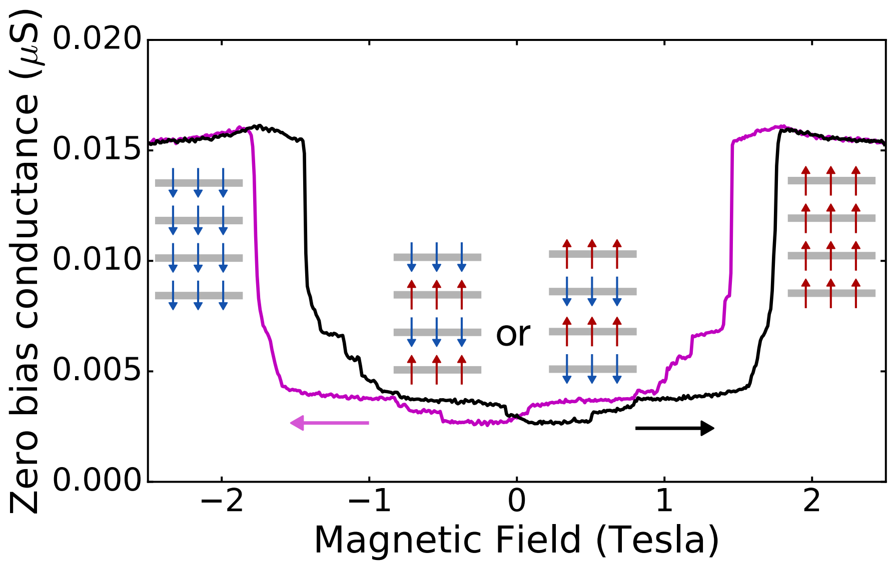
95% Magnetoresistance

Estimated spin polarization:

$$\frac{G_\uparrow - G_\downarrow}{G_\uparrow + G_\downarrow} \approx 85\%$$

Klein *et al.*, *Science* (2018)

Tetralayer CrI_3 Junction



550% Magnetoresistance!

Estimated spin polarization:

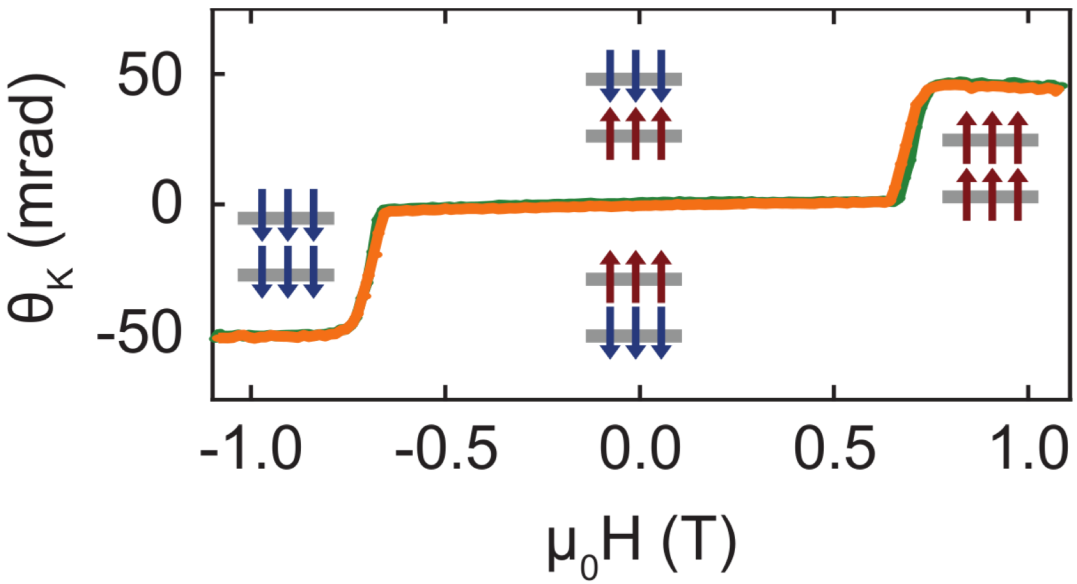
$$\frac{G_\uparrow - G_\downarrow}{G_\uparrow + G_\downarrow} \approx 99\%$$

Potential source of spin-polarized current

Klein *et al.*, *Science* (2018)

Mystery of Magnetism in CrI_3

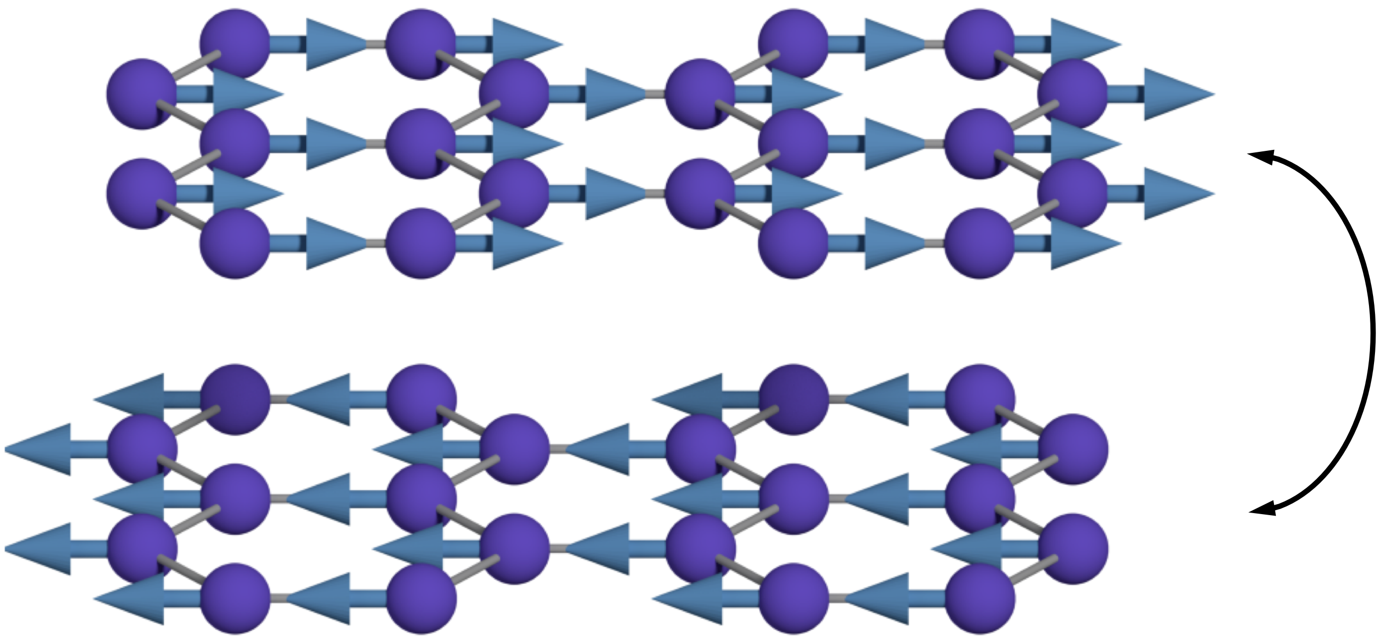
Why is ultrathin CrI_3 AFM if bulk is FM?



What about the other CrX_3?

