Electric Polarization Induced by Skyrmionic Order in GaV_4S_8: from First-Principles Calculations to Microscopic Models

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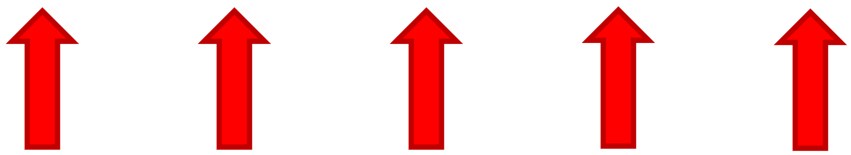
isotropic

$$\sum_{<ij>} -J_{ij}\boldsymbol{e}_i\boldsymbol{e}_j$$

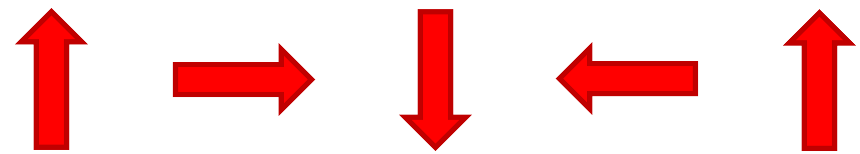


isotropic

$$\sum_{<ij>} -J_{ij}\boldsymbol{e}_i\boldsymbol{e}_j$$

Dzyaloshinskii-Moriya

$$\sum_{<ij>} \boldsymbol{d}_{ij}[\boldsymbol{e}_i\times\boldsymbol{e}_j]$$

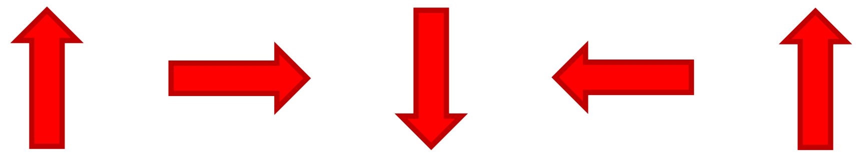


isotropic

$$\sum_{<ij>} -J_{ij}\boldsymbol{e}_i\boldsymbol{e}_j$$

Dzyaloshinskii-Moriya

$$\sum_{<ij>} \boldsymbol{d}_{ij}[\boldsymbol{e}_i \times \boldsymbol{e}_j]$$



both

spin spiral

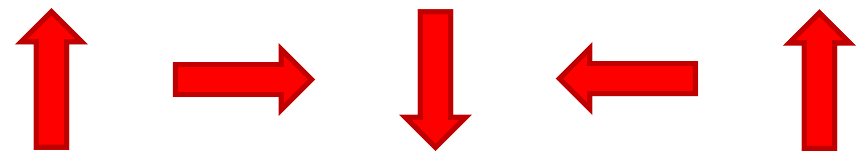
$$\sum_{<ij>} -J_{ij}\boldsymbol{e}_i\boldsymbol{e}_j + \boldsymbol{d}_{ij}[\boldsymbol{e}_i \times \boldsymbol{e}_j]$$

isotropic

$$\sum_{<ij>} -J_{ij}\boldsymbol{e}_i\boldsymbol{e}_j$$

Dzyaloshinskii-Moriya

$$\sum_{<ij>} \boldsymbol{d}_{ij}[\boldsymbol{e}_i\times\boldsymbol{e}_j]$$



spin spiral

both

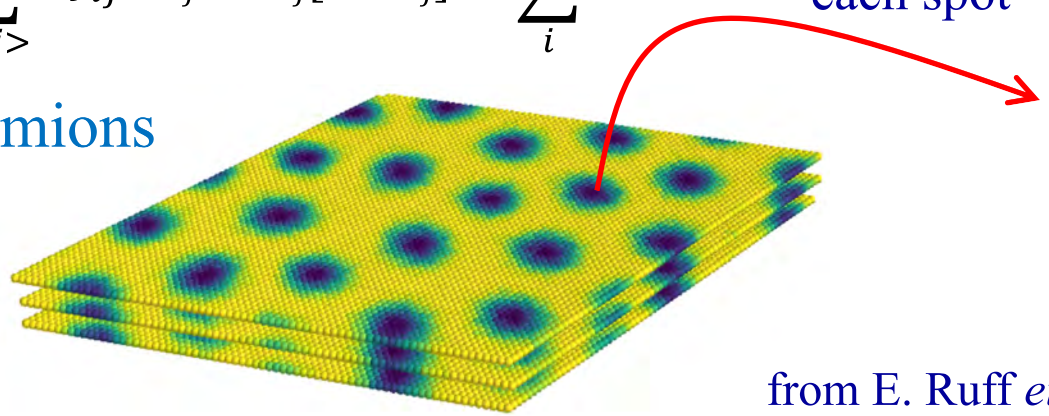
$$\sum_{<ij>} -J_{ij}\boldsymbol{e}_i\boldsymbol{e}_j + \boldsymbol{d}_{ij}[\boldsymbol{e}_i\times\boldsymbol{e}_j]$$

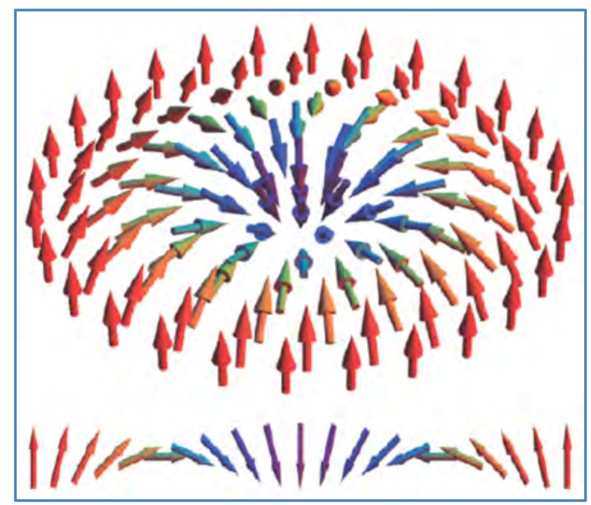
and … plus magnetic field

$$\sum_{<ij>} -J_{ij}\boldsymbol{e}_i\boldsymbol{e}_j + \boldsymbol{d}_{ij}[\boldsymbol{e}_i\times\boldsymbol{e}_j] + \sum_{i} \boldsymbol{H}\boldsymbol{e}_i$$

each spot

skyrmions



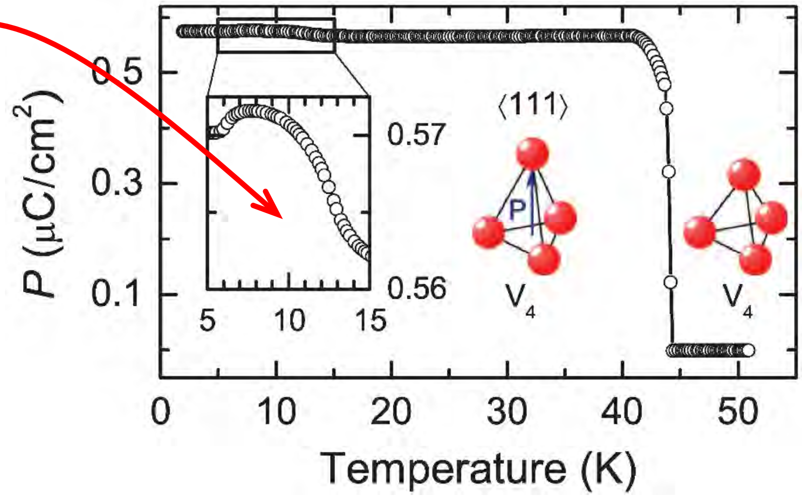


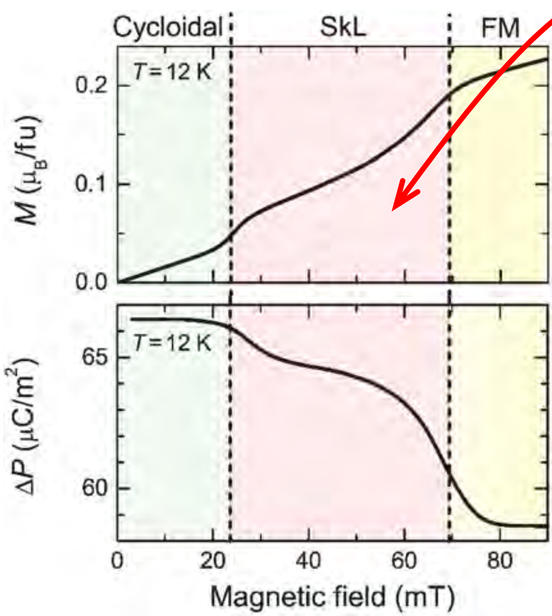
from E. Ruff *et al.*, Sci. Adv. **1**, e1500916 (2015)

