SPIN-ORBIT COUPLING: AN ENDLESS SOURCE OF EXOTIC MAGNETISM IN 2D MAGNETS

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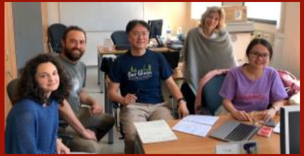
OUTLINE:

- **Introduction**: *Spin-orbit coupling*
- **Focus** on: "Rashba Physics" in Ferroelectrics
  Exotic Spin texture in 2D magnets
  Multiferroicity in 2D magnets

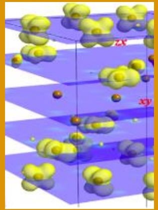
MODEM
(MOdelling and Design of functional Materials)

https://sites.google.com/site/silviapicozzi/

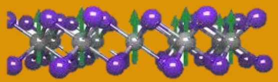
LOCATION & PEOPLE



MATERIALS

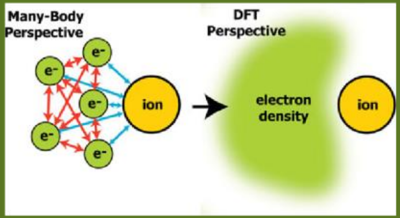


- Oxides
- Organics, hybrid
- Interfaces/surfaces
- 2D magnets



METHODS

- Density Functional Theory

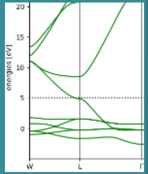


... but also:

- Symmetry analysis
- Model Hamiltonian

FOCUS

- Electronic Structure Theory

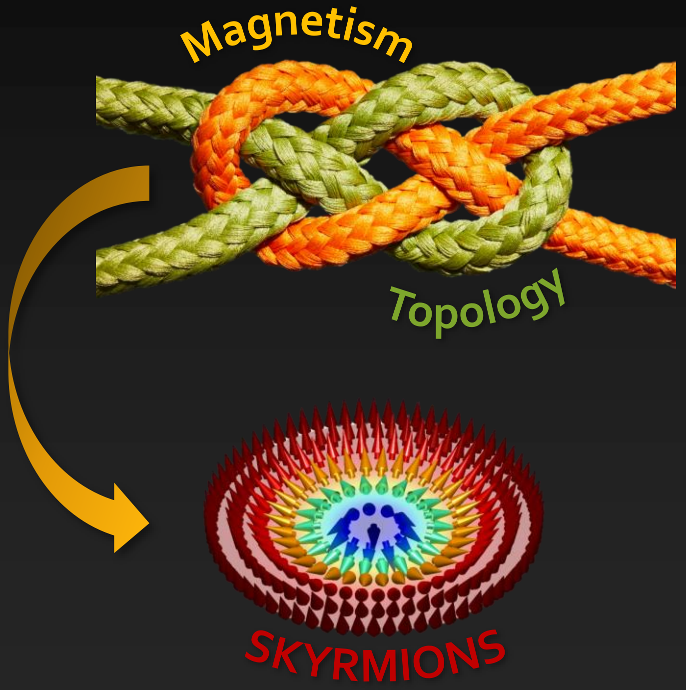


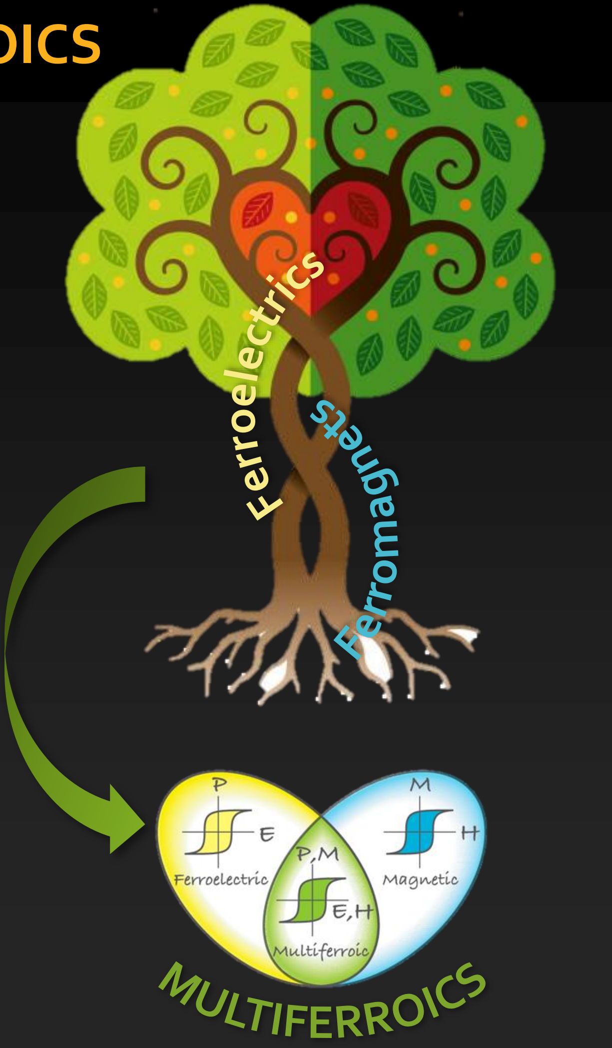
- Understanding Underlying Microscopic Mechanisms

✓ Optimization
✓ Materials Design

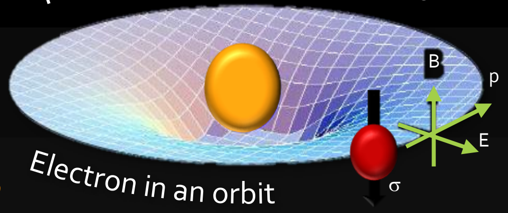
CROSS-COUPLING IN MULTIFUNCTIONAL FERROICS

Our expertise: **study *intertwined* phenomena**





SPIN-ORBIT COUPLING



Relativistic interaction linking spin and orbital momenta (i.e. spin space and real space)

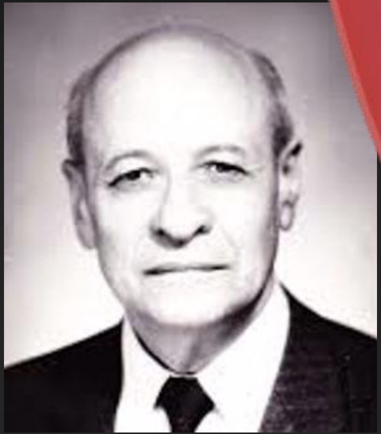
$$\underbrace{\frac{\mu_B}{2mcr}\frac{dV(r)}{dr}}_{\xi}\vec{\sigma}\cdot\left(\vec{r}\times\vec{p}\right)=\xi\vec{\sigma}\cdot\vec{L}$$

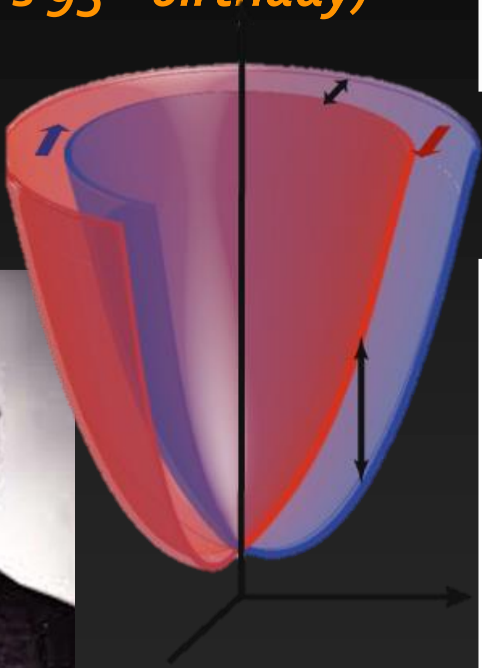
*.... a **small** interaction leading to rich physics ....*

Spin-Orbit Coupling in Solids

THE RASHBA EFFECT

(on the occasion of Rashba's 95th birthday)





EDITORIAL | Published: 09 December 2022

95th Birthday of Emmanuel Rashba

Journal of Experimental and Theoretical Physics **135**, 387 (2022)

2022 Oliver E. Buckley Condensed Matter Physics Prize Recipient

Emmanuel I. Rashba

Harvard University

APS physics

Citation:

"For pioneering research on spin-orbit coupling in crystals, particularly the foundational discovery of chiral spin-orbit interactions, which continue to enable new developments in spin transport and topological materials."