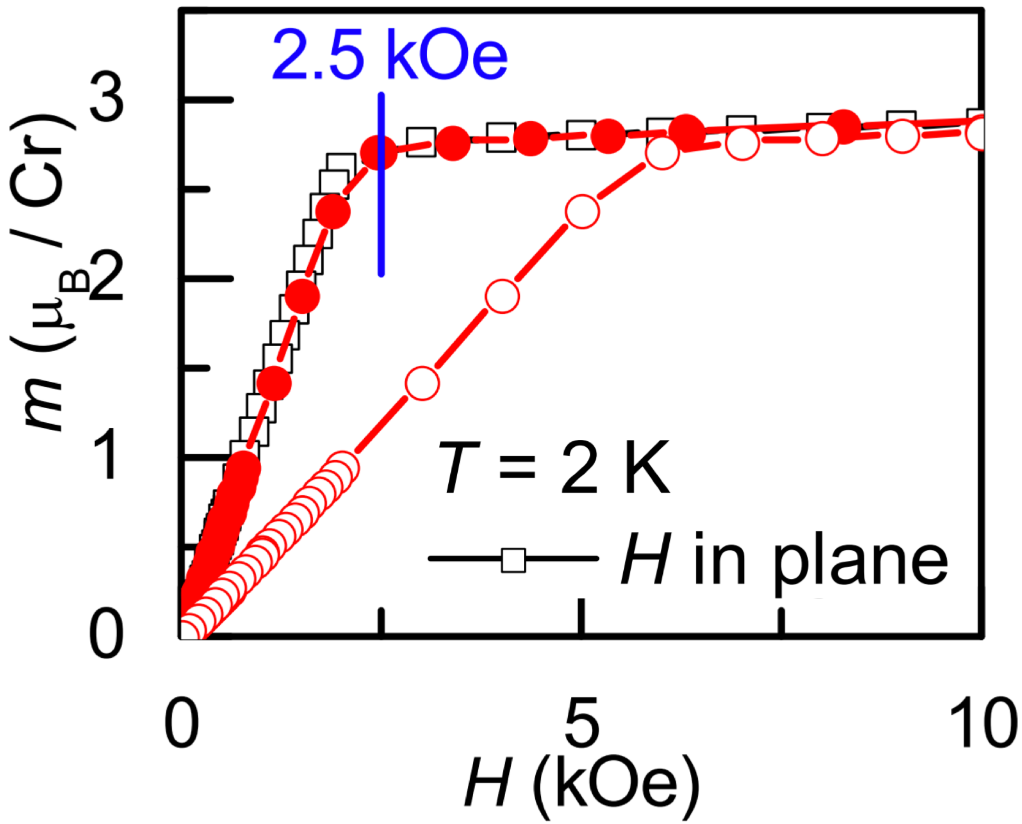
$CrCl_3$: Layered Antiferromagnet

Analogous crystal structure to CrI_3
In-plane magnetic moments



AFM
interlayer coupling

$CrCl_3$: Layered Antiferromagnet

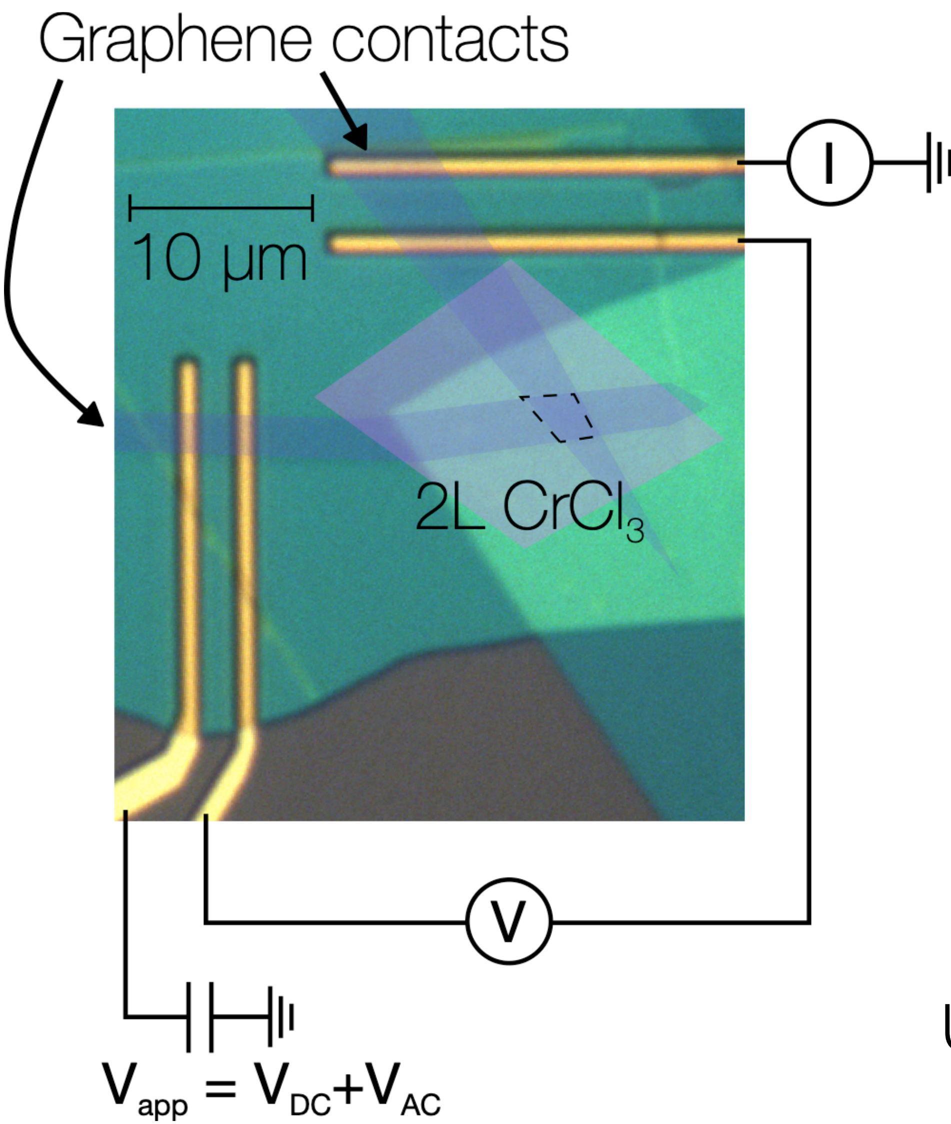


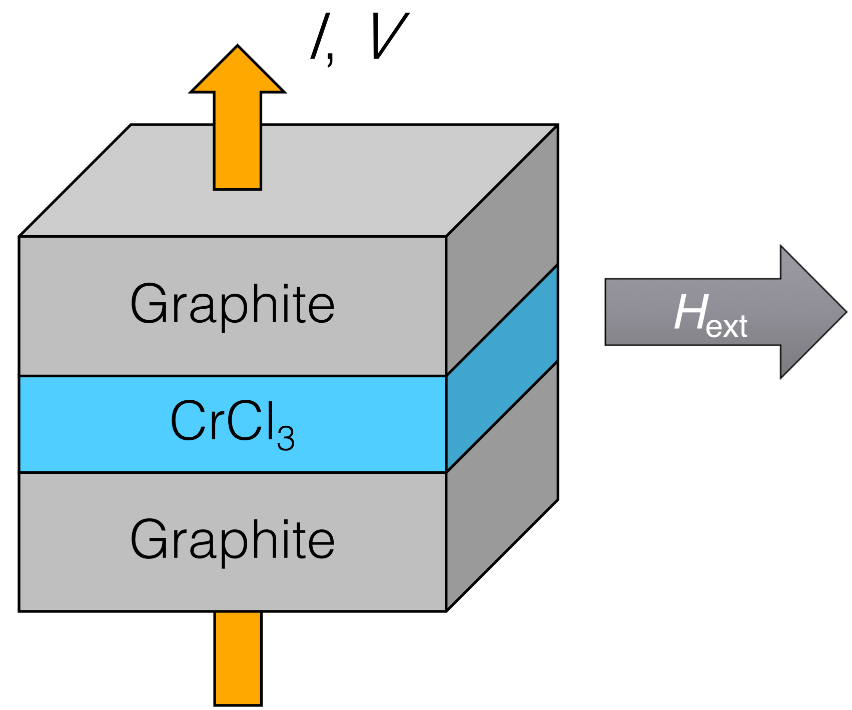
Bulk magnetization saturates with in-plane field of 0.25 T

Is the magnetic behavior the same in few-layer $CrCl_3$?

McGuire *et al.*, *Phys. Rev. Mater.* (2018)