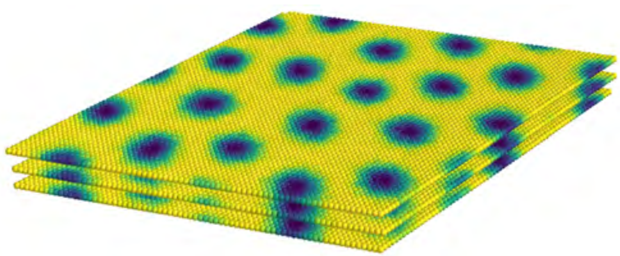
What is interesting about GaV_4S_8?

structural transition, T_{JT}=44 K
magnetic transition, T_C=13 K

magnetic contribution
to the electric polarization

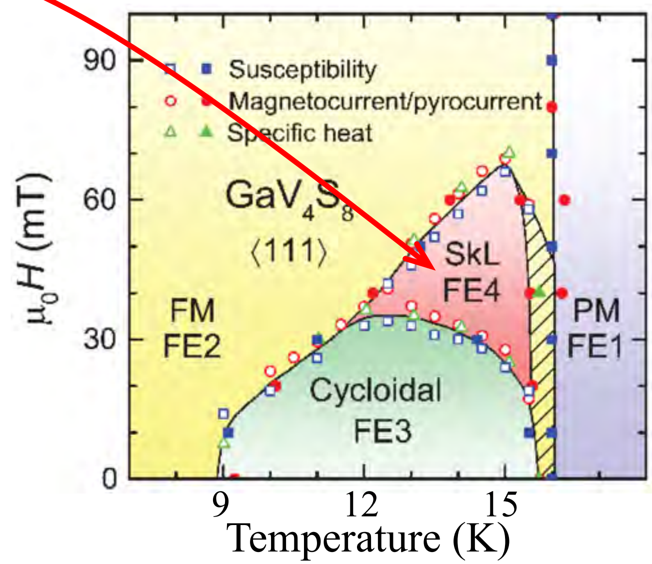






skyrmion phase

phase diagram



E. Ruff *et al.*, Sci. Adv. **1**, e1500916 (2015)

Outline

1. Electronic model in molecular orbital basis
2. Superexchange theory for exchange interactions
   Can we do the same for the polarization?
3. "Correct" formulas for the polarization starting from the general Berry-phase theory
4. spin-dependence of polarization:
   2D skyrmion texture vs. stacking misalignment
5. Model parameters and Monte-Carlo simulations
6. Comparison with GaV_4Se_8 and $GaMo_4S_8$

Collaboration with Dr. S. A. Nikolaev,
Now: Tokyo Institute of Technology

PHYSICAL REVIEW B **99**, 100401(R) (2019)

Rapid Communications

Microscopic theory of electric polarization induced by skyrmionic order in GaV_4S_8

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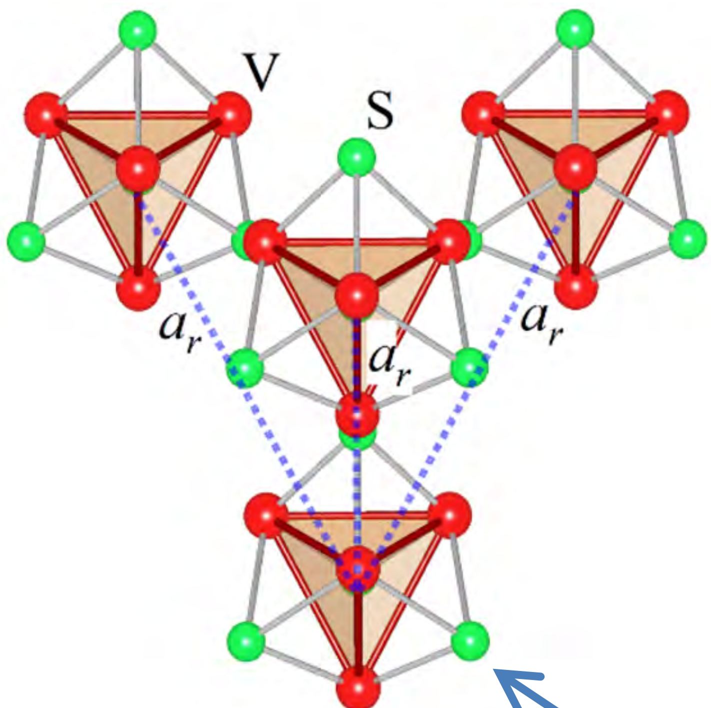
The lacunar spinel GaV_4S_8 was recently suggested to be a prototype multiferroic material hosting skyrmion lattice states with a sizable polarization $\boldsymbol{P}$ coupled to magnetic order. We explain this phenomenon on the microscopic level. On the basis of density functional theory, we construct an effective model describing the behavior of magnetically active electrons in a weakly coupled lattice formed by *molecular* orbitals of the $(V_4S_4)^{5+}$ clusters. By applying superexchange theory combined with the Berry-phase theory for $\boldsymbol{P}$, we derive a compass model relating the energy *and polarization* change with the directions of spins $\boldsymbol{e}_i$ in magnetic bonds. We argue that, although each skyrmion layer is mainly formed by superexchange interactions in the same plane, the spin dependence of $\boldsymbol{P}$ arises from the stacking misalignment of such planes in the perpendicular direction, which is inherent to the lacunar spinel structure. We predict a strong competition of isotropic, $\sim\boldsymbol{e}_i\boldsymbol{e}_j$, and antisymmetric, $\sim\boldsymbol{e}_i \times \boldsymbol{e}_j$, contributions to $\boldsymbol{P}$ that explains the experimentally observed effect.

DOI: 10.1103/PhysRevB.99.100401

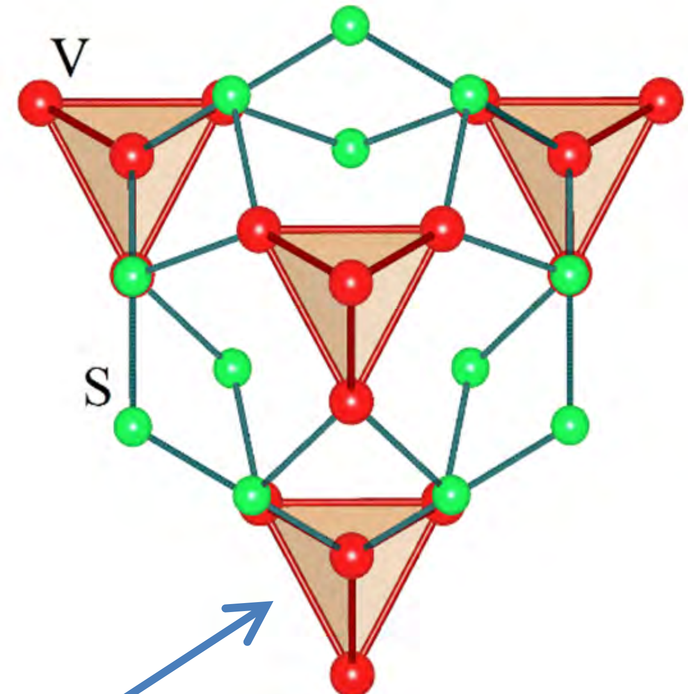
only 5 pages, but +18 additional pages of Supplementary!