SYMMETRY PROPERTIES IN BAND STRUCTURE : SPACE/TIME INVERSION

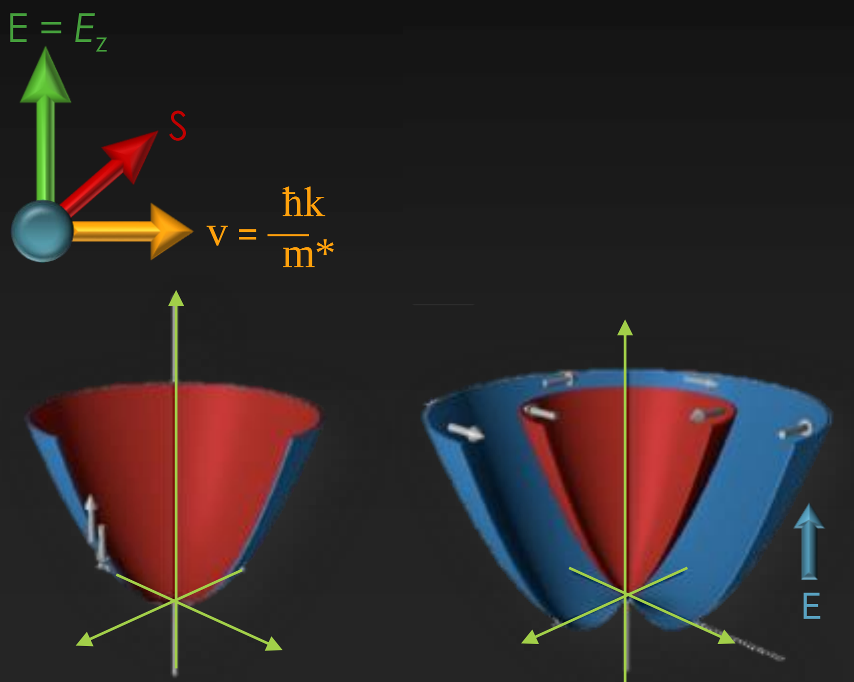
Time reversal symmetry: $\varepsilon_{k\uparrow} = \varepsilon_{-k\downarrow}$

(Space) inversion symmetry: $\varepsilon_{k\uparrow} = \varepsilon_{-k\uparrow}$

WHAT IS THE RASHBA EFFECT ?

SOC effect: particle in **electric field E** experiences internal **effective magnetic field $\mathbf{B}_{\mathbf{eff}} \propto \mathbf{v} \times \mathbf{E}$** in its moving frame

NB: **E** could be external (i.e. 2DEG), or "effective" (as in FE)

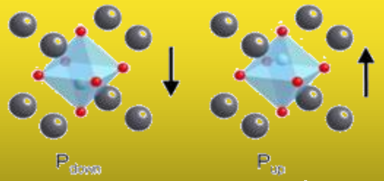


E. Rashba, Sov. Phys. Solid State 2, 1109 (1960)

KEY CONCEPT & MAIN MESSAGE

(S. Picozzi, Frontiers in Physics 2, 10 (2013))

FERROELECTRICITY



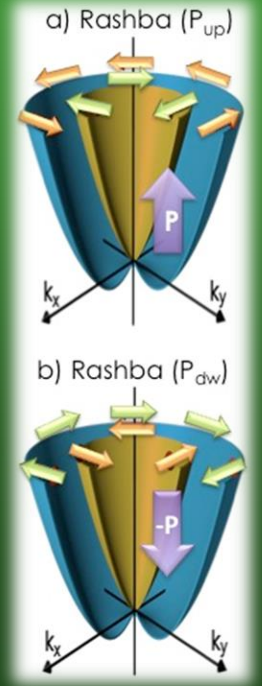
Permanent and switchable P, controllable via E

SPIN-ORBIT COUPLING

Relativistic inte-raction linking spin and lattice

RASHBA EFFECT

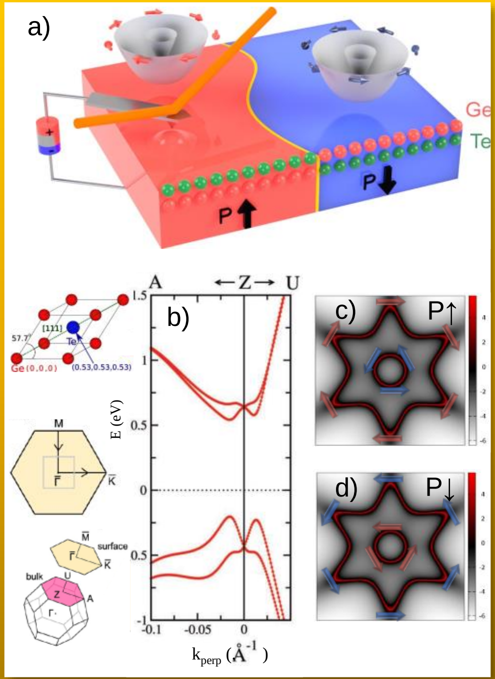
SPIN TEXTURE: LINKED to P (via SOC)→ CONTROL and SWITCH via E in a permanent (non volat.) way



The tale of GeTe

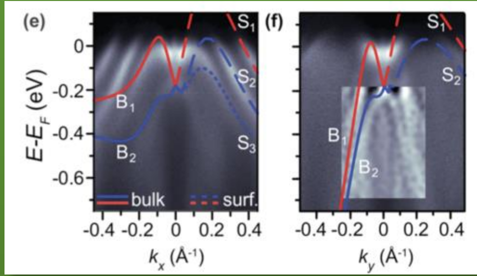
2013 — 2016-18 — 2021

THEORY & MODELLING

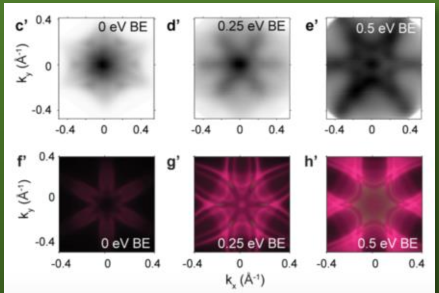


Di Sante,… Bertacco, SP,
Adv Mat (2013)

ADVANCED CHARACTERIZ.

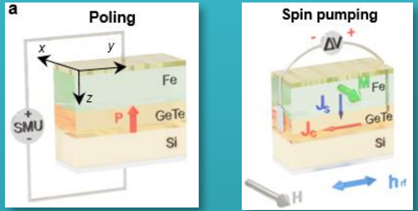


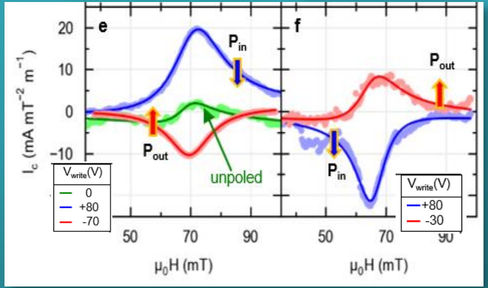
Liebmann ... Bertacco, Panaccione,
SP, ... Adv Mat (2016)

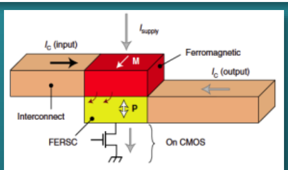


Rinaldi, …., Panaccione, SP,
Bertacco, Nanoletters (2018)

TOWARDS DEVICES







Varotto, … SP, … Bertacco,
Nature Electronics (2021)

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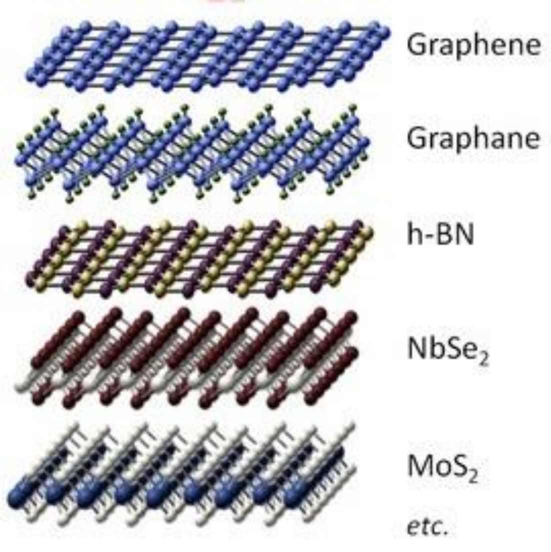
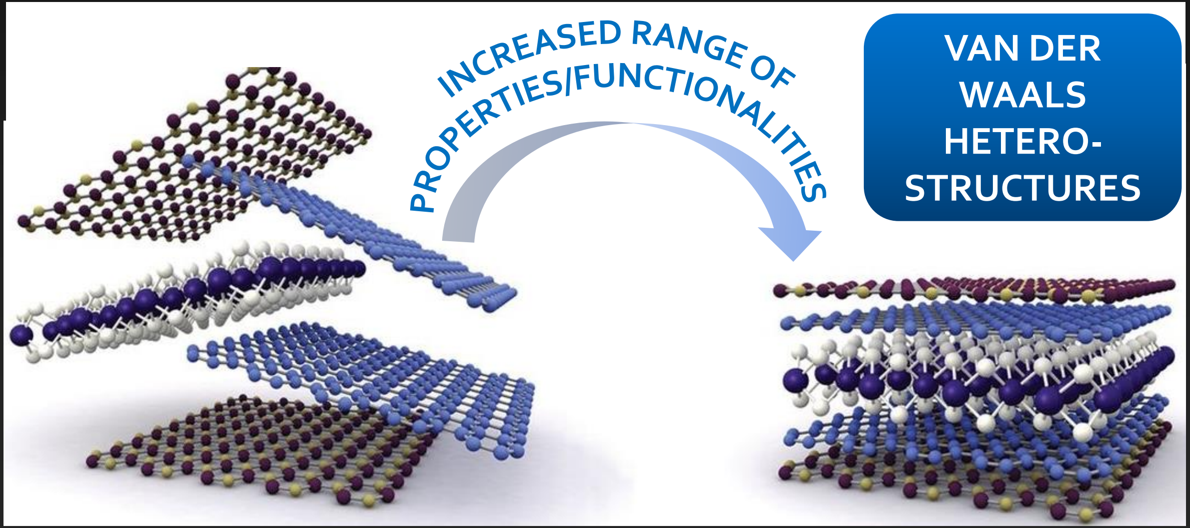
Exotic Spin texture in 2D magnets