Tunneling through $CrCl_3$

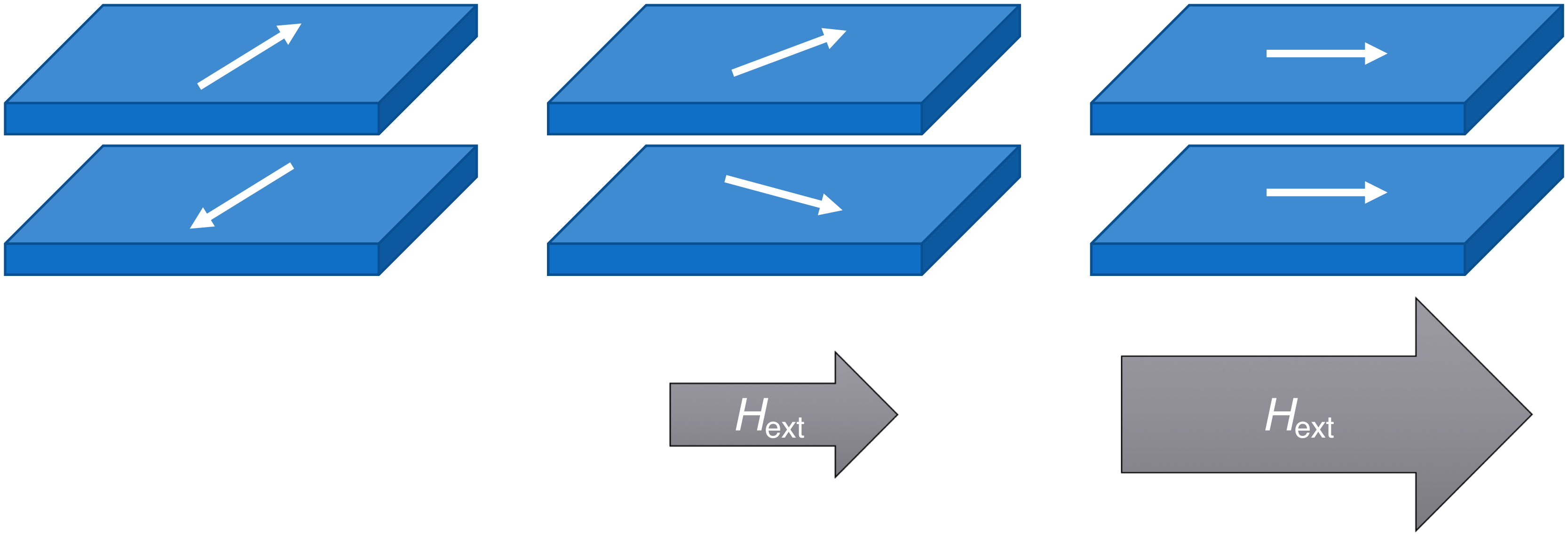




MTJs with 2-4 layer $CrCl_3$ barrier

Use MR to measure interlayer exchange coupling

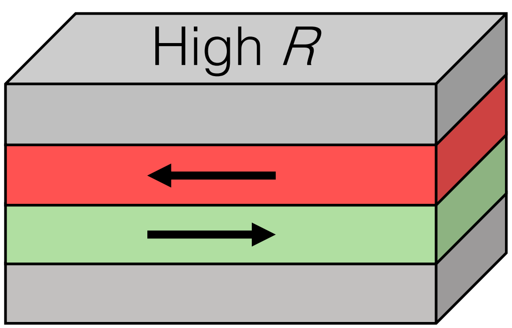
Tunneling through $CrCl_3$



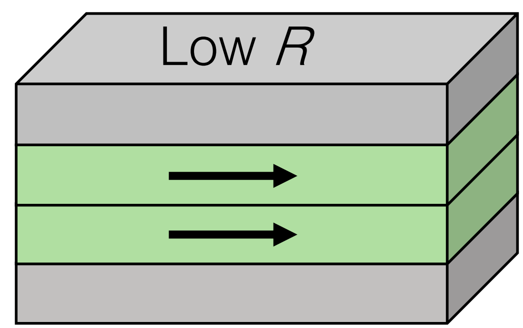
AFM ground state

Spins begin to cant towards field

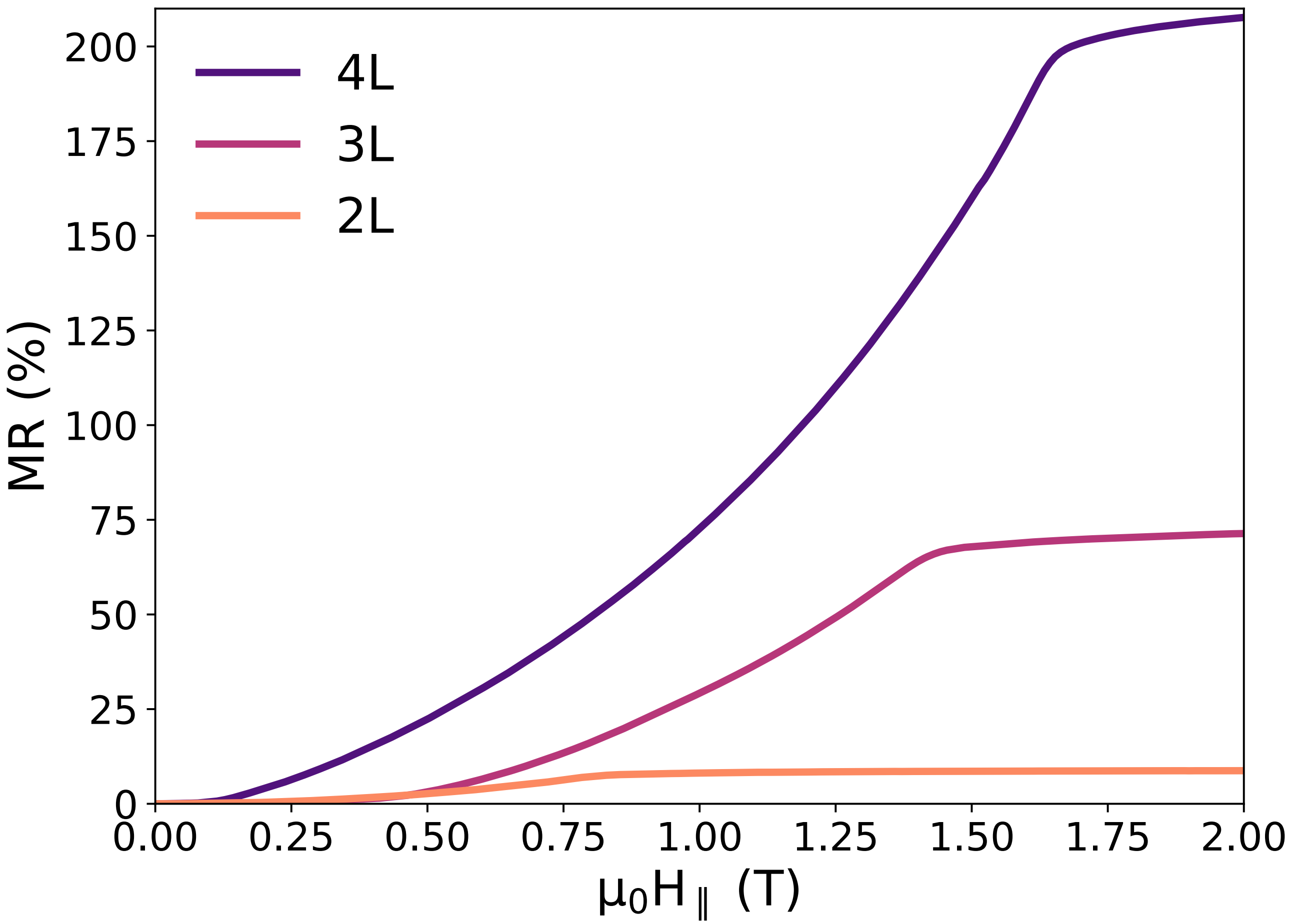
Spins fully aligned at saturation field H_{sat}



Use MR to read out H_{sat}

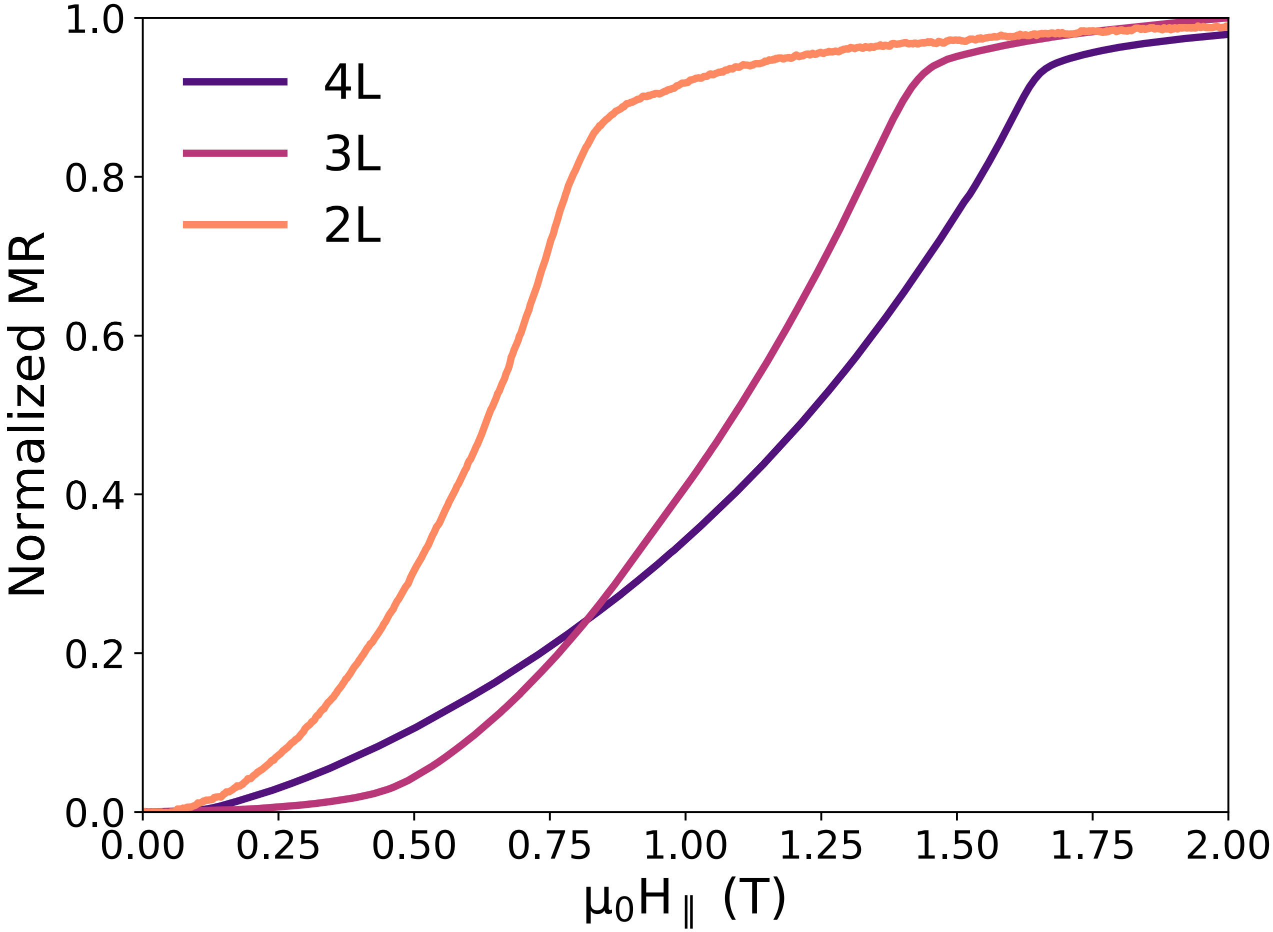


Magnetoresistance



Klein *et al.*, *Nat. Phys.* (2019)

Magnetoresistance



$\mu_0 H_{sat}$:
1.65 T
1.45 T
0.85 T

Much larger than bulk $\mu_0 H_{sat}$ ~0.25 T

Klein *et al.*, *Nat. Phys.* (2019)

Interlayer Exchange

Extract interlayer exchange $\mu_0 H_E$ from $\mu_0 H_{sat}$:

0.97 T (4L)
0.96 T (3L)
0.86 T (2L)

Magnetization models:

$$H_{sat} = (1 + \sqrt{2}/2) H_E \quad (4L)$$

$$H_{sat} = \frac{3}{2} H_E \quad (3L)$$

$$H_{sat} = H_E \quad (2L)$$

Klein *et al.*, *Nat. Phys.* (2019)

Interlayer Exchange

Extract interlayer exchange
$\mu_0 H_E$ from $\mu_0 H_{sat}$:

0.97 T (4L)

0.96 T (3L)

0.86 T (2L)

0.084 T (bulk)
[Narath & Davis, *Phys. Rev.* (1965)]

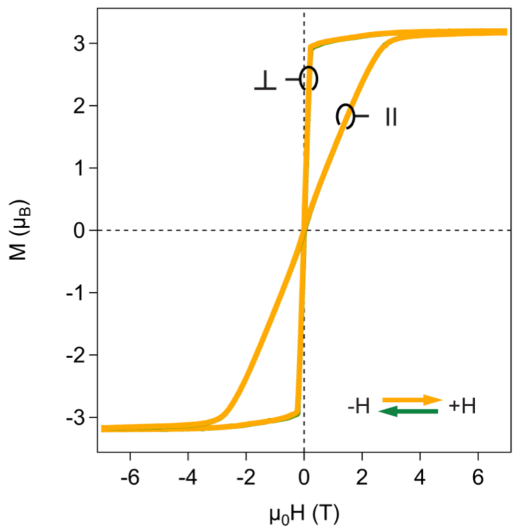
10x increase in interlayer exchange in ultrathin $CrCl_3$!