Model for interconnected $(V_4S_4)^{5+}$ clusters

S-atoms forming clusters



S-atoms connecting clusters



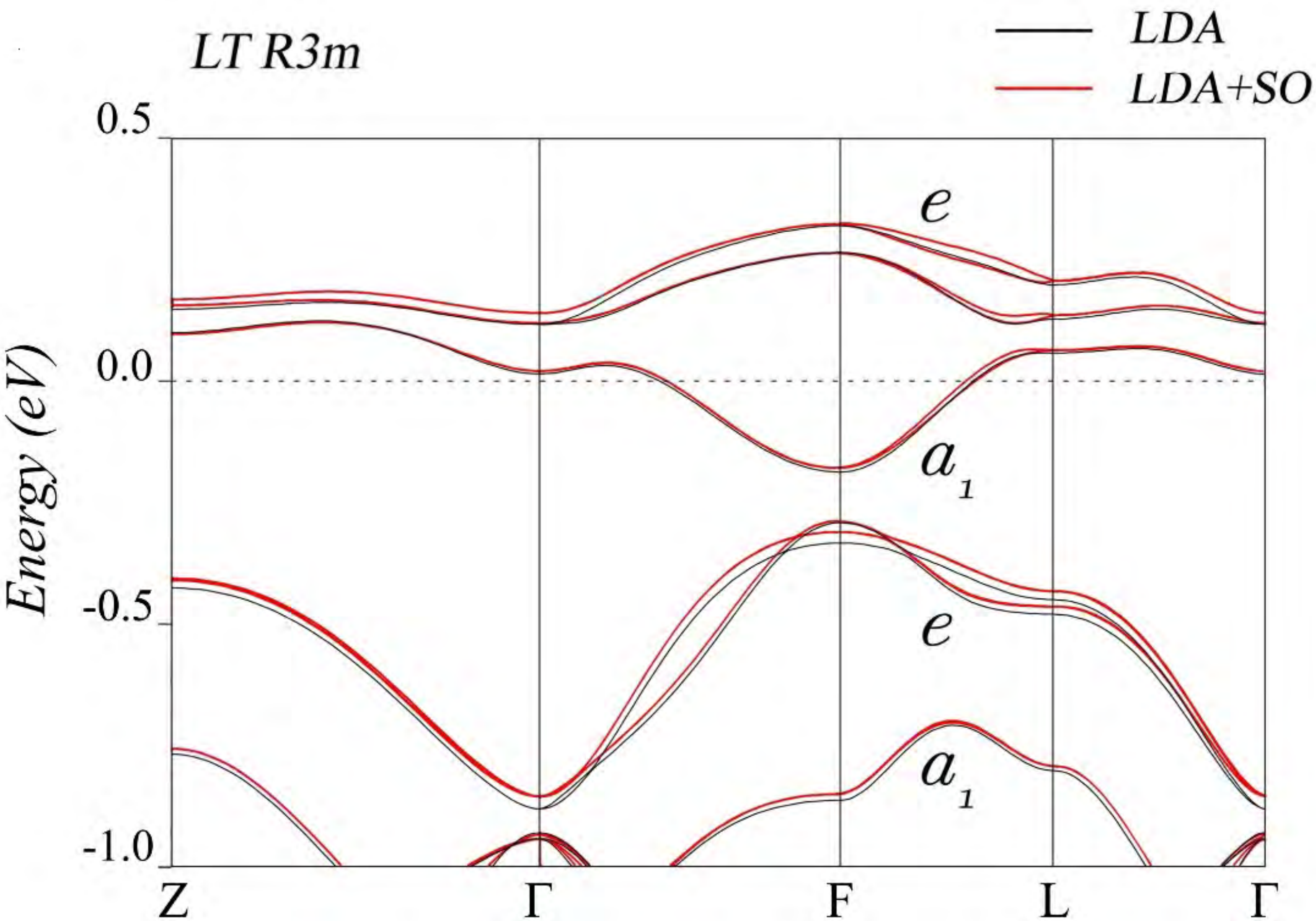
"building blocks" or
"lattice points" in the Hubbard model

What can we do?

- Thousands of magnetic atoms
- Noncollinear magnetism
- Coulomb correlations in molecular $(V_4S_4)^{5+}$clusters

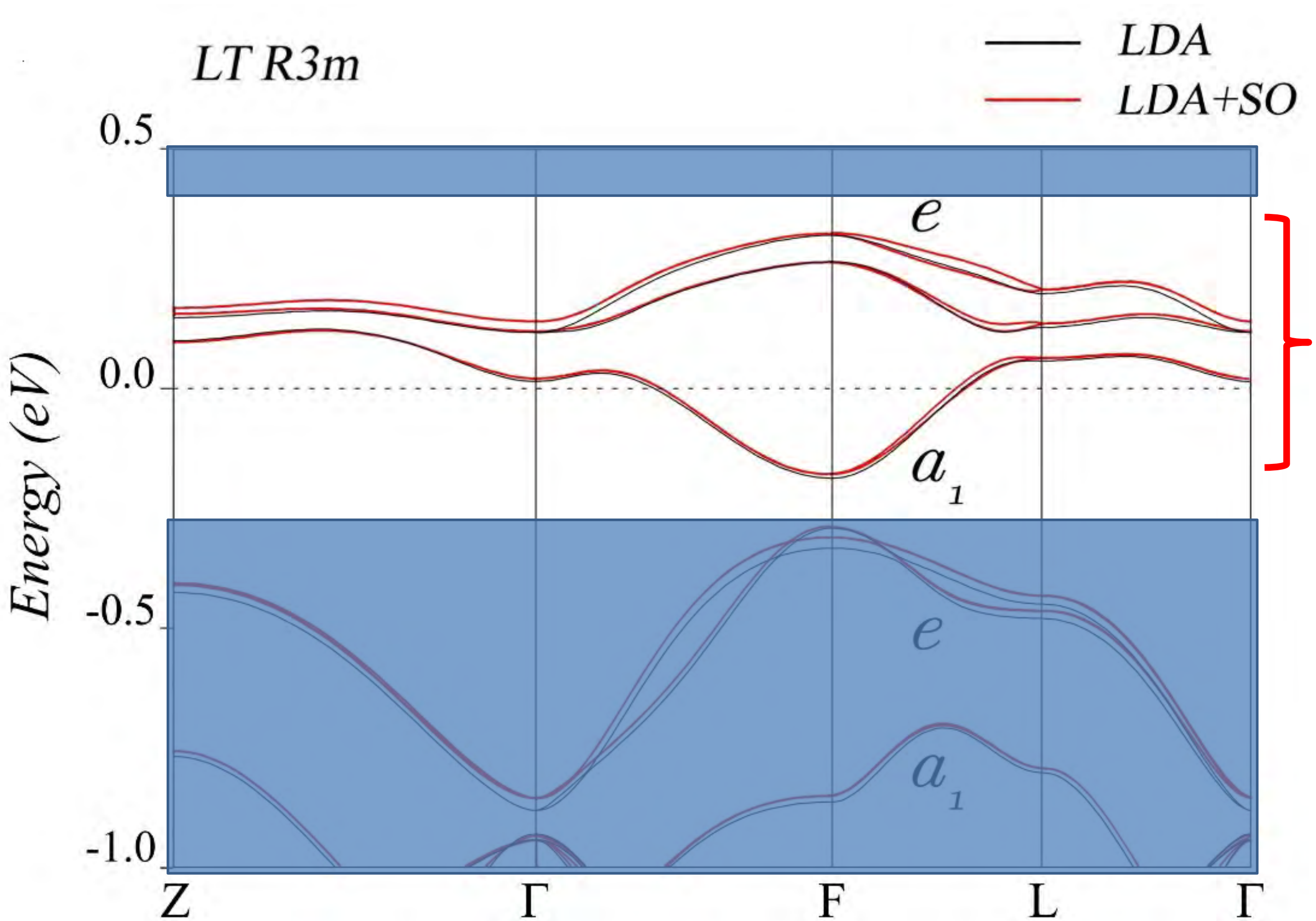
Too heavy for conventional
electronic structure calculations …

Electronic structure of GaV_4S_8 in LDA



S. A. Nikolaev and IVS, Phys. Rev. B **99**, 100401(R) (2019)

Electronic structure of GaV_4S_8 in LDA



target bands for the model

and … hope it is enough!

S. A. Nikolaev and IVS, Phys. Rev. B **99**, 100401(R) (2019)

Details

VASP or QUANTUM ESPRESSO

one-electron part

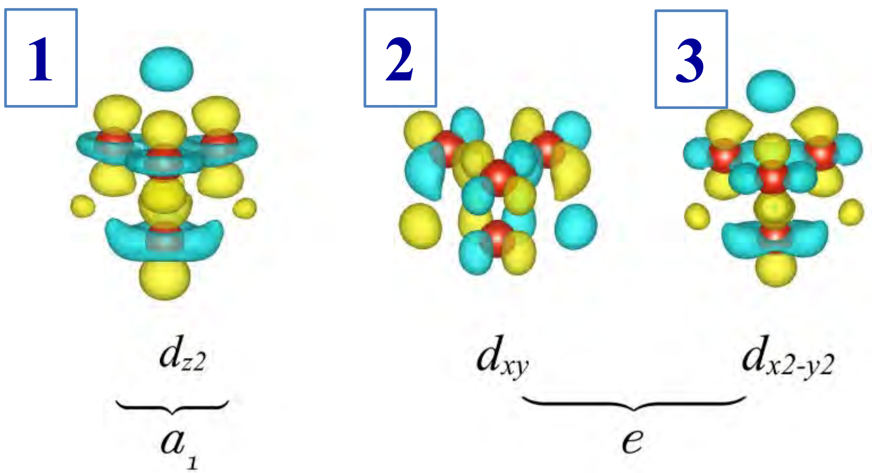
Coulomb interaction part

$$\hat{\mathcal{H}}_e = \sum_{ij}\sum_{\alpha\beta} t_{ij}^{\alpha\beta}\hat{c}^{\dagger}_{i\alpha}\hat{c}_{j\beta} + \frac{1}{2}\sum_{i}\sum_{\alpha\beta\gamma\delta} U_{\alpha\beta\gamma\delta}\hat{c}^{\dagger}_{i\alpha}\hat{c}^{\dagger}_{i\gamma}\hat{c}_{i\beta}\hat{c}_{i\delta}$$