Multiferroicity in 2D magnets



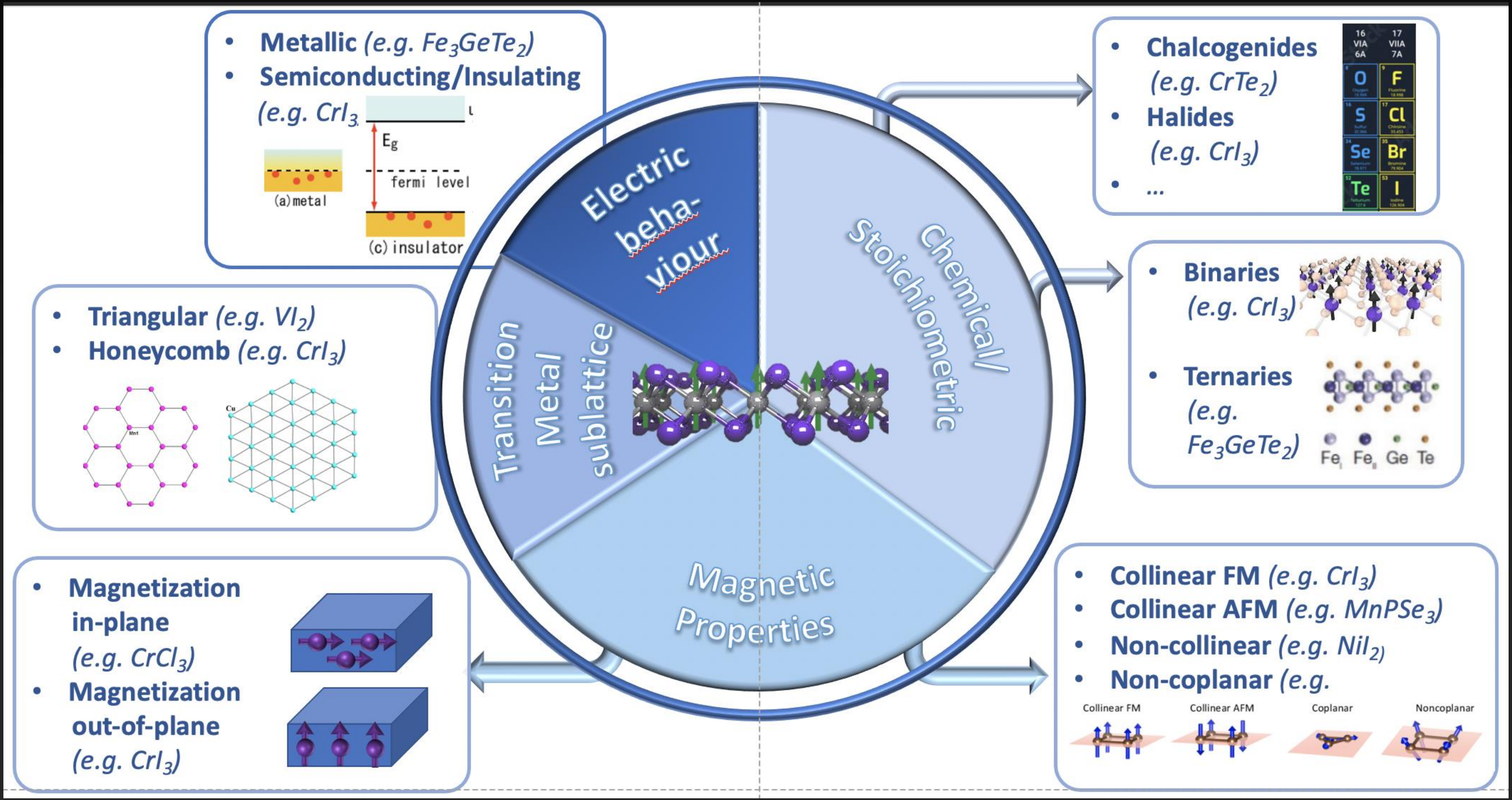
THE FLAT-LAND

- ✓ One–atom-thick (or *few-atoms-thick*) systems
- ✓ Layers held together by (weak) Van der Waals forces
- ✓ Extended range of properties and functionalities
- ✓ Properties of 2D materials different from 3D counterparts



…. and you can play LEGO with 2D-materials !!

2D MAGNETS: A RICH PLAYGROUND



CHALLENGES IN 2D MAGNETS & MERMIN WAGNER THEOREM

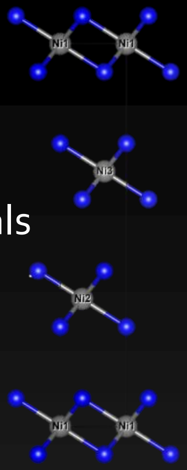
- Need to **increase Curie temperature** T_C
- Need to **improve air-stability & scalability**
- **Need for improved understanding/modelling**

*"At any non-zero temperature, a **one- or two-dimensional isotropic** spin **Heisenberg** model with **finite-range exchange interaction** can be neither ferromagnetic nor antiferromagnetic."*

N.D. Mermin and H. Wagner, Phys. Rev. Lett. 17, 1133 (1996)

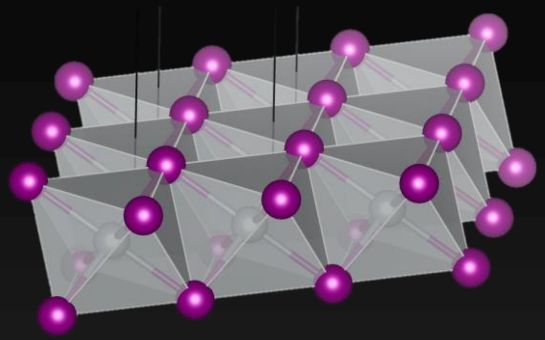
☞ 2D magnetism relies on **Anisotropic effects** ☞ **Spin-orbit Coupling**

BACKGROUND ON NiX2 (X = Cl, Br, I): 3D vs 2D (ML)



MONOLAYER STRUCTURE

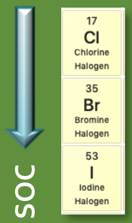
✓ Triangular lattice
✓ Edge-Shared octahedra:
- small trigonal compression

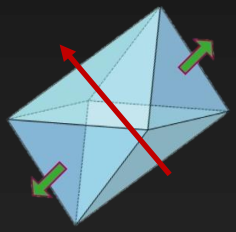


3D layered
Van der Waals
crystal

ELECTRON FILLING

- Ni $3p^6 3d^8 4s^2$
- Cl $3s^2$ **$3p^5$**
- Br $4s^2$ **$4p^5$**
- I $5s^2$ **$5p^5$**





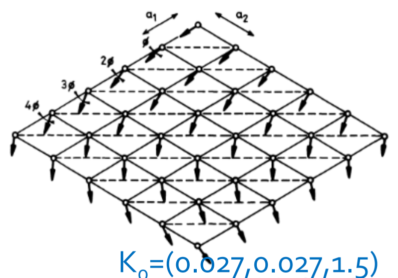


Fig. 1. — Helimagnetic ordering within the basal plane for $NiBr_2$ at $T = 4.2$ K.

Régnault et al, J. Physique (1982)

CRYSTAL FIELD SPLITTING: Ni d^8

eg ↑ ↑
t2g ↑↓ ↑↓ ↑↓
→ high spin $S = 1$ → $M = 2\mu_B$

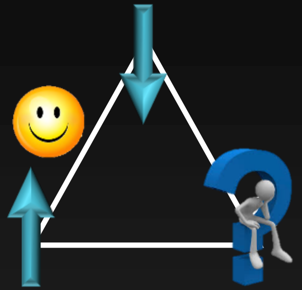
MAGNETIC MOMENTS

- **Localized moments on TM (high spin)**
- Sizeable (**positive**) **moment** on **halogen**

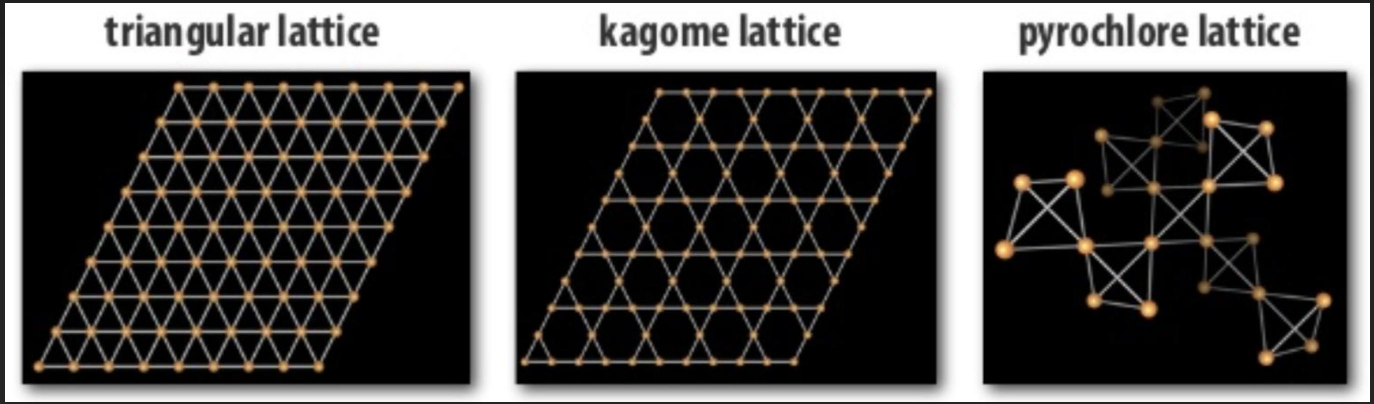
☞ **COMPLEX MAGNETISM!**

FRUSTRATION IN MAGNETS: TRIANGLE

Spins on a triangular lattice with AFM coupling

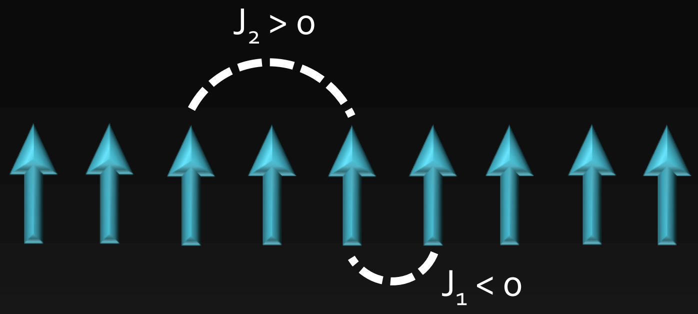


What about the third spin ????