Klein *et al.*, *Nat. Phys.* (2019)

Bulk vs. Thin Films of CrX_3

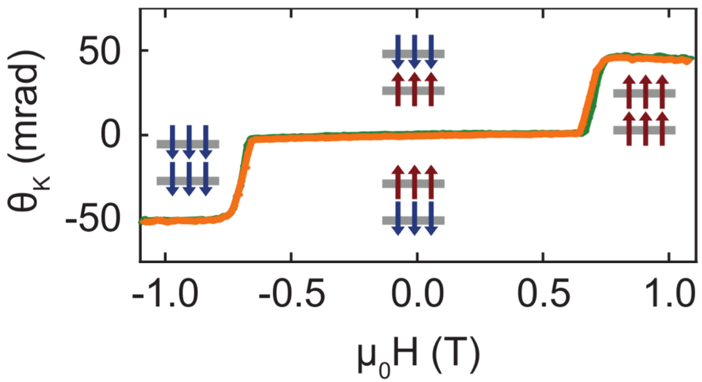
Bulk $CrCl_3$:
Small AFM interlayer coupling

Bulk CrI_3:
FM interlayer coupling



Few-layer $CrCl_3$:
Large AFM interlayer coupling

Few-layer CrI_3:
AFM interlayer coupling



Huang *et al.*, *Nature* (2017)

Mystery of Magnetism in CrX_3

arXiv.org > cond-mat > arXiv:1806.09274

Condensed Matter > Materials Science

Stacking tunable interlayer magnetism in bilayer CrI3

Peiheng Jiang, Cong Wang, Dachuan Chen, Zhicheng Zhong, Zhe Yuan, Zhong-Yi Lu, Wei Ji

(Submitted on 25 Jun 2018 (v1), last revised 2 Mar 2019 (this version, v2))

arXiv.org > cond-mat > arXiv:1807.00357

Condensed Matter > Mesoscale and Nanoscale Physics

Interplay between interlayer exchange and stacking in CrI_3 bilayers

D. Soriano, C. Cardoso, J. Fernández-Rossier

(Submitted on 1 Jul 2018 (v1), last revised 25 Mar 2019 (this version, v2))

arXiv.org > cond-mat > arXiv:1808.06559

Condensed Matter > Materials Science

Stacking-Dependent Magnetism in Bilayer CrI_3

Nikhil Sivadas, Satoshi Okamoto, Xiaodong Xu, Craig. J. Fennie, Di Xiao

(Submitted on 20 Aug 2018 (v1), last revised 15 Nov 2018 (this version, v2))

arXiv.org > cond-mat > arXiv:1809.01388

Condensed Matter > Materials Science

Microscopic understanding of magnetic interactions in bilayer CrI_3

Seung Woo Jang, Min Yong Jeong, Hongkee Yoon, Siheon Ryee, Myung Joon Han

(Submitted on 5 Sep 2018)

arXiv.org > cond-mat > arXiv:1901.09525

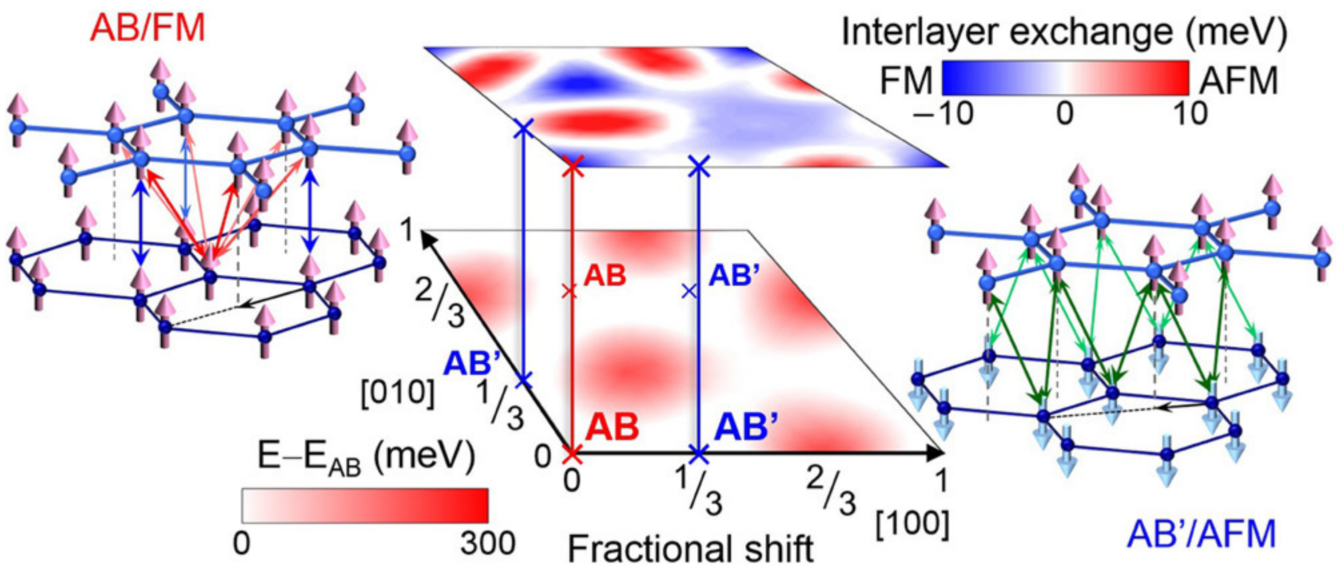
Condensed Matter > Materials Science

Microscopic origin of ferromagnetism in trihalides $CrCl_3$ and CrI_3

Omar Besbes, Sergey Nikolaev, Igor Solovyev

(Submitted on 28 Jan 2019)

Hypothesis: Stacking Order in CrX_3

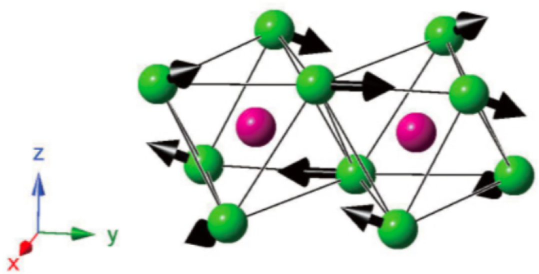


First principles calculations: interlayer coupling in 2L CrI_3

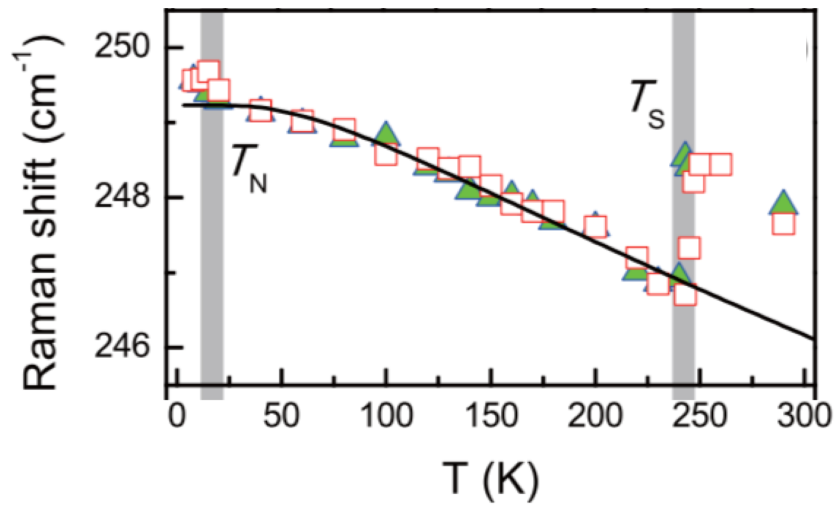
Could stacking order play a role in $CrCl_3$ interlayer exchange?

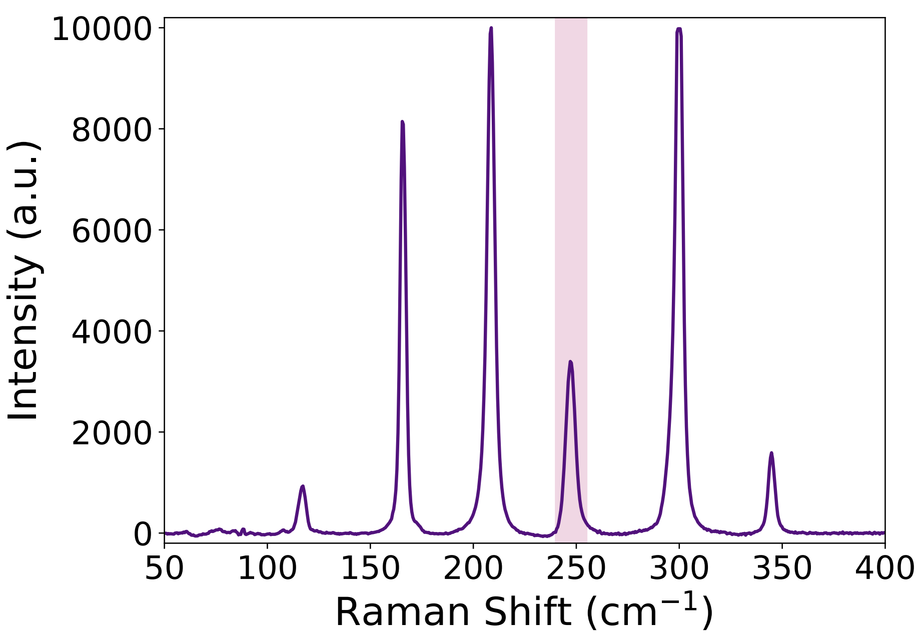
Sivadas *et al.*, *Nano Lett.* (2018)