wannier90

wannier90 + cRPA

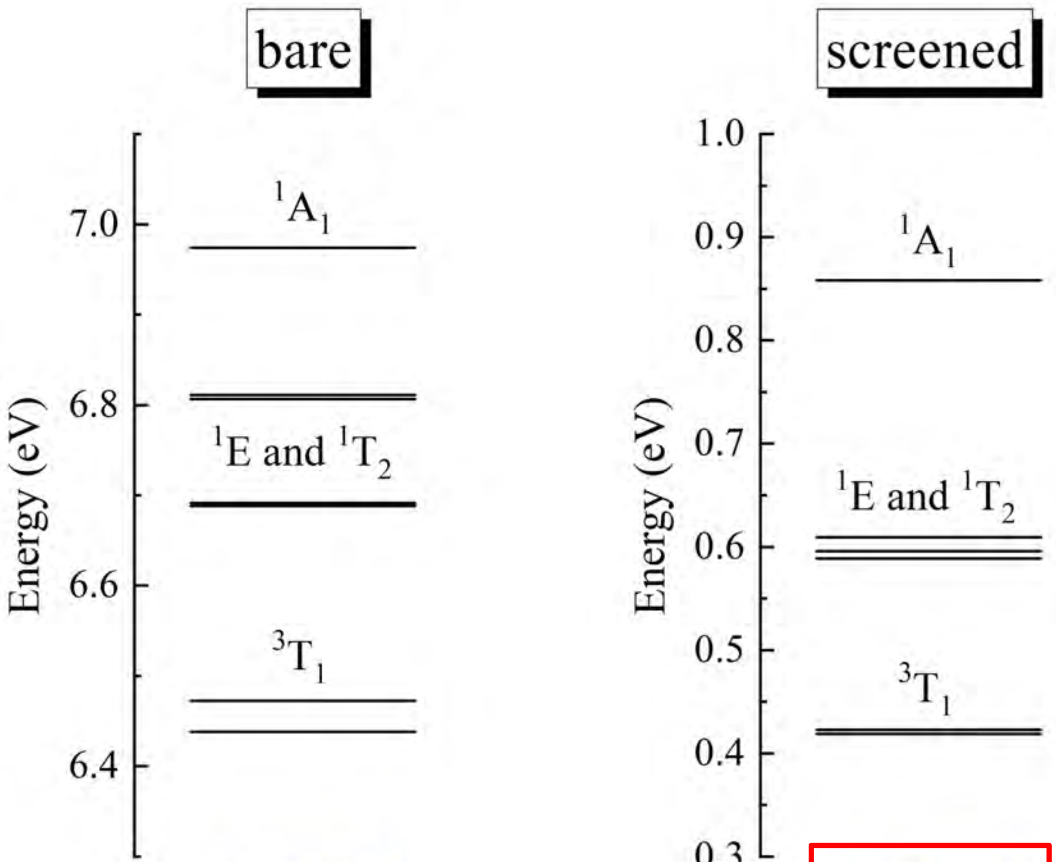
Wannier functions (MLWF)



Parameters

(excited) two-electron states

one can derive
Kanamori's U and J



$U = 6.968$ eV
$J = 0.182$ eV

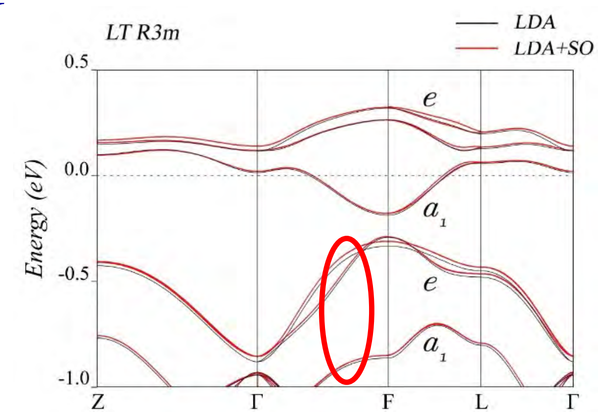
$U = 0.684$ eV
$J = 0.087$ eV

so small!

$U+2J$

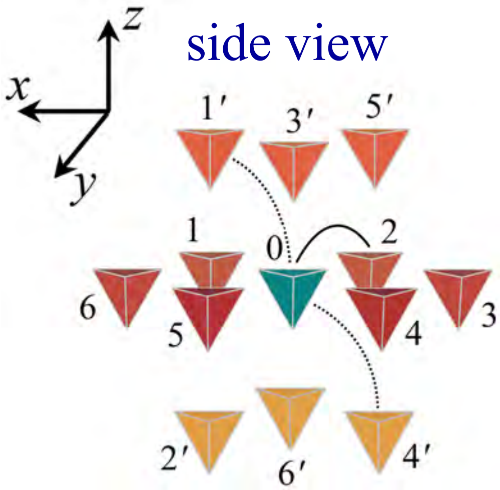
$U-J$

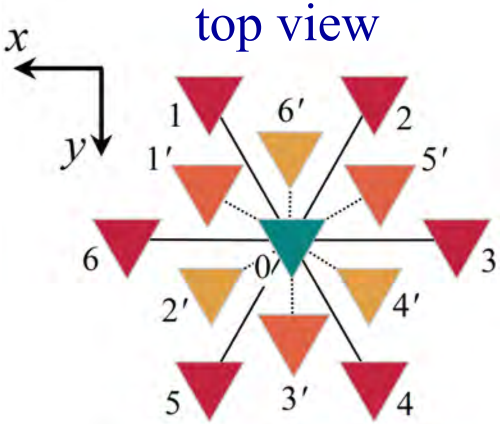
$U-3J$



delocalization +
strong screening
due to proximity
of other V *3d* states

But… the transfer integrals are also small!





in-plane (j=1-6)

$$\hat{t}_{0j} = \begin{pmatrix} t_{\parallel}^{1} & s_{\parallel}^{3}\sin\frac{2\pi j}{3} - u_{\parallel}^{3}\cos\frac{\pi j}{3} & -s_{\parallel}^{3}\cos\frac{2\pi j}{3} + u_{\parallel}^{3}\sin\frac{\pi j}{3} \\ s_{\parallel}^{3}\sin\frac{2\pi j}{3} + u_{\parallel}^{3}\cos\frac{\pi j}{3} & t_{\parallel}^{2} - s_{\parallel}^{2}\cos\frac{2\pi j}{3} & s_{\parallel}^{2}\sin\frac{2\pi j}{3} + (-1)^{j}u_{\parallel}^{2} \\ -s_{\parallel}^{3}\cos\frac{2\pi j}{3} - u_{\parallel}^{3}\sin\frac{\pi j}{3} & s_{\parallel}^{2}\sin\frac{2\pi j}{3} - (-1)^{j}u_{\parallel}^{2} & t_{\parallel}^{2} + s_{\parallel}^{2}\cos\frac{2\pi j}{3} \end{pmatrix}$$

(in meV)

$t_{\parallel}^{1}$	$s_{\parallel}^{3}$	$u_{\parallel}^{3}$	$t_{\parallel}^{2}$	$s_{\parallel}^{2}$	$u_{\parallel}^{2}$
4.0	25.5	16.2	−0.4	−10.5	18.7

out-of-plane (j=1′-6′)

$$\hat{t}_{0j} = \begin{pmatrix} t_{\perp}^{1} & s_{\perp}^{3}\sin\frac{2\pi j}{3} - u_{\perp}^{3}\sin\frac{\pi j}{3} & s_{\perp}^{3}\cos\frac{2\pi j}{3} + u_{\perp}^{3}\cos\frac{\pi j}{3} \\ s_{\perp}^{3}\sin\frac{2\pi j}{3} + u_{\perp}^{3}\sin\frac{\pi j}{3} & t_{\perp}^{2} + s_{\perp}^{2}\cos\frac{2\pi j}{3} & s_{\perp}^{2}\sin\frac{2\pi j}{3} \\ s_{\perp}^{3}\cos\frac{2\pi j}{3} - u_{\perp}^{3}\cos\frac{\pi j}{3} & s_{\perp}^{2}\sin\frac{2\pi j}{3} & t_{\perp}^{2} - s_{\perp}^{2}\cos\frac{2\pi j}{3} \end{pmatrix}$$

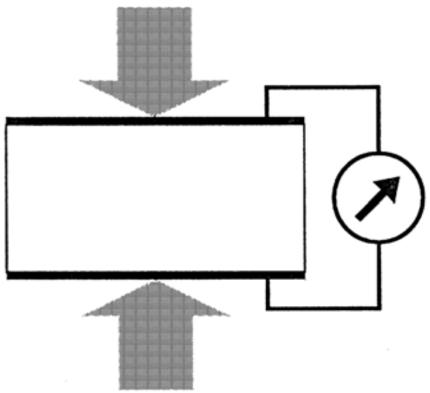
(in meV)

$t_{\perp}^{1}$	$s_{\perp}^{3}$	$u_{\perp}^{3}$	$t_{\perp}^{2}$	$s_{\perp}^{2}$
−3.3	−22.7	−21.6	2.3	21.7

The superexchange approximation (t/U <<1) is justified!