FRUSTRATION IN MAGNETS: SPIN-CHAIN

- ✓ Simplest case: Frustrated spin chains with the **nearest-neighbour FM J_1** and **next-nearest-neighbour AFM** interactions J_2 .



EXCHANGE COUPLING CONSTANTS

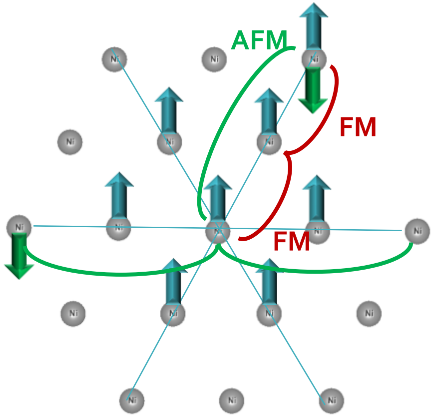
*Let's start with **Heisenberg Hamiltonian** (no SOC)*

$$\mathcal{H} = -\frac{1}{2}\sum_{\substack{i,j \\ i\neq j}} J(\vec{r}_{ij})\hat{\vec{S}}_i \cdot \hat{\vec{S}}_j$$

- ✓ Magnetic interaction strength varies with the ligand
- ✓ Longer ranged interaction in NiI2 (5p) than in NiCl2 (3p)

☞ Large exchange frustration J3/J1 (increases with ligand)

☞ EXPECTED NON-COLLINEARITY !!!



....NOT ONLY HEISENBERG

$$H = -\frac{1}{2}\sum_{i,j} J_{ij}\,\mathbf{S}_i \cdot \mathbf{S}_j$$

INTERSITE EXCHANGE-COUPLING MATRIX

isotropic | Antisymmetric | (Traceless) Symmetric

$$H = -\frac{1}{2}\sum_{i,j} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j + \sum_{i,j} \mathbf{D}_{ij}\, \mathbf{S}_i \times \mathbf{S}_j + \sum_{i,j} \mathbf{S}_i\, \Gamma_{ij}\, \mathbf{S}_j$$

Heisenberg | DM | Anisotropic exchange

INTERSITE EXCHANGE-COUPLING MATRIX

isotropic Antisymmetric (Traceless) Symmetric

$$H = -\frac{1}{2}\sum_{i,j} J_{ij}\,\mathbf{S}_i \cdot \mathbf{S}_j + \sum_{i,j} \mathbf{D}_{ij}\,\mathbf{S}_i \times \mathbf{S}_j + \sum_{i,j} \mathbf{S}_i\,\Gamma_{ij}\,\mathbf{S}_j$$

Heisenberg DM Anisotropic exchange

NiX2: ANISOTROPIC EXCHANGE AND SINGLE-ION ANISOTROPY

$$\mathcal{H} = \mathcal{H}_{ex} + \mathcal{H}_{si} = \frac{1}{2}\sum_{i,j} S_i \cdot \mathcal{J}_{ij} \cdot S_j + \sum_{i} S_i \cdot \mathcal{A}_{ii} \cdot S_i$$

J_{xx}	0	0
0	J_{yy}	J_{yz}
0	J_{yz}	J_{zz}

Symmetry-allowed exchange tensor

(Inter-site) Symmetric Anisotropic Exchange matrix (in meV)

-5.1	0	0
0	-5.1	0
0	0	-5.1

NiCl2

-6.0	0	0
0	-5.8	-0.1
0	-0.1	-5.9

NiBr2

-8.0	0	0
0	-5.6	-1.4
0	-1.4	-7.3

NiI2

17
Cl
Chlorine
Halogen

35
Br
Bromine
Halogen

53
I
Iodine
Halogen

✓ **Anisotropies** in 1st NN interaction in **NiI_2 : anisotropic diagonal** and **large off-diagonal.** ☞ **SOC of ligand: important!**

FROM EXCHANGE CONSTANTS TO THE SPIN-TEXTURE

$$\mathcal{H} = \mathcal{H}_{ex} + \mathcal{H}_{si} = \frac{1}{2}\sum_{i,j} S_i \cdot \mathcal{J}_{ij} \cdot S_j + \sum_i S_i \cdot \mathcal{A}_{ii} \cdot S_i$$

Exchange Coupling Tensor *Single-Ion Anisotropy (SIA)*

MULTISCALE APPROACH

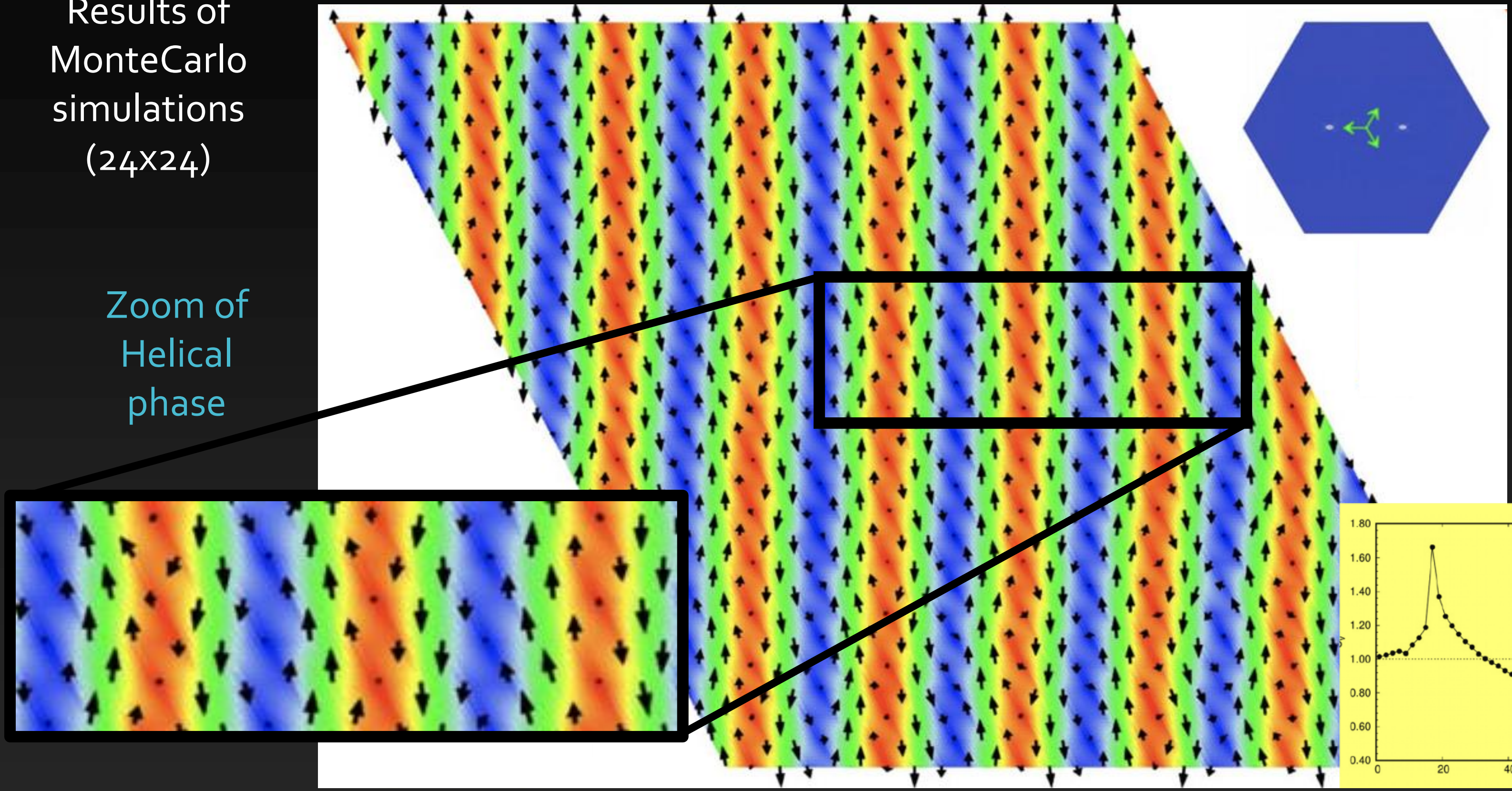
Plug DFT values into MonteCarlo simulations
☞ access to:
1) Larger (space) scales
2) Finite temperatures