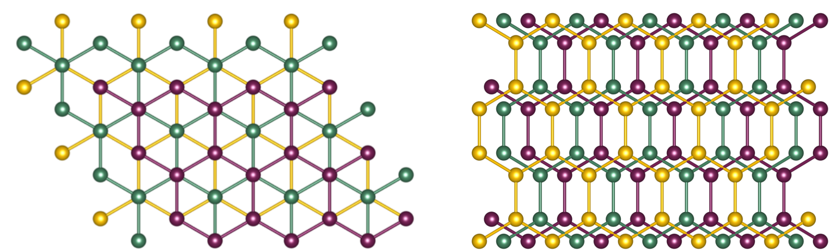
Raman Spectroscopy of $CrCl_3$



247 cm^{-1} Raman peak
sensitive to stacking





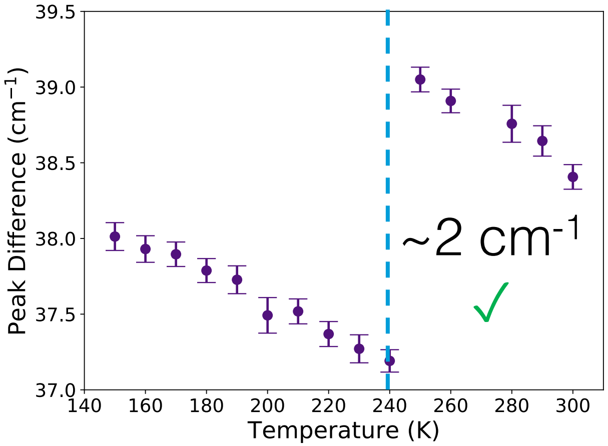


Bulk peak jumps at T_S
by ~2 cm^{-1}

Glamazda *et al.*, *Phys. Rev. B* (2017)

Investigating Phase Transition

Use relative shift from constant reference peak at 209 cm^{-1}

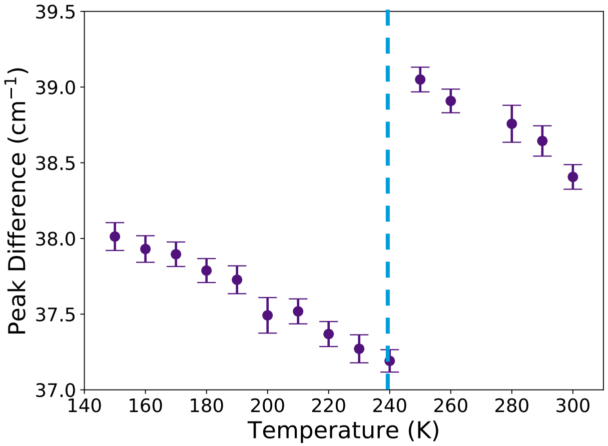


Bulk

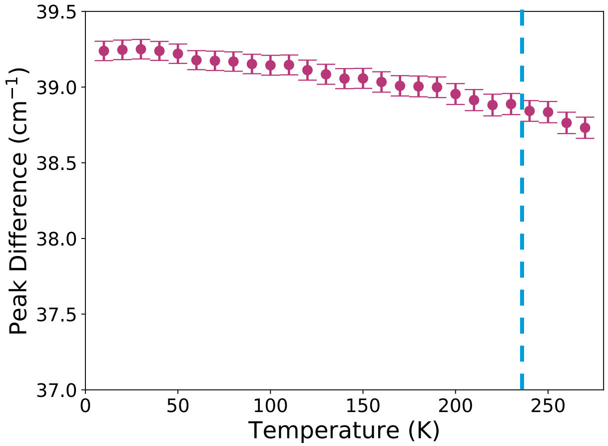
Klein *et al.*, *Nat. Phys.* (2019)

Investigating Phase Transition

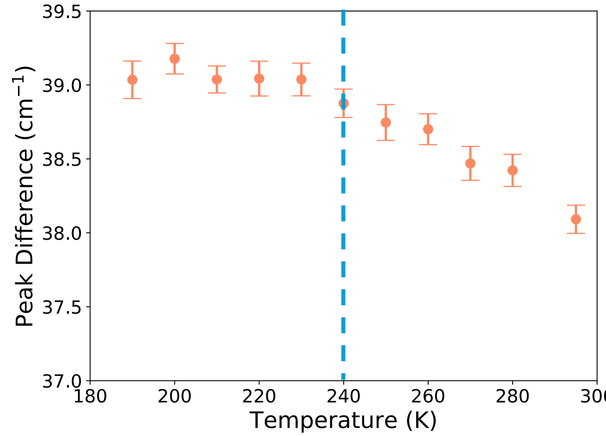
Use relative shift from constant reference peak at 209 cm^{-1}



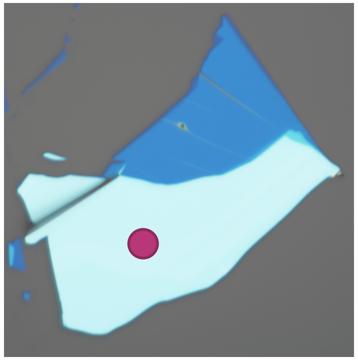
Bulk

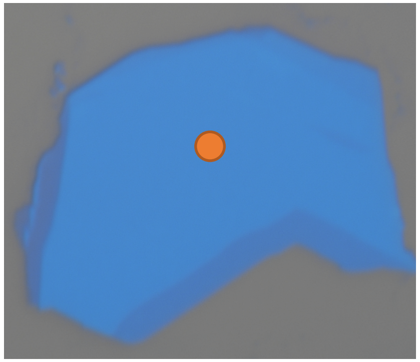


35 nm Flake



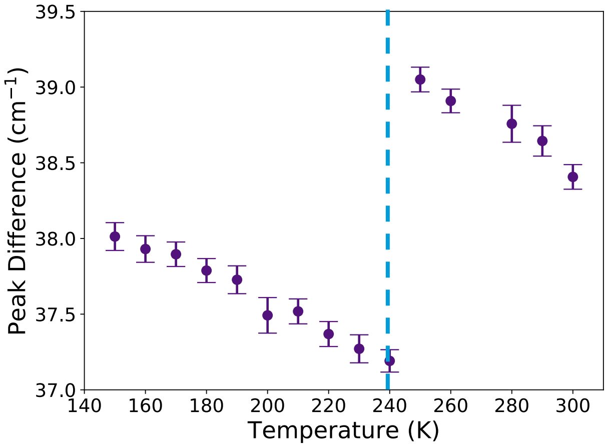
8 nm Flake



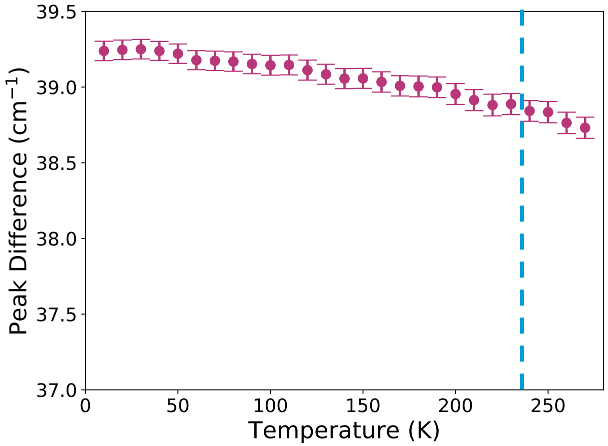


Klein *et al.*, *Nat. Phys.* (2019)

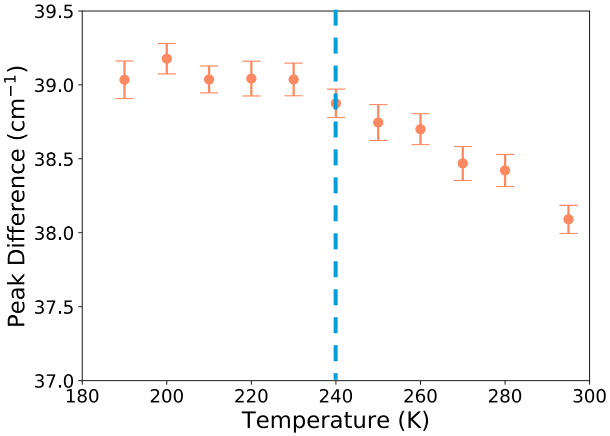
Investigating Phase Transition



Bulk



35 nm Flake



8 nm Flake

No evidence of phase transition in thin flakes even down to 10 K!

Does thin $CrCl_3$ remain in the monoclinic phase at low T?

Klein *et al.*, *Nat. Phys.* (2019)

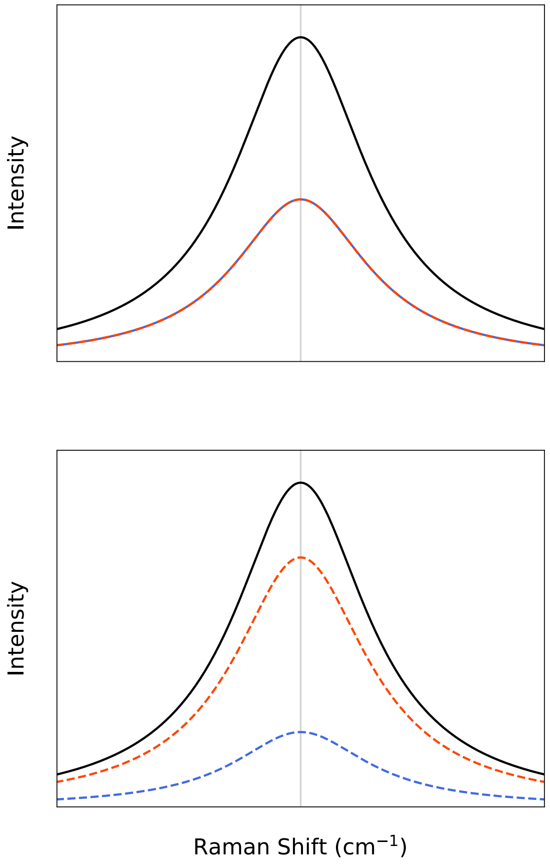
Symmetry of 247 cm^{-1} Peak

Peak energy vs. Raman polarization angle

Rhombohedral Phase (Low T):
$^{1}E_g + {}^{2}E_g$

Degenerate phonon modes

No polarization dependence in peak energy



Symmetry of 247 cm^{-1} Peak

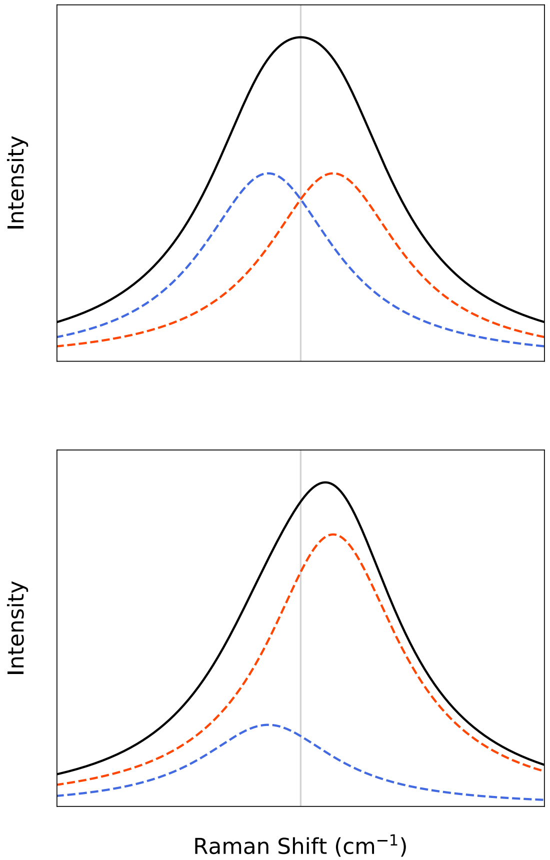
Peak energy vs. Raman polarization angle