Polarization:
General Properties
and
Implications for Skyrmion Textures

Berry-phase theory of Polarization for Periodic Systems



in periodic systems, P is related to the current flowing through the sample

$$\Delta \mathbf{P} = \mathbf{P}(\Delta t) - \mathbf{P}(0) = \int_0^{\Delta t} \mathrm{d}t\, \mathbf{j}(t)$$

- depends on the phase of the wavefunction (Berry phase)
- only difference is measurable

$$\mathbf{P} = -\frac{ie}{(2\pi)^3} \sum_{n=1}^{M} \int_{\mathrm{BZ}} \langle n\mathbf{k}|\nabla_{\mathbf{k}}|n\mathbf{k}\rangle d\mathbf{k}$$

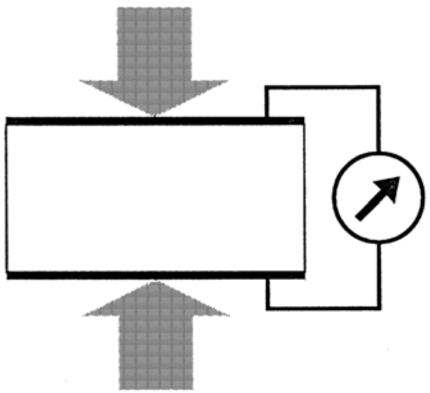
in **k**-space (via Berry connection)

$$\mathbf{P} = -\frac{e}{V} \sum_{n=1}^{M} \int \mathbf{r}\, w_n^2(\mathbf{r})\, d\mathbf{r}$$

in **r**-space (via Wannier functions)

D. Vanderbilt and R. D. King-Smith, Phys. Rev. B **48**, 4442 (1993);
R. Resta, Rev. Mod. Phys. **66**, 899 (1994); J. Phys.: Condens. Matter **22**, 123201 (2010).

Berry-phase theory of Polarization



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- depends on the phase of the wavefunction (Berry pha
- only differ

All information about the magnetic state dependence or the effect of spin-orbit interaction is here

$$\mathbf{P} \;= -\frac{ie}{(2\pi)^3} \sum_{n=1}^{M} \int_{\mathrm{BZ}} \langle n\mathbf{k}|\nabla_{\mathbf{k}}$$

$$\mathbf{P} = -\frac{e}{V} \sum_{n=1}^{M} \int \mathbf{r}\, w_n^2(\mathbf{r})\, d\mathbf{r}$$

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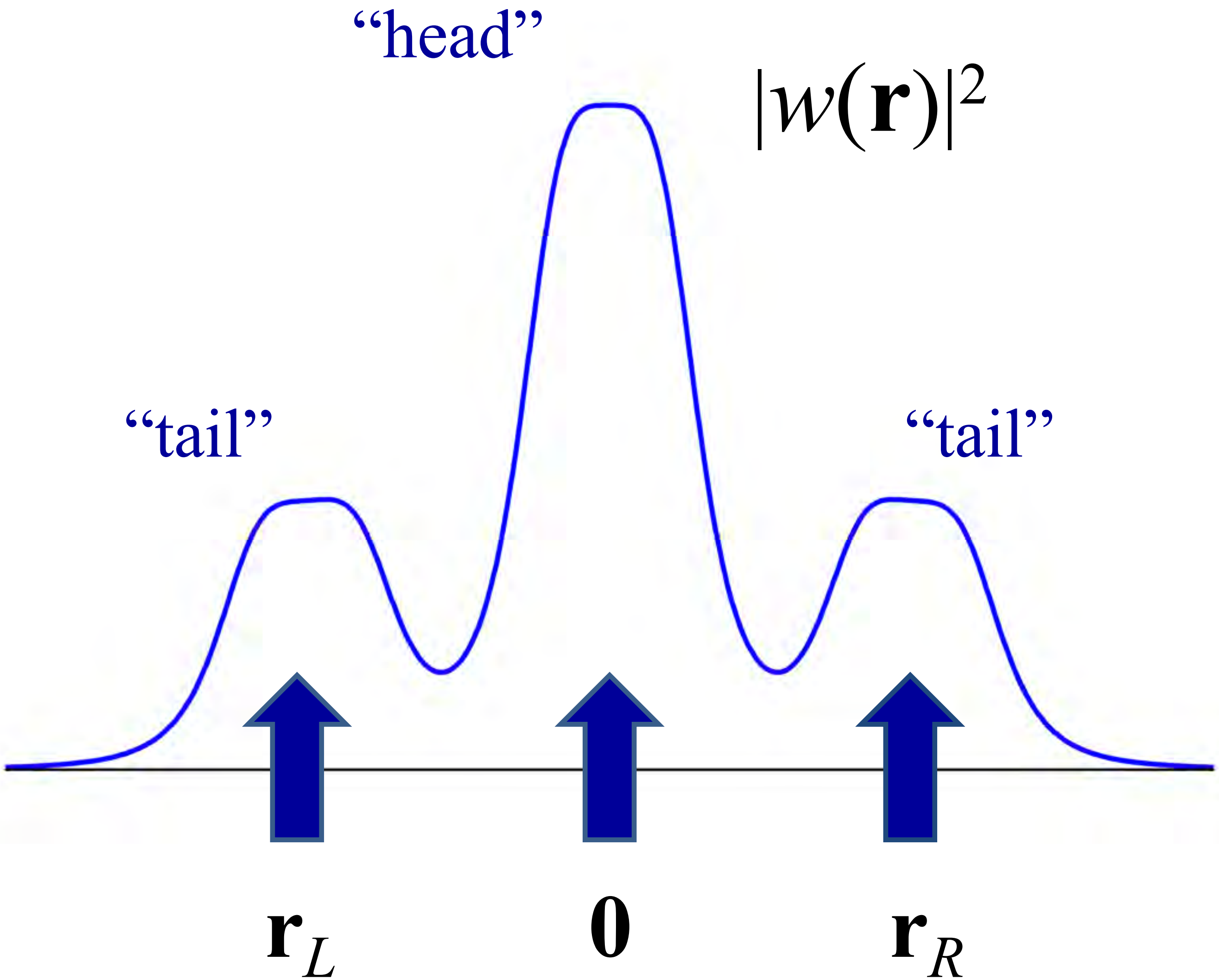
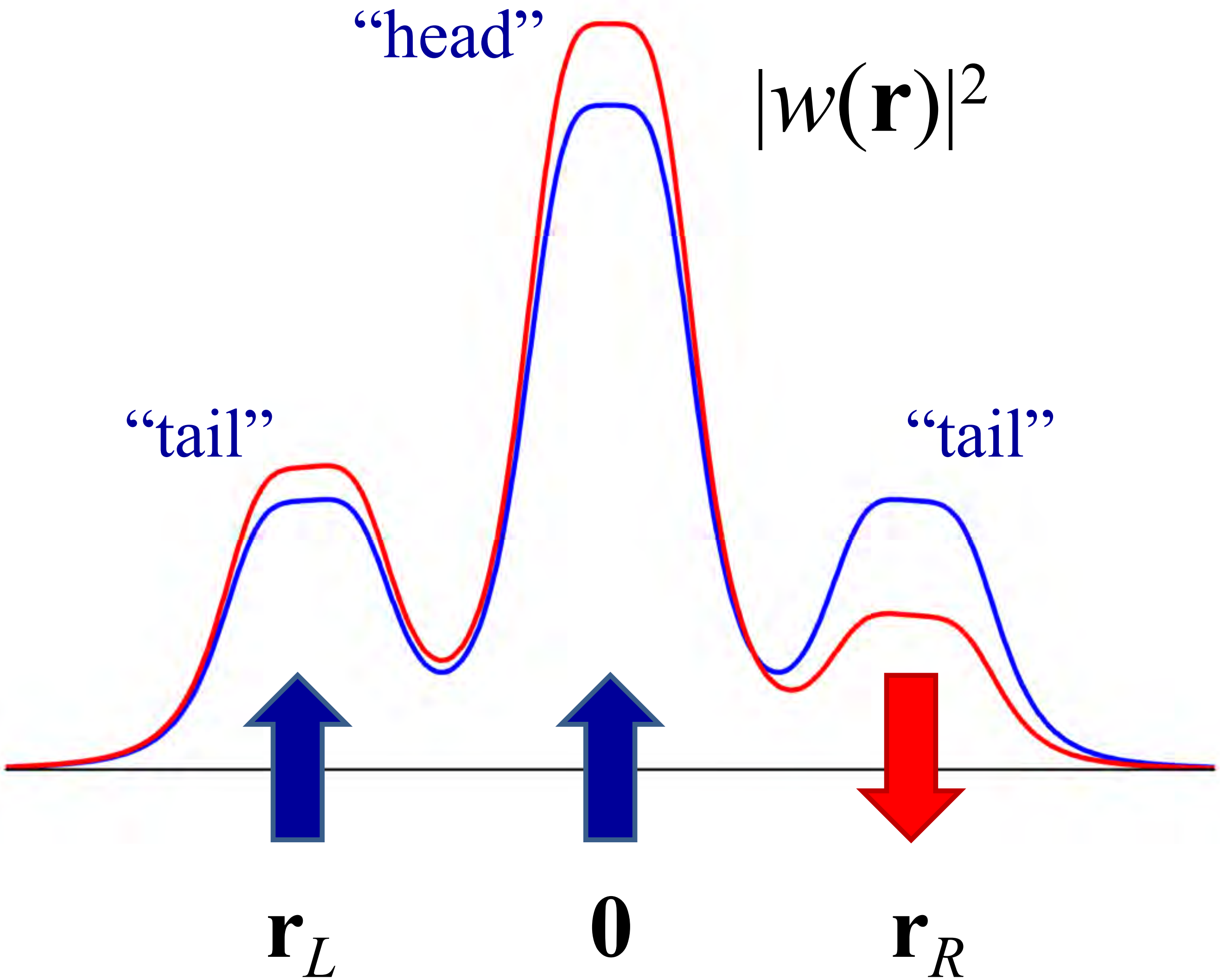
What does it mean in practice?