➡ (Real-space) SPIN TEXTURE

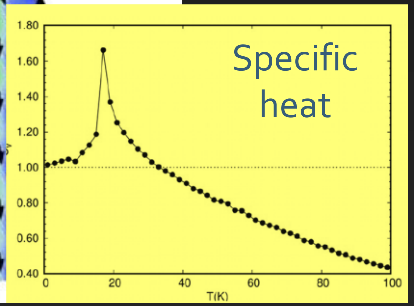
NON-COLLINEARITY IN $NiBr_2$

Results of MonteCarlo simulations (24x24)

Color scale: S_z (out-of-plane spins)

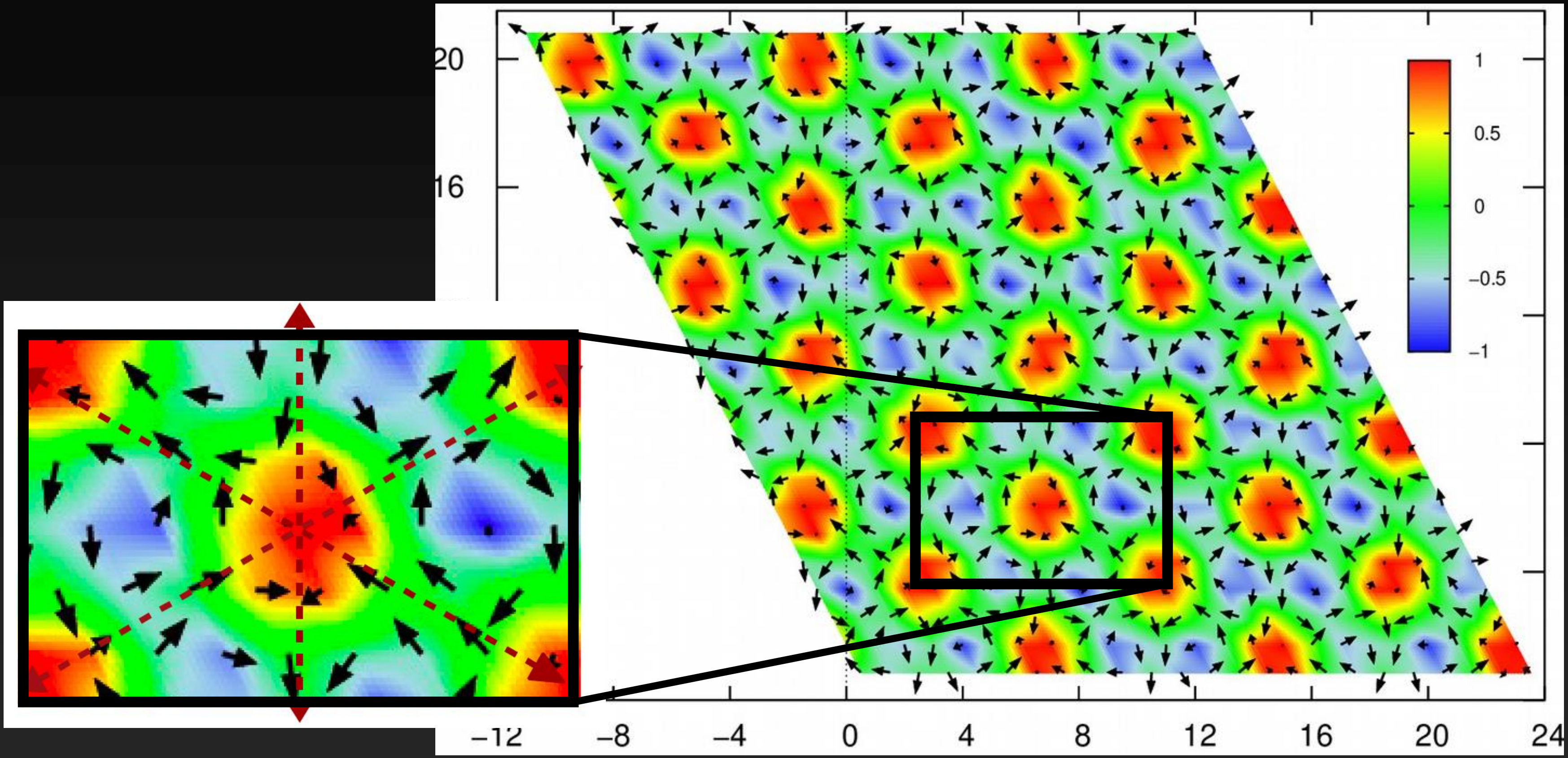


Zoom of Helical phase



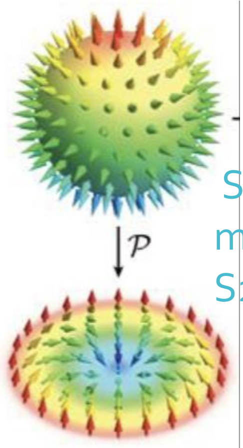
Single-q state along **q3** = (−2δ, δ) ☞ **SPIN HELIX**

NiI2: EXOTIC NON-COPLANAR SPIN-ORDER !!!

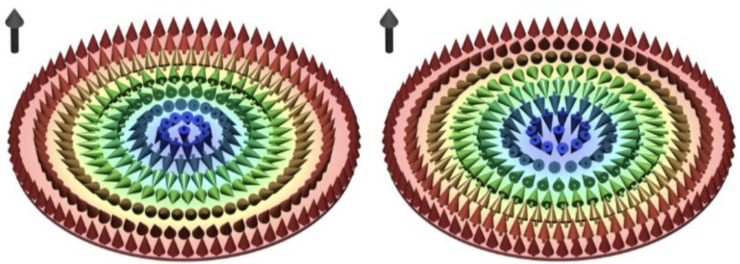


WHAT IS A MAGNETIC SKYRMION ?

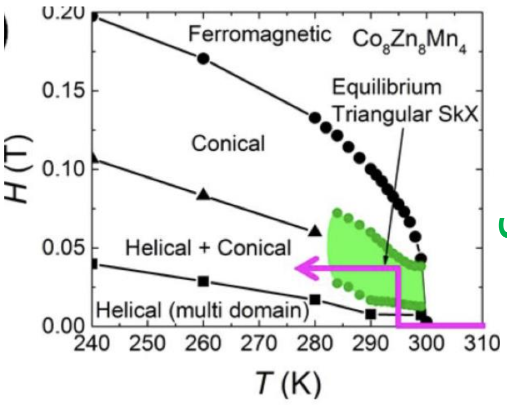
Particle-like nanometre-sized **spin texture** of **topological** origin *(Bogdanov, 1989)*



Smooth mapping S2 ⇔ R2



Different handedness (or rotational sense): Counterlockwise vs clockwise



Phase diagram

TOPOLOGICAL CHARGE (discrete approx.)

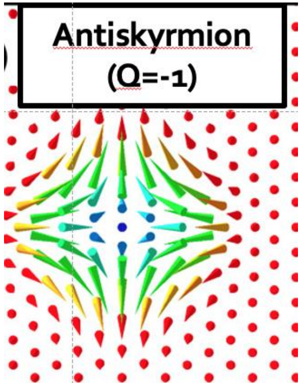
- (**Classical) Spins $\mathbf{m}_i$** on atomic sites
- **Topological charge Q = Σ q_i**

$$\tan\left(\frac{1}{2}q\right) = \frac{[\mathbf{m}_1\mathbf{m}_2\mathbf{m}_3]}{1 + \mathbf{m}_1\mathbf{m}_2 + \mathbf{m}_1\mathbf{m}_3 + \mathbf{m}_2\mathbf{m}_3}$$

Triple-scalar product (or **scalar spin-chirality**)

$= \mathbf{m}_1 \cdot (\mathbf{m}_2 \times \mathbf{m}_3)$

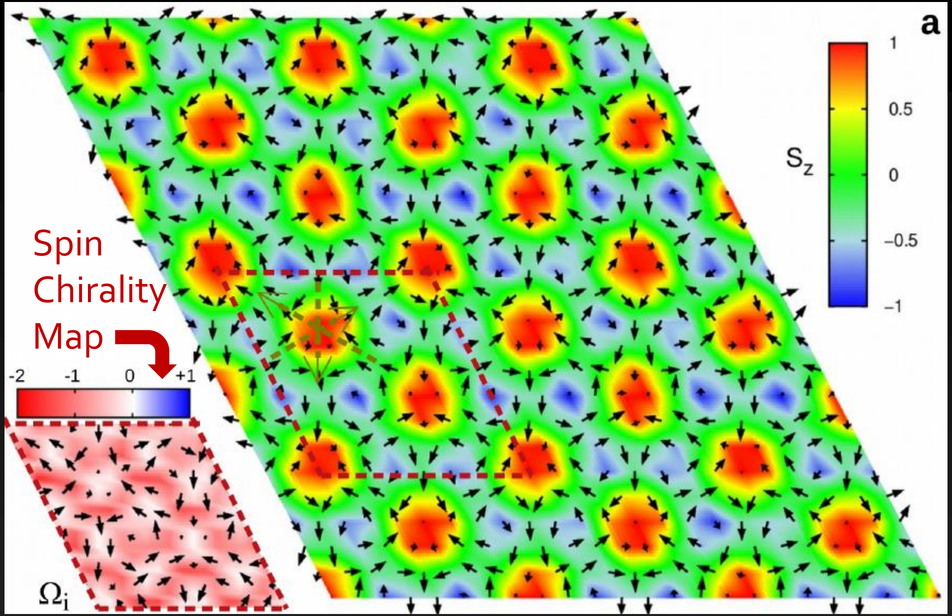
Antiskyrmion: change of rotational sense for two high symmetry directions