Monoclinic Phase (High T):

$A_g + B_g$

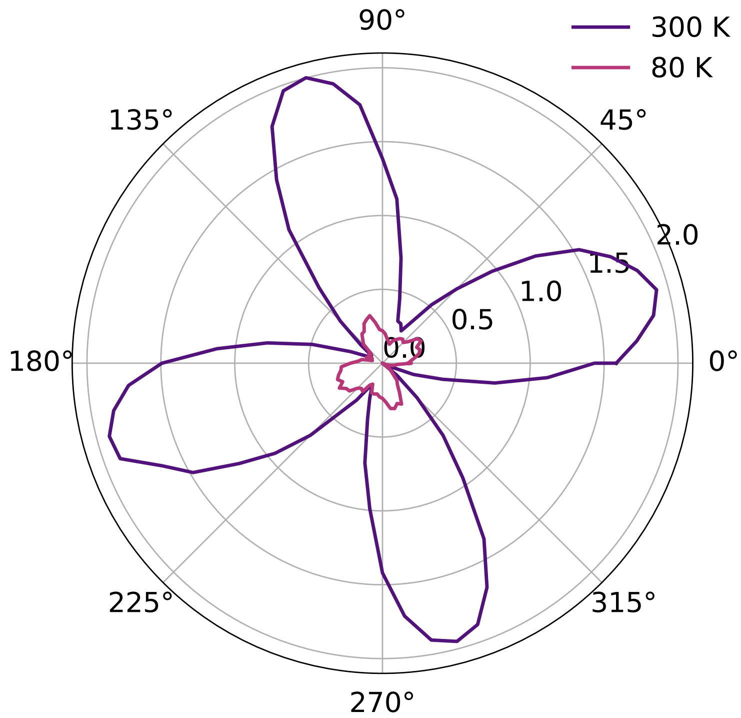
Phonon modes split

4-fold peak energy oscillation



Symmetry of 247 cm^{-1} Peak

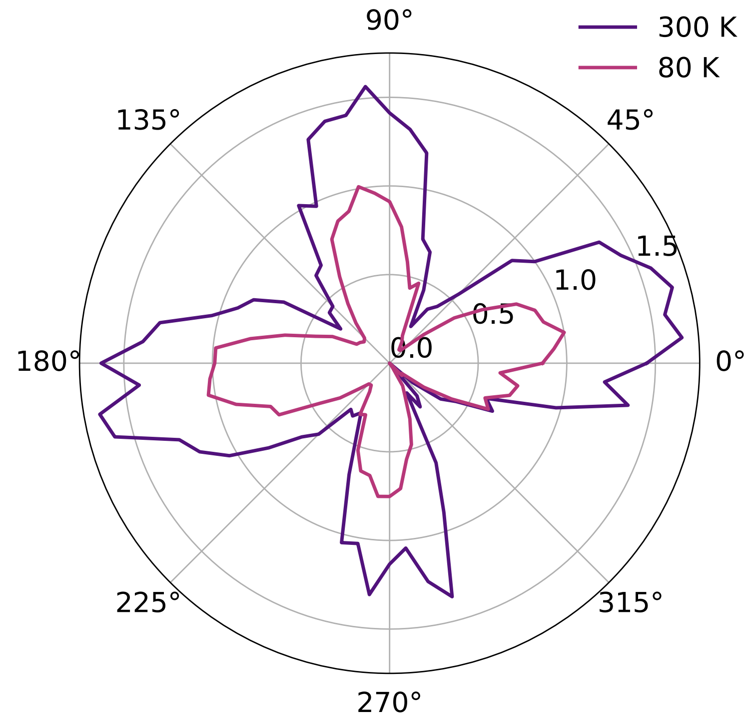
Bulk



✓ 4-fold symmetry at 300 K

✓ No symmetry at 80 K

17 nm Flake



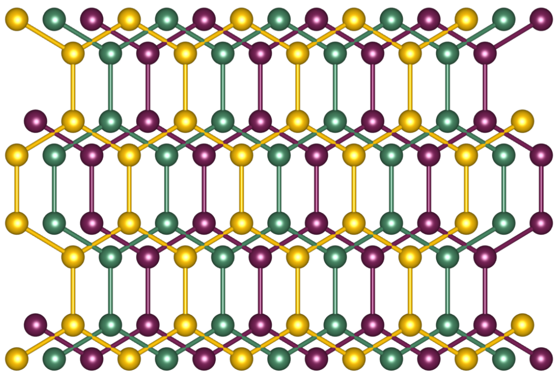
✓ 4-fold symmetry at 300 K

? 4-fold symmetry at 80 K!

Klein *et al.*, *Nat. Phys.* (2019)