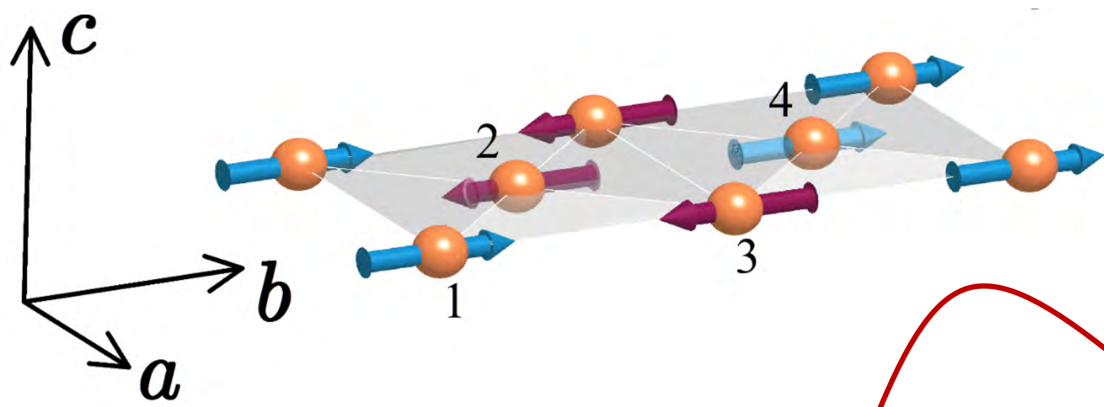
$\mathbf{P} = 0$

What does it mean in practice?



$$\mathbf{P} \approx \mathbf{r}_L |w(\mathbf{r}_L)|^2 + \mathbf{r}_R |w(\mathbf{r}_R)|^2$$

Simplest Example: E-phase of manganites



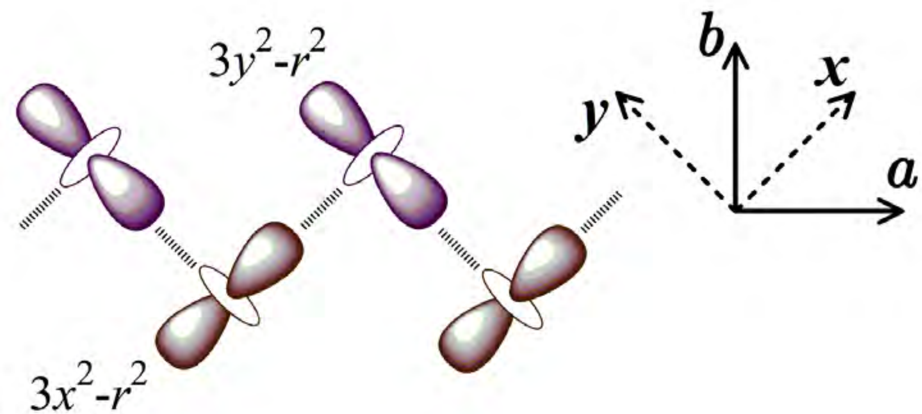
$YMnO_3$
$HoMnO_3$

all information about spins is here

double exchange physics: $\hat{t}_{ij} \longrightarrow \xi_{ij}\hat{t}_{ij}$

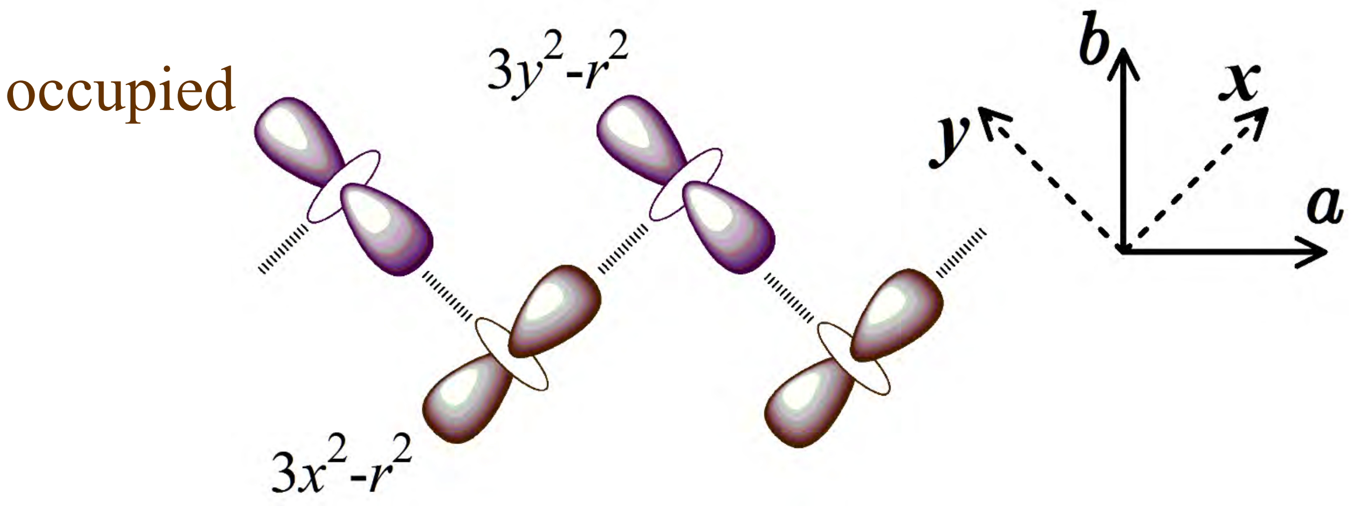
$\xi_{ij} = 0$ for ↑↓ bonds

orbitally ordered
ferromagnetic zigzag chain



see also P. Barone *et al.*, Phys. Rev. Lett. **106**, 077201 (2011)

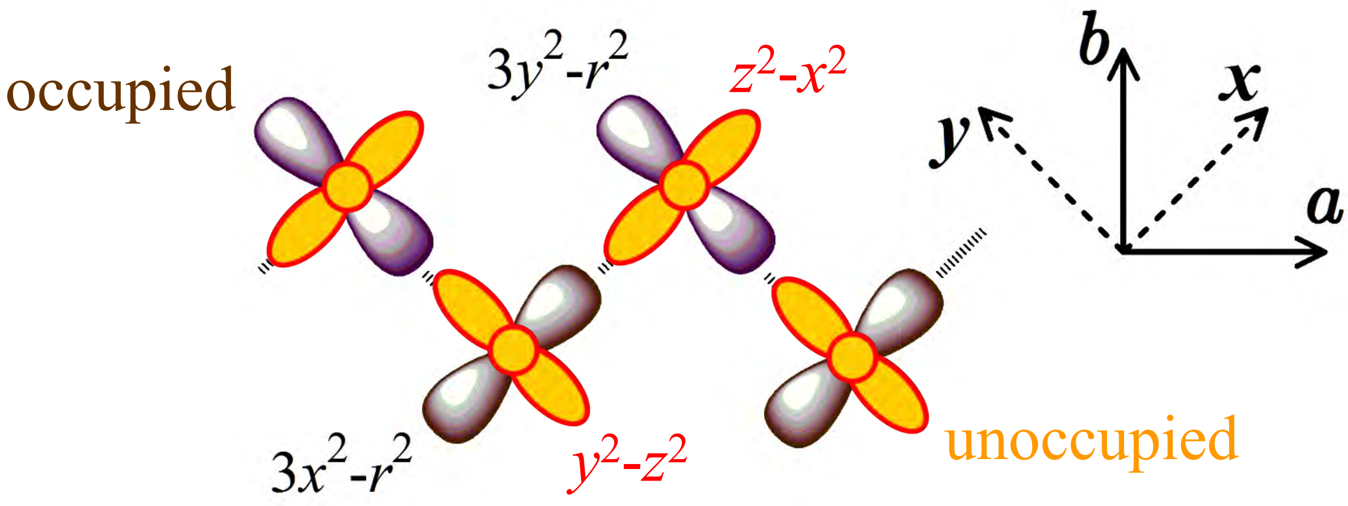
$$\mathbf{P} = -\frac{e}{V}\sum_{n=1}^{M}\int \mathbf{r}\, w_n^2(\mathbf{r})\, d\mathbf{r}$$