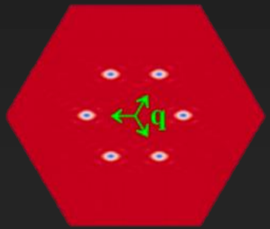


TOPOLOGICAL CHARGE

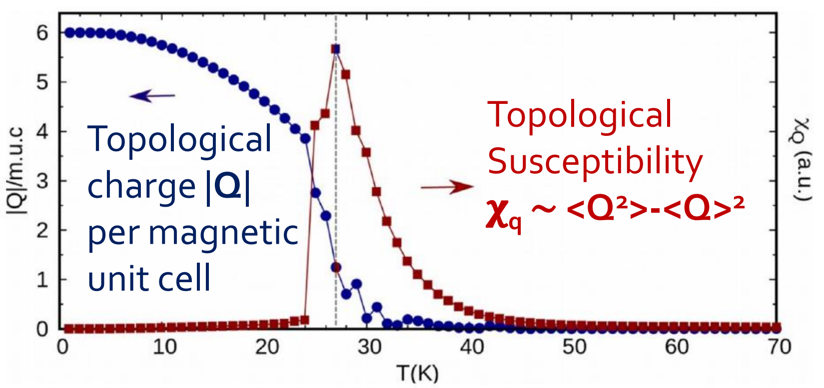
☞ |Q|=2 Higher-order antiskyrmion!

- ✓ Topological state without B field
- ✓ First example in 2D magnets
- ✓ Not driven by Dzyaloshinskii-Moriya

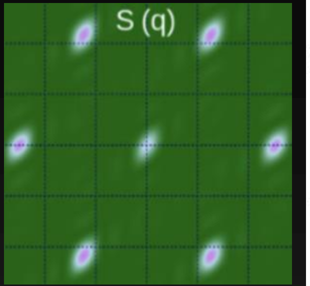


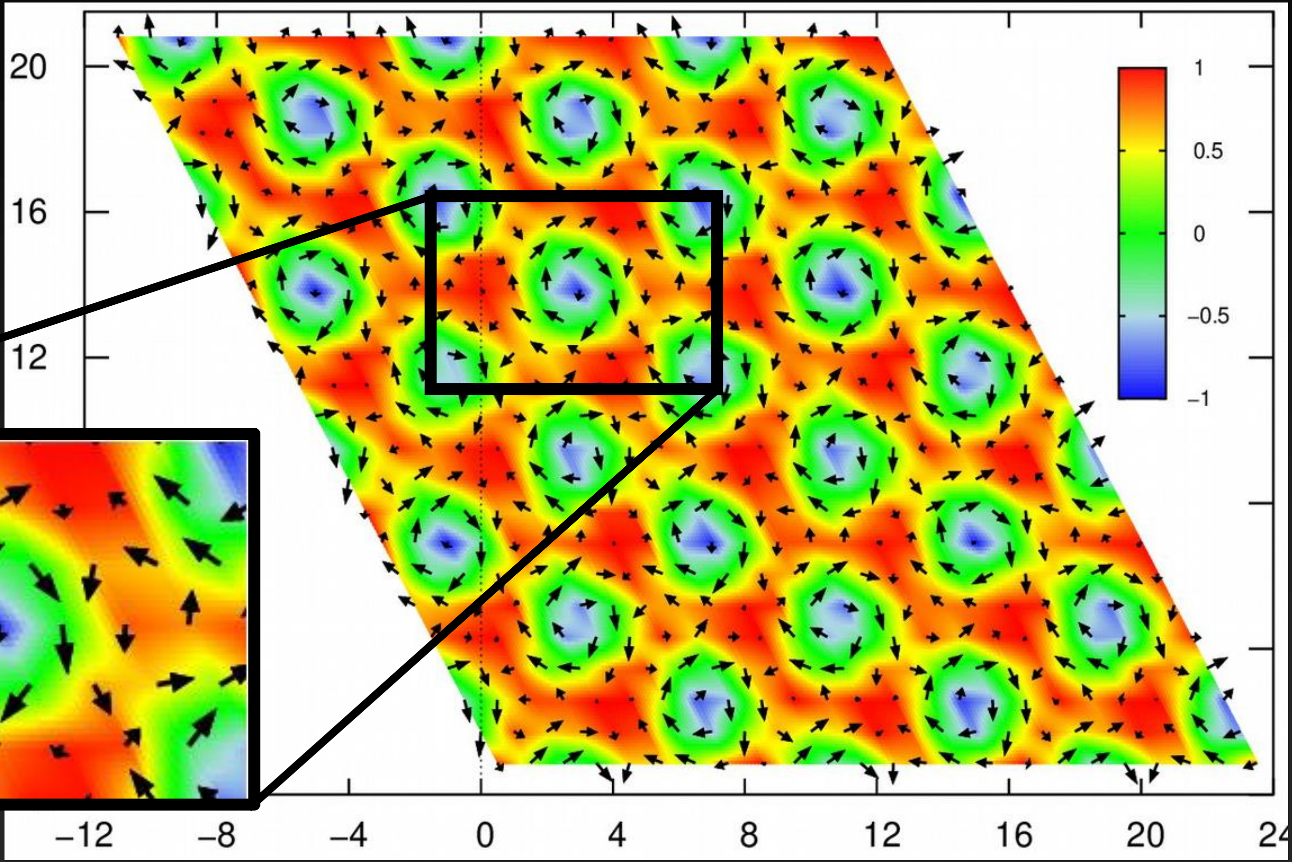


Spin-structure factor S(q)



WHAT HAPPENS UNDER MAGNETIC FIELD?





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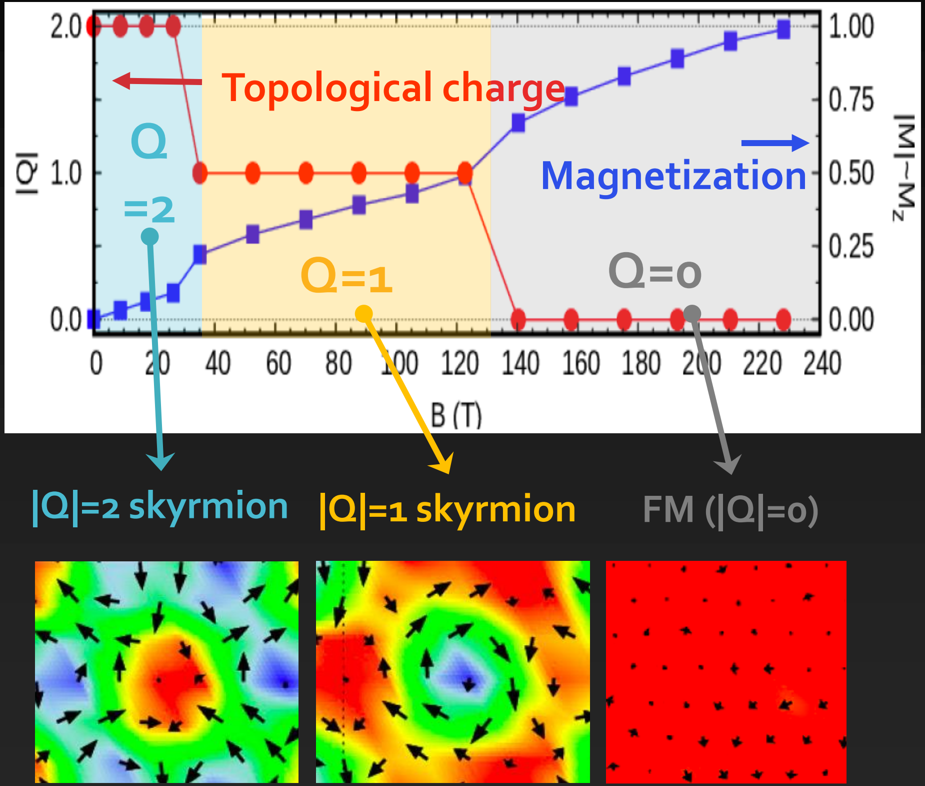
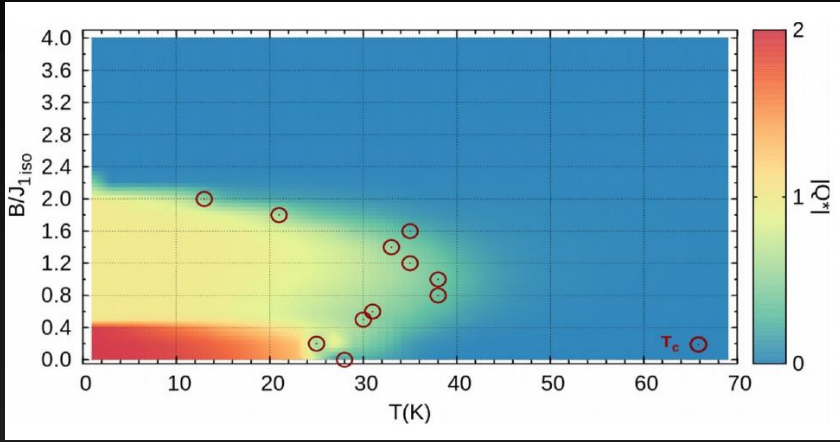


Phase Diagram of **B/J_{iso}** vs **Temperature**



☞ Sharp topological transition to «conventional» (Q=1) skyrmion!