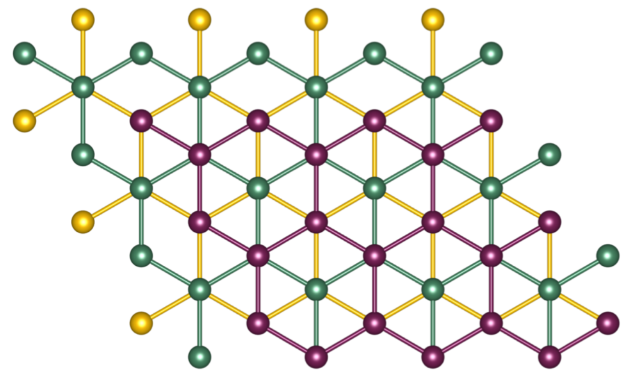
Raman Conclusions

Bulk $CrCl_3$



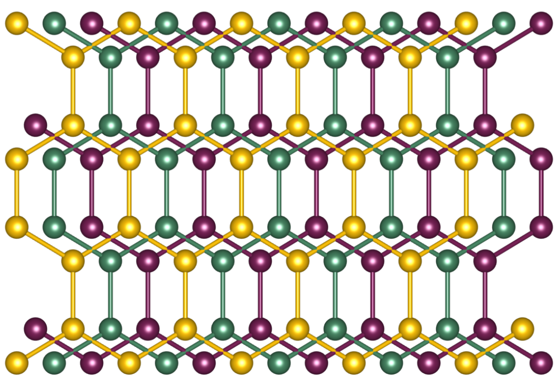
Monoclinic

Cool below 240 K



Rhombohedral

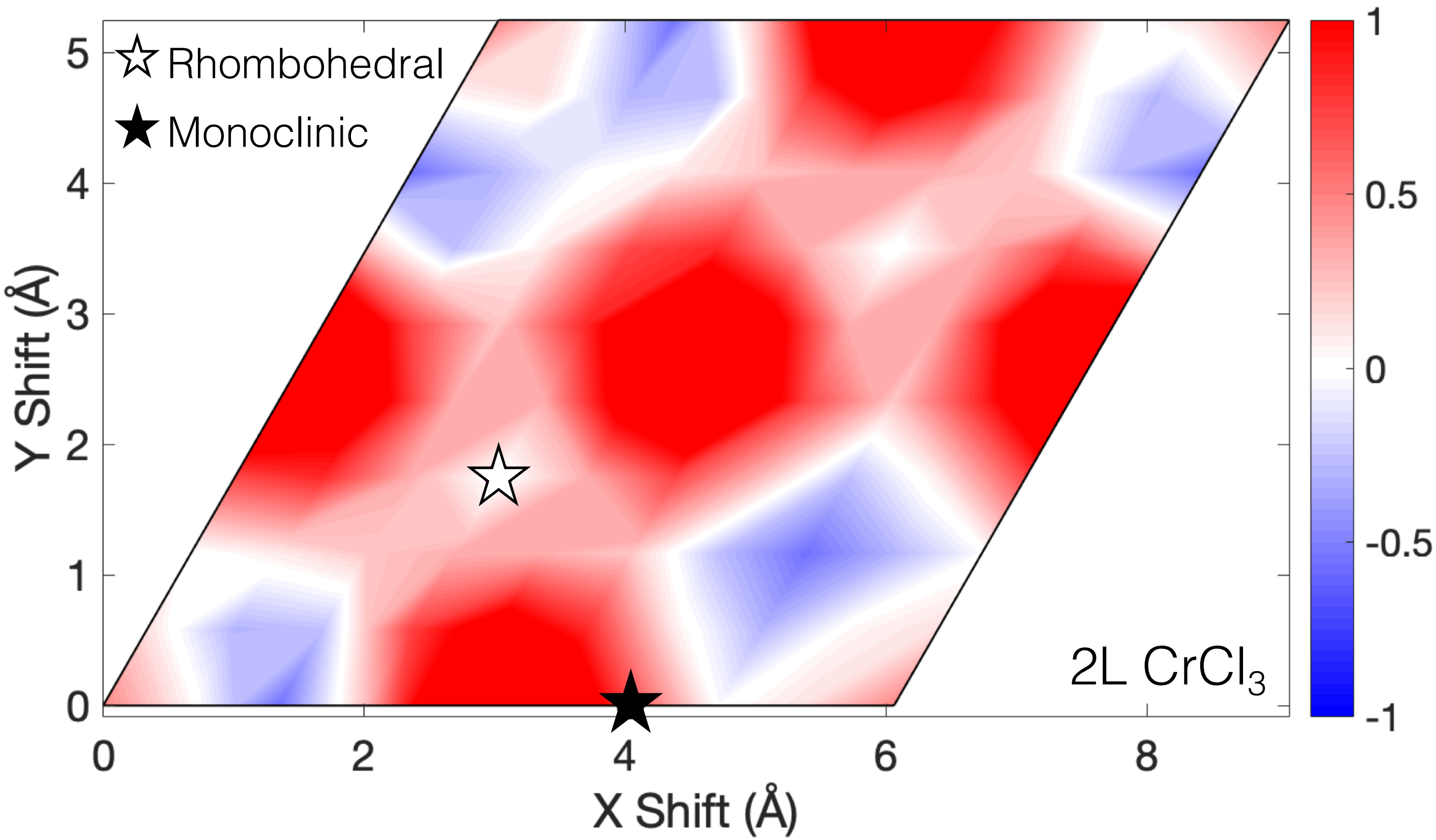
Ultrathin $CrCl_3$



Monoclinic

At all T

DFT Calculations



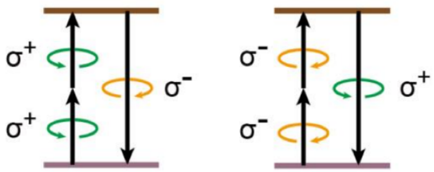
$\Delta E = E$(FM) – E(AFM) for fixed layer spacing d = 6 Å

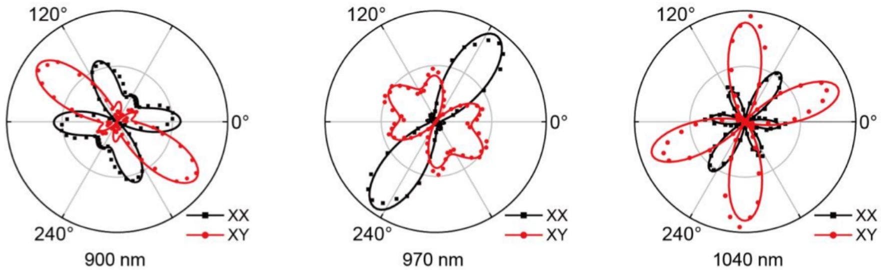
✓ Supports larger AFM exchange for monoclinic phase

Klein *et al.*, *Nat. Phys.* (2019)

Further Stacking Evidence in CrI_3

Second Harmonic Generation (SHG) of 2L CrI_3



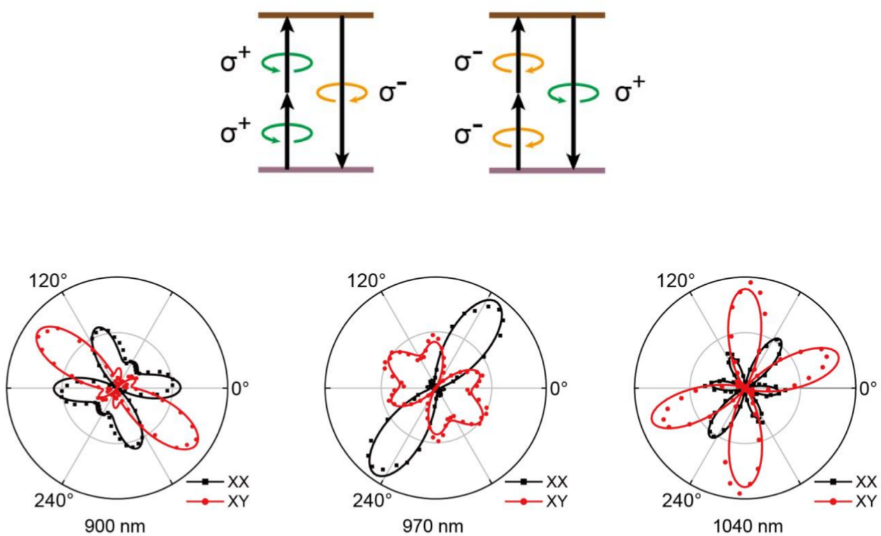


Consistent with monoclinic symmetry
Rules out rhombohedral (C_3 symmetry axis)

Sun *et al.*, *Nature* (2019)

Further Stacking Evidence in CrI_3

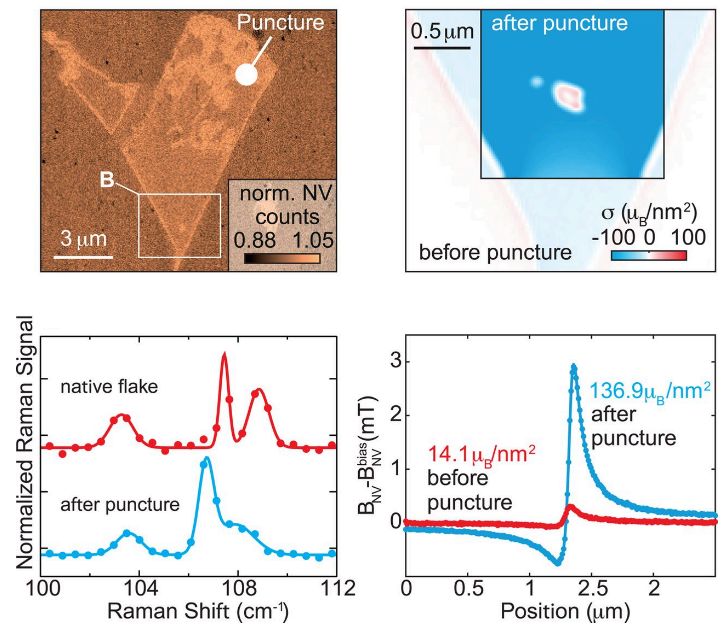
Second Harmonic Generation (SHG) of 2L CrI_3



Consistent with monoclinic symmetry
Rules out rhombohedral (C_3 symmetry axis)

Sun *et al.*, *Nature* (2019)

Scanning NV Magnetometry of 9L CrI_3

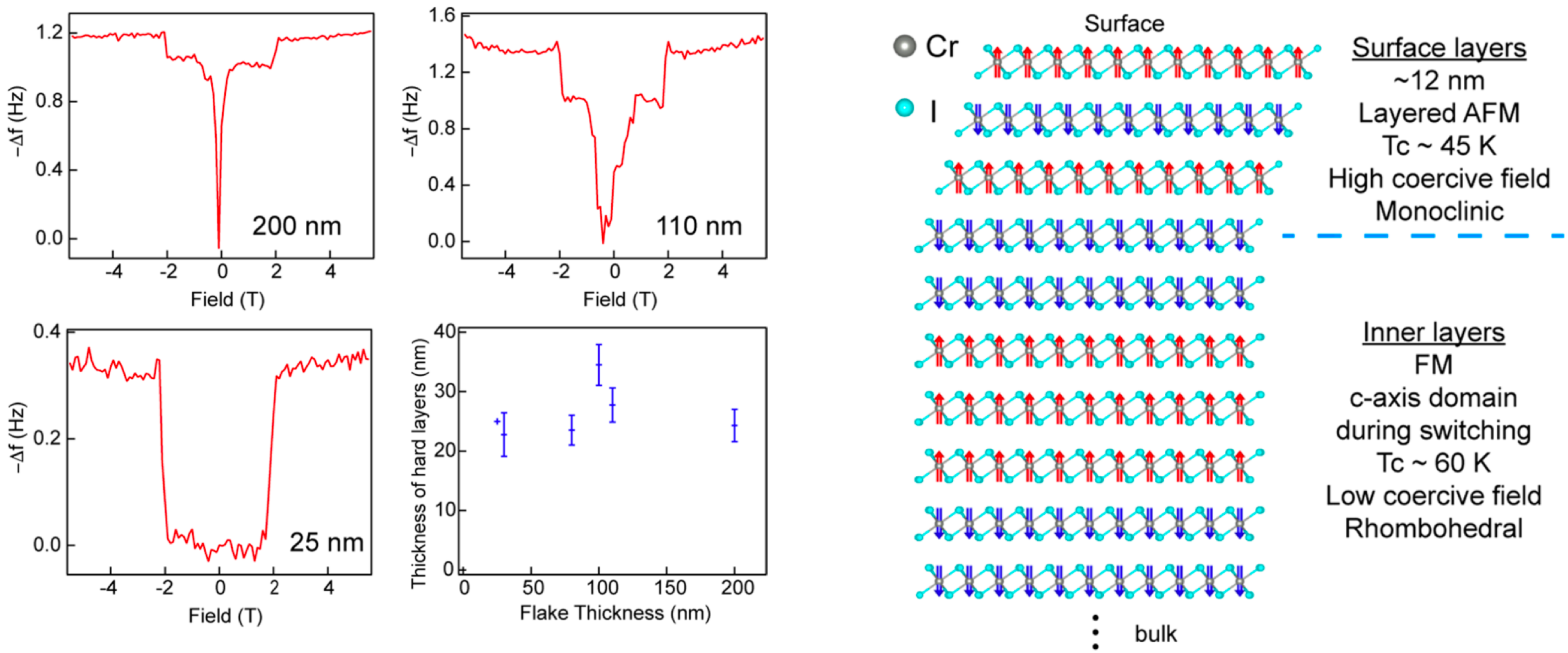


Increased *M* and shifted Raman signal after flake puncture → AFM-to-FM transition

Thiel *et al.*, *Science* (2019)

Further Stacking Evidence in CrI_3

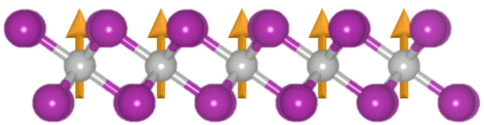
Magnetic Force Microscopy (MFM)
of thicker CrI_3 flakes (25-200 nm)