atomic limit: $\mathbf{P} = 0$

Phys. Rev. B **87**, 144424 (2013)

$$\mathbf{P} = -\frac{e}{V}\sum_{n=1}^{M}\int \mathbf{r}\, w_n^2(\mathbf{r})\, d\mathbf{r}$$



atomic limit: **P** = 0

Phys. Rev. B **87**, 144424 (2013)

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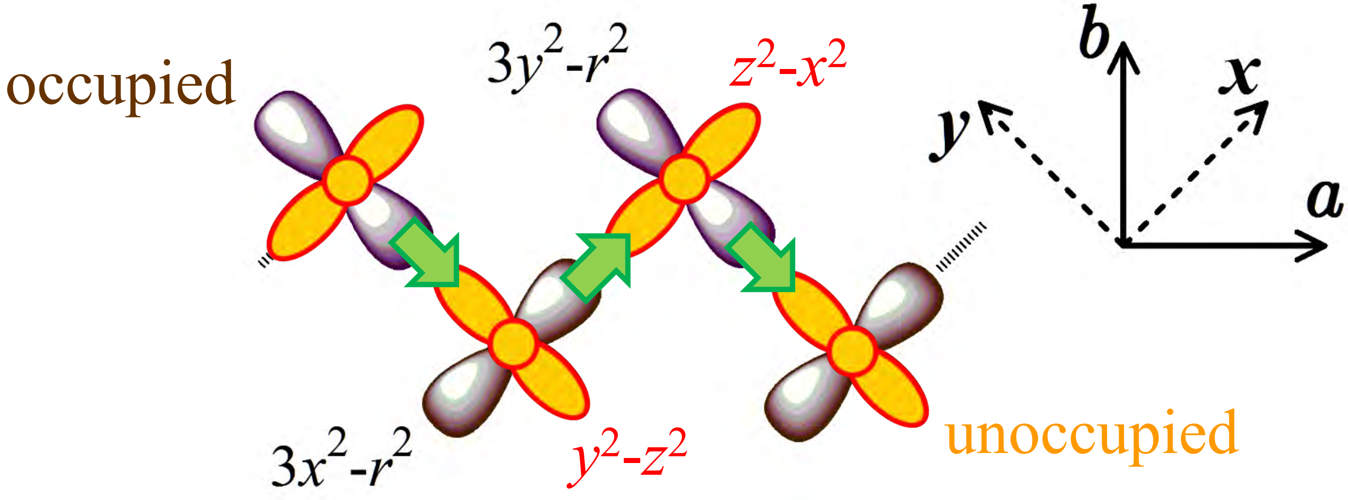


atomic limit: $\mathbf{P} = 0$

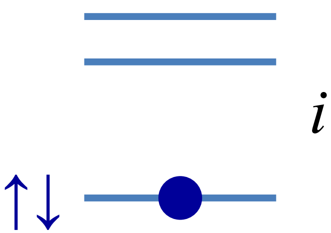
asymmetric Wannier transfer: $\delta w_{i\rightarrow i+1} = (t_{ii+1}/\Delta)^2$, but $\delta w_{i\rightarrow i\text{-}1} = 0$

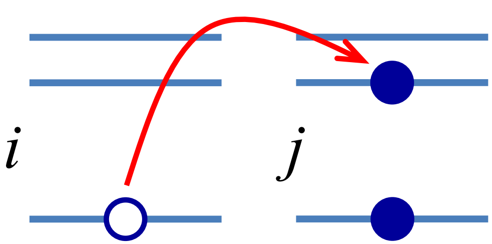
polarization: $\delta\mathbf{P} \sim (\boldsymbol{R}_{i+1}\text{-}\boldsymbol{R}_i)\delta w_{i\rightarrow i+1}$

Phys. Rev. B **87**, 144424 (2013)

Superexchange theory for magentic interactions *and* electric polarization

Kramer's doublets





"atomic" limit:

occupied orbital: $\alpha_i = c_\uparrow \chi_\uparrow + c_\downarrow \chi_\downarrow$

direction of spin: $\boldsymbol{e}_i = \langle \alpha_i | \boldsymbol{\sigma} | \alpha_i \rangle / |\langle \alpha_i | \boldsymbol{\sigma} | \alpha_i \rangle|$

perturbation:

$$|w_i\rangle \approx |\alpha_i\rangle + |\alpha_{i\to j}\rangle$$

$$|\alpha_{i\to j}\rangle = \hat{\mathcal{M}}_j \hat{t}_{ji} |\alpha_i\rangle$$ (new WF)

$$\hat{\mathcal{M}}_j = \sum_M \frac{\hat{\mathcal{P}}_j |jM\rangle\langle jM| \hat{\mathcal{P}}_j}{E_{jM}}$$ $\sim 1/U$

kinetic energy:

$$E_{\rm kin} = \sum_{\langle ij \rangle} \left(\langle \alpha_i | \hat{t}_{ij} | \alpha_{i\to j} \rangle + i \leftrightarrow j \right)$$

polarization:

$$\boldsymbol{P} = \sum_{\langle ij \rangle} \frac{e}{V} \boldsymbol{\tau}_{ji} \left(\langle \alpha_{j\to i} | \alpha_{j\to i} \rangle - \langle \alpha_{i\to j} | \alpha_{i\to j} \rangle \right)$$

Wannier weight transfer: $\langle \alpha_{i\to j} | \alpha_{i\to j} \rangle = \langle \alpha_i | \hat{t}_{ij} \hat{\mathcal{M}}_j^2 \hat{t}_{ji} | \alpha_i \rangle$ $\quad \boldsymbol{\tau}_{ji} = \boldsymbol{R}_j - \boldsymbol{R}_i$

kinetic energy:

polarization:

mapping, considering the directions of spins $\boldsymbol{e}_i \parallel x$, y, and z

$$\mathcal{H}^{\mathrm{S}} = \sum_{\langle ij \rangle} \boldsymbol{e}_i \overleftrightarrow{\mathscr{J}}_{ij} \boldsymbol{e}_j \qquad \boldsymbol{P} = \sum_{\langle ij \rangle} \boldsymbol{\epsilon}_{ji} (\boldsymbol{e}_i \overleftrightarrow{\mathscr{P}}_{ij} \boldsymbol{e}_j)$$

unit vector in the direction of the bond ij

antisymmetric

$$\mathcal{H}^{\mathrm{S}} = \sum_{\langle ij \rangle} (-J_{ij} \boldsymbol{e}_i \boldsymbol{e}_j + \boldsymbol{D}_{ij} \boldsymbol{e}_i \times \boldsymbol{e}_j + \boldsymbol{e}_i \overleftrightarrow{\Gamma}_{ij} \boldsymbol{e}_j) \qquad \boldsymbol{P} = \sum_{\langle ij \rangle} \boldsymbol{\epsilon}_{ji} (P_{ij} \boldsymbol{e}_i \boldsymbol{e}_j + \boldsymbol{\mathcal{P}}_{ij} \boldsymbol{e}_i \times \boldsymbol{e}_j + \boldsymbol{e}_i \overleftrightarrow{\Pi}_{ij} \boldsymbol{e}_j)$$

isotropic

traceless anisotropic symmetric

S. A. Nikolaev and IVS, Phys. Rev. B **99**, 100401(R) (2019)

Inverse Dzyaloshinskii-Moriya mechanism (or spin-current mechanism)

unit vector connecting two magnetic sites

pseudovector (depends on the symmetry)

$$\boldsymbol{\varepsilon}_{ji}\mathcal{P}_{ij}[\boldsymbol{e}_i \times \boldsymbol{e}_j]$$