D. Amoroso, P. Barone and SP, Nature Communications 11, 5784 (2020)

ROLE OF ANISOTROPIC EXCHANGE IN EXOTIC MAGNETISM

J_{xx}	0	0
0	J_{yy}	J_{yz}
0	J_{yz}	J_{zz}

Diagonalize →

J_{α}	0	0
0	J_{β}	0
0	0	J_{γ}

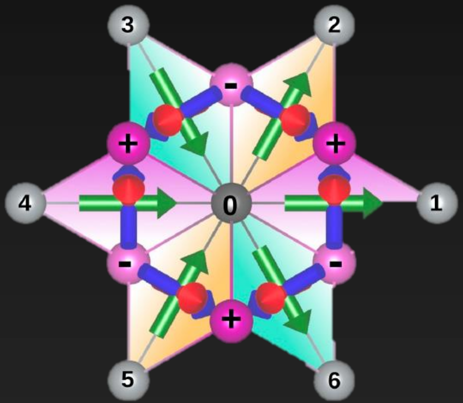
Roughly $J_{\alpha} \approx J_{\beta}$

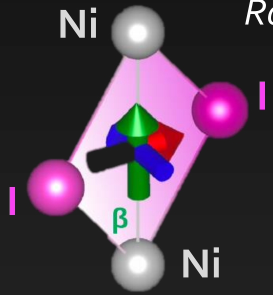
☞ **Two eigenvectors** in the **Ni-I-Ni plane**

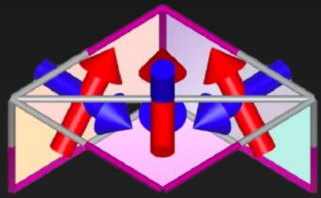
- **One along I-I ligands**
- **One along Ni-Ni**

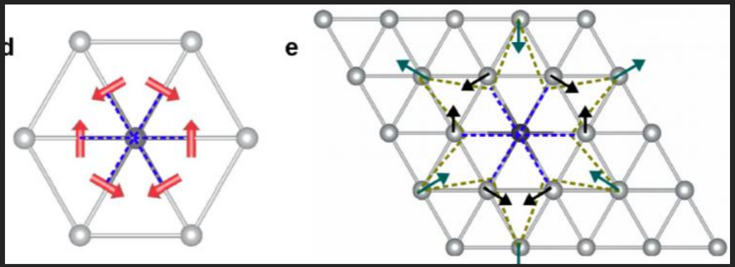
☞ **Third eigenvector**

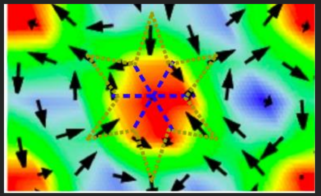
⊥ to the Ni-I-Ni-I plaquette



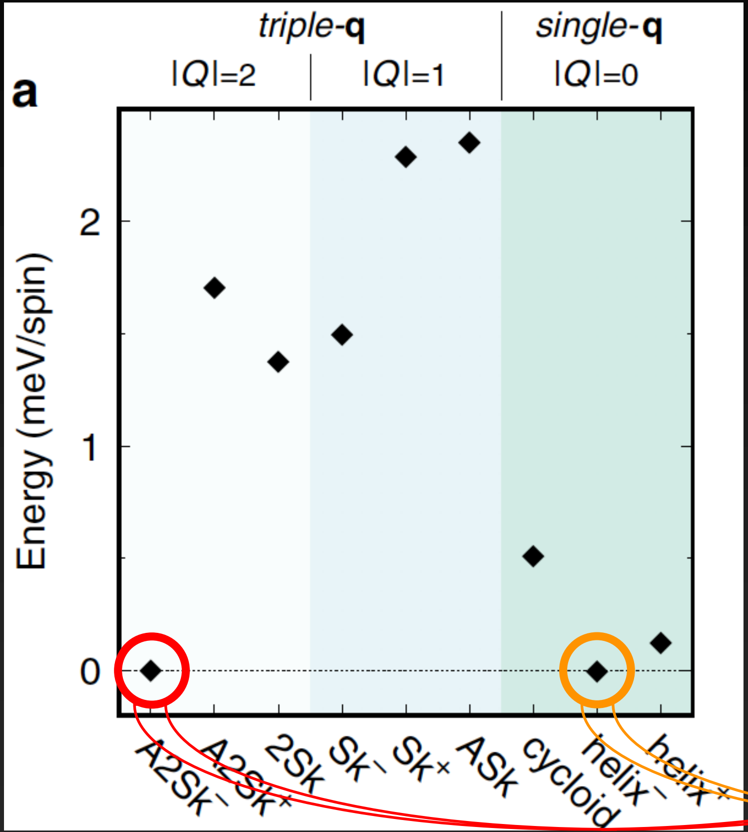






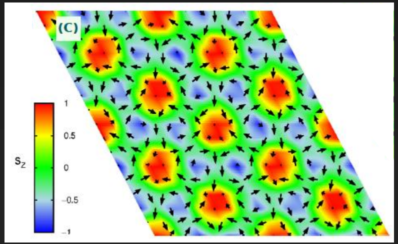


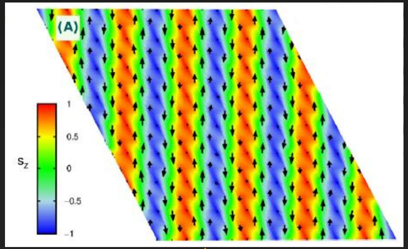
TOTAL ENERGIES OF SELECTED SPIN CONFIGURATIONS



- Superscript ± : chiral partners of the given spin texture, related by a reflection with respect to the xy plane
- Single-q spin configurations generated by MC simulations artificially tuning the two-site anisotropy term.

Energy degeneracy between Antiskyrmion and Spin-Helix !





SPIN-ORBIT COUPLING: AN ENDLESS SOURCE OF EXOTIC MAGNETISM IN 2D MAGNETS

OUTLINE:

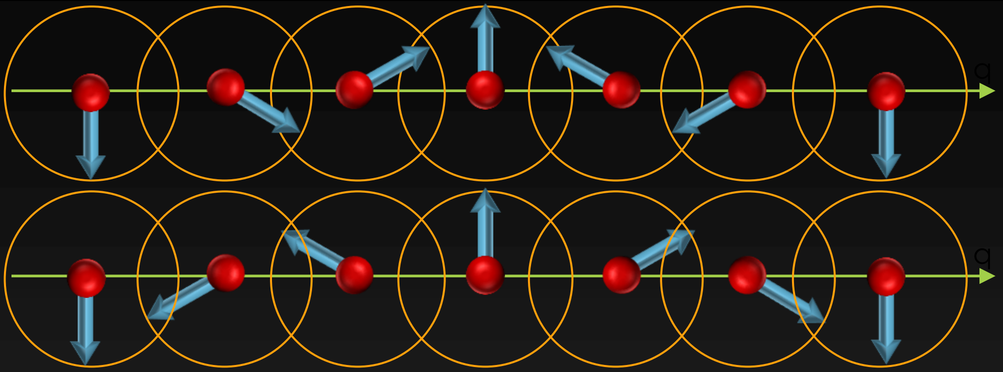
- Introduction: *Spin-orbit coupling*
- Focus on: "Rashba Physics" in Ferroelectrics