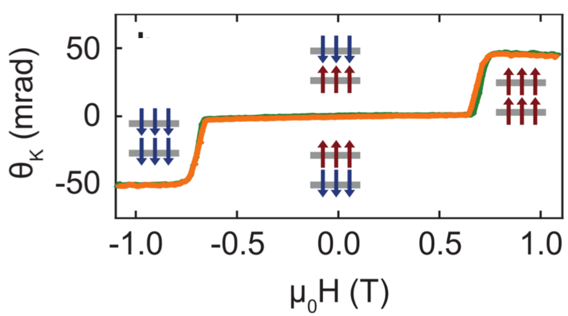


Niu *et al.*, *Nano Lett.* (2020)

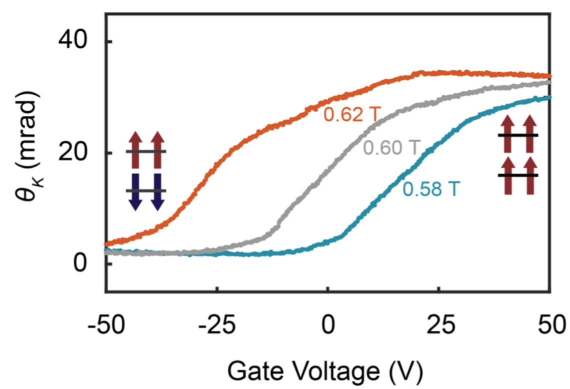
Chromium Trihalides: 2D Magnetic Insulators

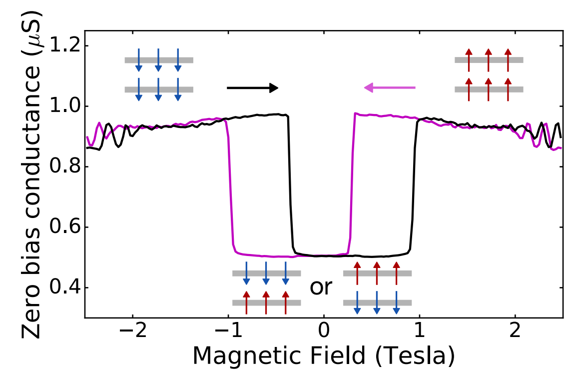
Ultrathin CrI_3: Layered AFM vs. bulk FM



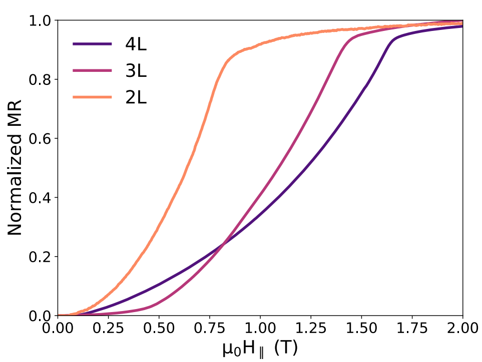


Electrical control & readout of 2D magnetic states

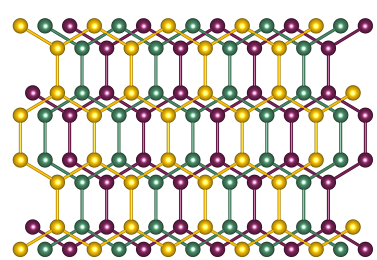




Ultrathin $CrCl_3$: 10x AFM interlayer exchange

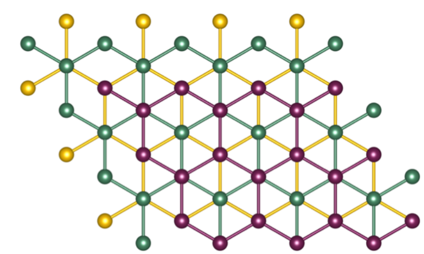


Stacking & magnetic orders strongly linked



Monoclinic

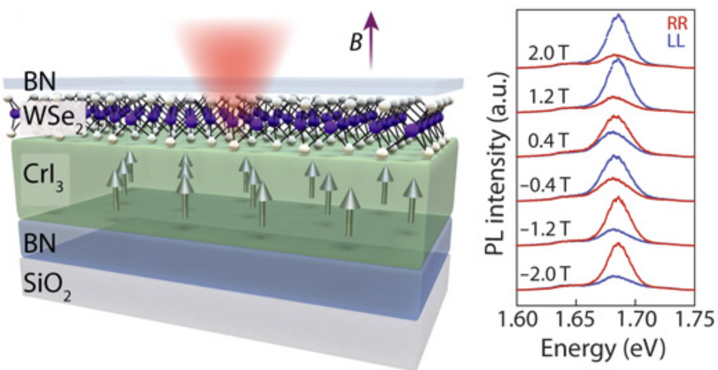
vs.



Rhombohedral

Outlook

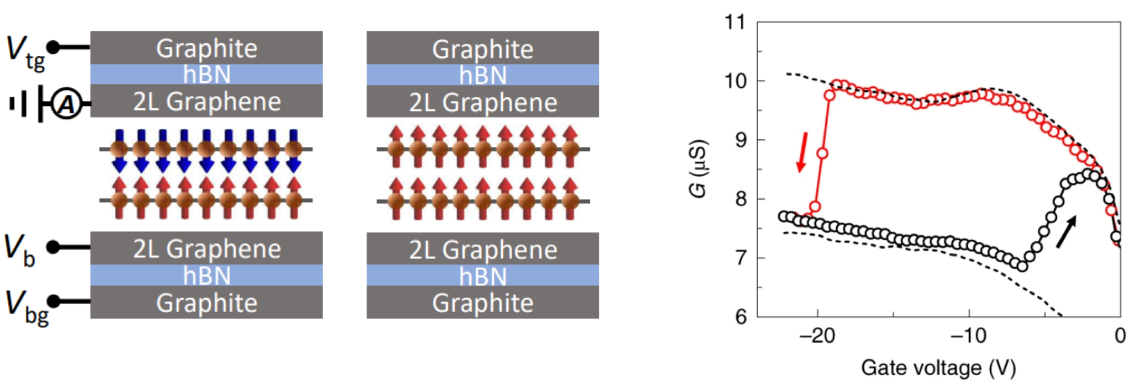
Assemble vdW heterostructures incorporating 2D magnets



Proximity magnetism in WSe_2/CrI_3 heterostructure

Zhong *et al.*, *Sci. Adv.* (2017)

Explore van der Waals spintronics using MTJs to generate & detect spin-polarized currents

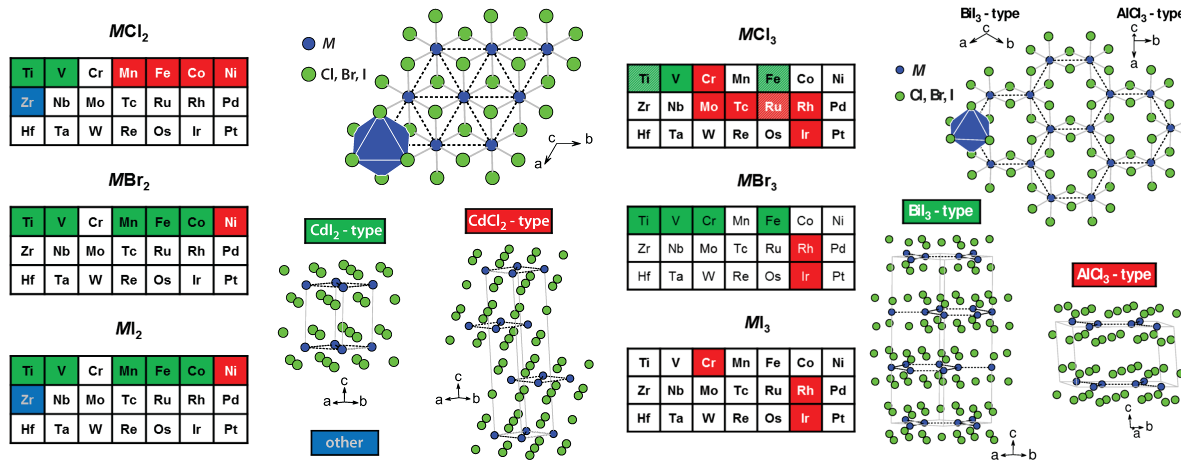


2L CrI_3 “Spin Transistor”

Jiang *et al.*, *Nat. Electron.* (2019)

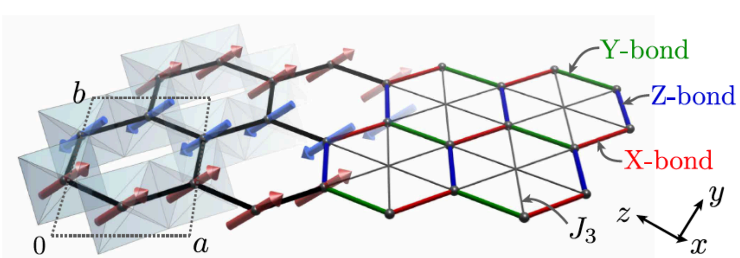
Outlook

Developed techniques for fabricating devices
& probing states in air-sensitive 2D magnets



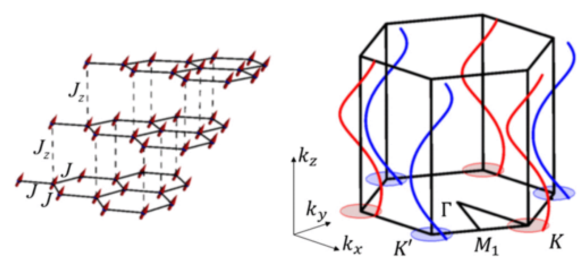
McGuire, *Crystals* (2017)

Kitaev Quantum Spin Liquid state in α-$RuCl_3$



Winter *et al.*, *Nat. Commun.* (2017)

Dirac magnon-magnon interactions in honeycomb FMs



Pershoguba *et al.*, *PRX* (2018)

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Jose L. Lado

David Soriano

Efthimios Kaxiras

Daniel Larson

Shiang Fang

BN Crystal Growth

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