Exotic Spin texture in 2D magnets

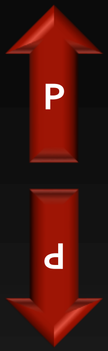
Multiferroicity in 2D magnets

HOW THE HYPE ON (ELECTRONIC) MULTIFERROICS STARTED …

Spin spiral

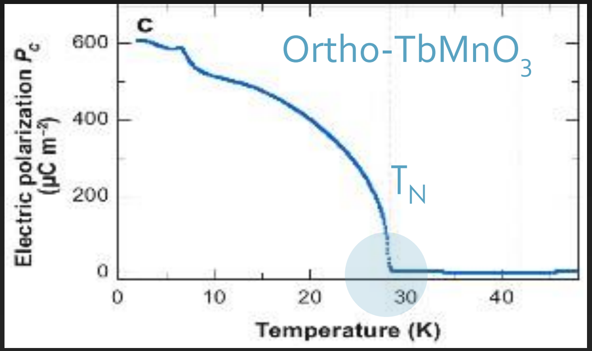


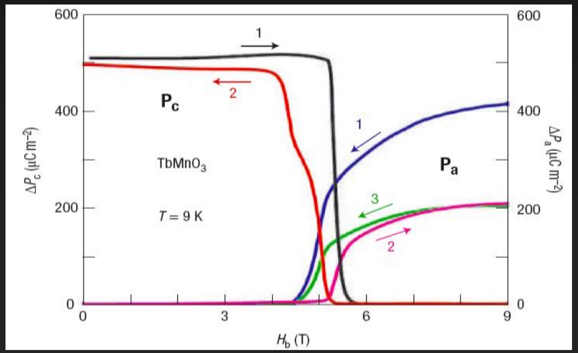
Left handed



Left handed

☞ Right handed





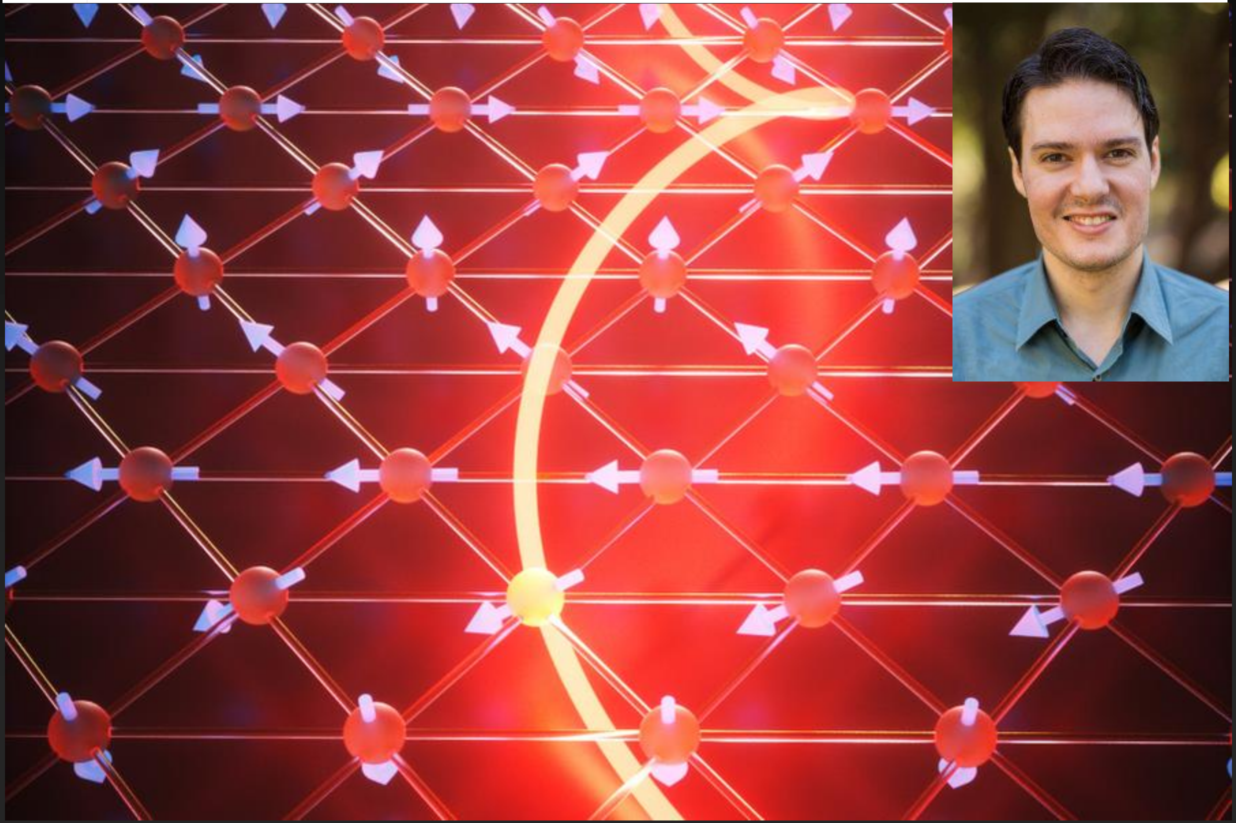
T.Kimura & al., Nature 425, 55 (03);
S.W.Cheong & M.Mostovoy, Nature Mater. 6, 13 (07)

Can **Multi-Ferroicity** persist down to the ultimate monolayer limit ?

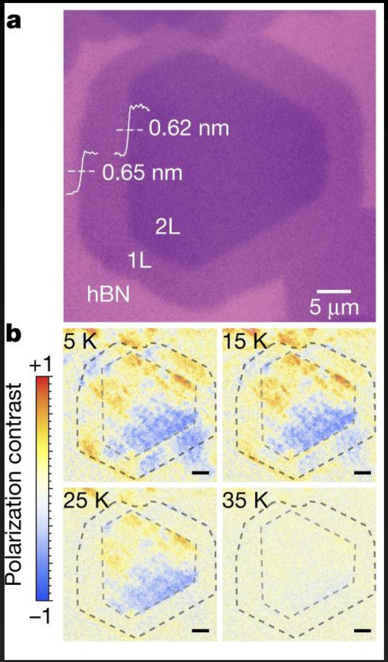
Evidence for a single-layer van der Waals multiferroic

Qian Song, Connor A. Occhialini, Emre Ergeçen, Batyr Ilyas, Danila Amoroso, Paolo Barone, Jesse Kapeghian, Kenji Watanabe, Takashi Taniguchi, Antia S. Botana, Silvia Picozzi, Nuh Gedik & Riccardo Comin

Nature **602**, 601–605 (2022) | Cite this article

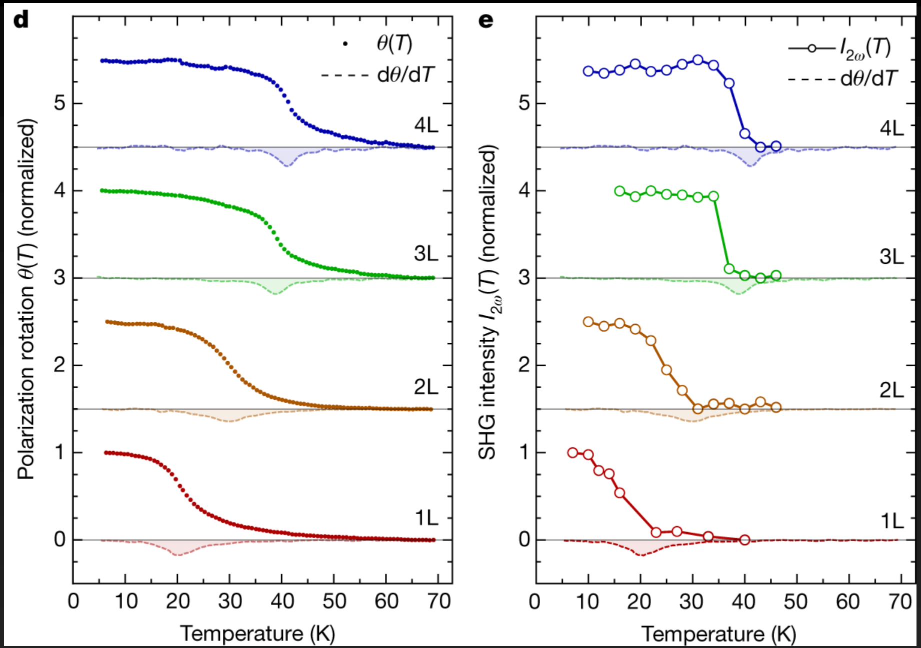


OPTICAL CHARACTERIZATION OF FEW-LAYERS NiI_2

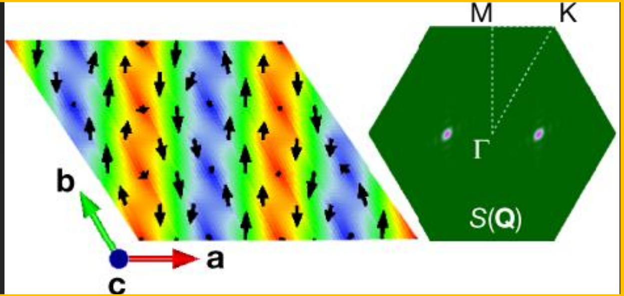


Optical image NiI_2 samples grown on hBN

Temperature-dependent polarized microscopy



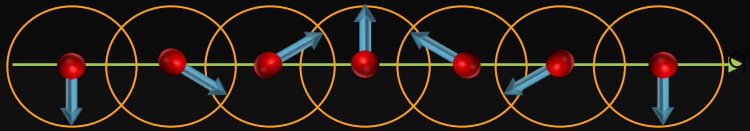
Spin-helix: likely spin ground state!



d. Temperature-dependent, birefringence-induced polarization rotation $\vartheta(T)$ in monodomain regions.
e. Temperature-dependent ED-SHG. Data normalized to value at 5 K and offset vertically for clarity.

SPIN-INDUCED FERROELECTRICITY: SPIN CURRENT MODEL

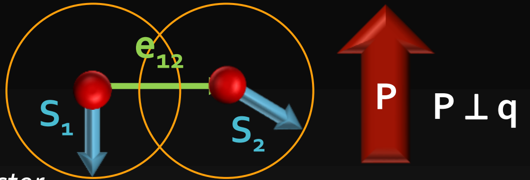
Spin cycloid (spins in a plane containing e_{12})



Katsura, Nagaosa, Balatsky (PRL 2005)

$$P_{12} = e_{12} \times (S_1 \times S_2)$$

e_{12}: spiral propagation vector



MAGNETOELECTRIC TENSOR (DFT)

$$\boldsymbol{P}_{12} = \boldsymbol{M}(\boldsymbol{S}_1 \times \boldsymbol{S}_2)$$

$$\begin{pmatrix} M_{11} & M_{12} & M_{13} \\ M_{21} & M_{22} & M_{23} \\ M_{31} & M_{32} & M_{33} \end{pmatrix} = \begin{pmatrix} 20 & 0 & 32 \\ 0 & 348 & -520 \\ 0 & 25 & 0 \end{pmatrix}$$

Units: 10^{-5} e Ang

Large "non-KNB" terms!

We now have a 2D multiferroic !