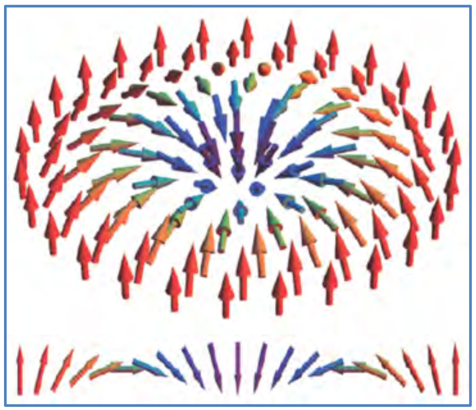
directions of spins

not $\mathbf{P}_{ij} \sim \boldsymbol{\varepsilon}_{ji} \times [\boldsymbol{e}_i \times \boldsymbol{e}_j]$, as in KNB, PRL **95**, 057205 (2005)

Phys. Rev. B **95**, 214406 (2017)

Skyrmion Texture and Polarization

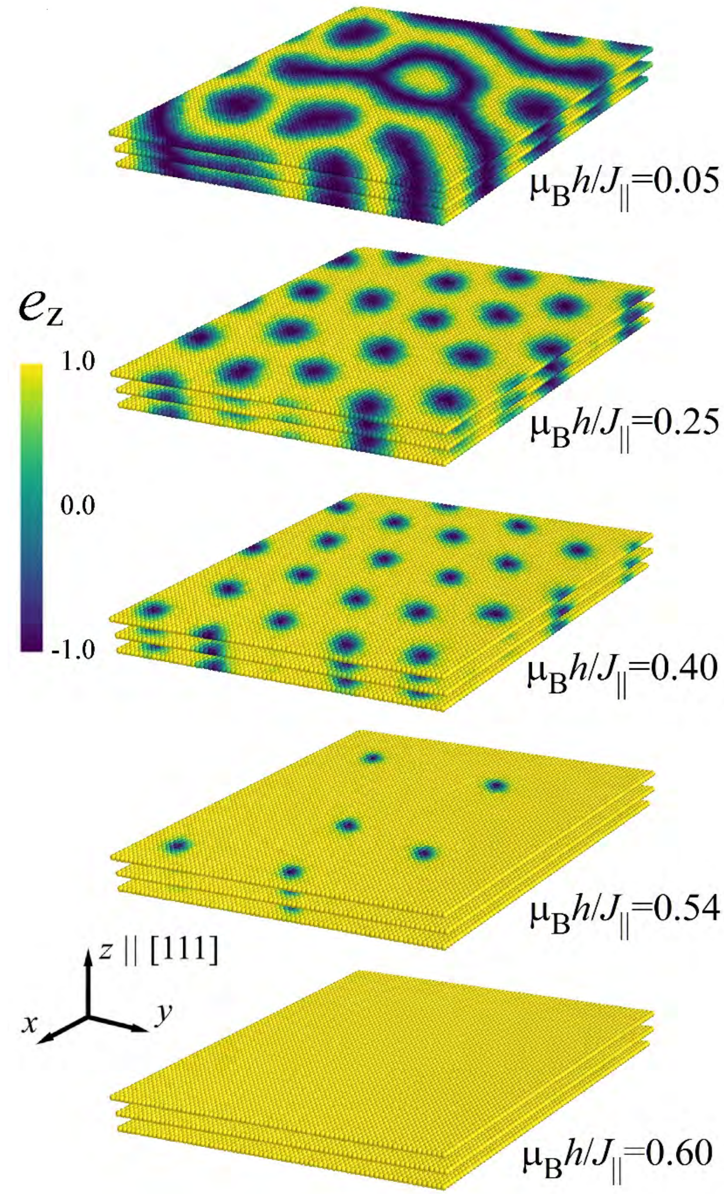
Results of Monte-Carlo simulations



in 2D

which form skyrmion tubes in 3D

What does it mean for the polarization?



$$\boldsymbol{P} = \sum\nolimits_{\langle ij \rangle} \boldsymbol{\epsilon}_{ji} (\boldsymbol{e}_i \overset{\leftrightarrow}{\mathscr{P}}_{ij} \boldsymbol{e}_j)$$

spin-dependence

$$\boldsymbol{P} = \sum_{\langle ij \rangle} \boldsymbol{\epsilon}_{ji} \boxed{(\boldsymbol{e}_i \overset{\leftrightarrow}{\mathscr{P}}_{ij} \boldsymbol{e}_j)}$$

spin-dependence

$$\boldsymbol{P} = \sum_{\langle ij \rangle} \boxed{\boldsymbol{\epsilon}_{ji}} \boxed{(\boldsymbol{e}_i \overleftrightarrow{\mathscr{P}}_{ij} \boldsymbol{e}_j)}$$

direction of bond

spin-dependence

$$\boldsymbol{P} = \sum_{\langle ij\rangle} \boxed{\epsilon_{ji}} \boxed{(\boldsymbol{e}_i \overset{\leftrightarrow}{\mathscr{P}}_{ij} \boldsymbol{e}_j)}$$

direction of bond

- $\boldsymbol{P}$ || direction of the bond

spin-dependence

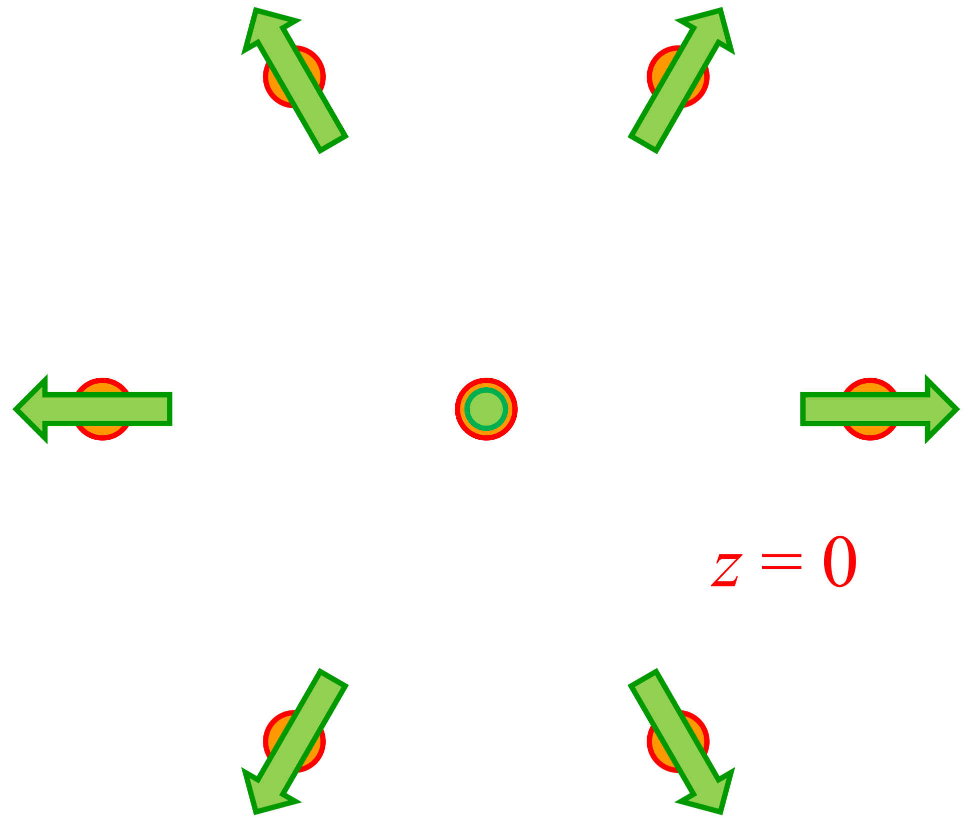
$$\boldsymbol{P} = \sum_{\langle ij \rangle} \boxed{\boldsymbol{\epsilon}_{ji}} \boxed{(\boldsymbol{e}_i \overset{\leftrightarrow}{\mathscr{P}}_{ij} \boldsymbol{e}_j)}$$

direction of bond

- $\boldsymbol{P}$ || direction of the bond
- only out-of-plane bonds contribute to P^z

$$\boldsymbol{P} = \sum_{\langle ij\rangle} \underbrace{\boxed{\boldsymbol{\epsilon}_{ji}}}_{\text{direction of bond}} \overbrace{\boxed{(\boldsymbol{e}_i \overleftrightarrow{\mathscr{P}}_{ij} \boldsymbol{e}_j)}}^{\text{spin-dependence}}$$

- ***P*** || direction of the bond
- only out-of-plane bonds contribute to P^z



$$\boldsymbol{P} = \sum_{\langle ij \rangle} \underbrace{\boxed{\boldsymbol{\epsilon}_{ji}}}_{\text{direction of bond}} \overbrace{\boxed{(\boldsymbol{e}_i \overleftrightarrow{\mathscr{P}}_{ij} \boldsymbol{e}_j)}}^{\text{spin-dependence}}$$

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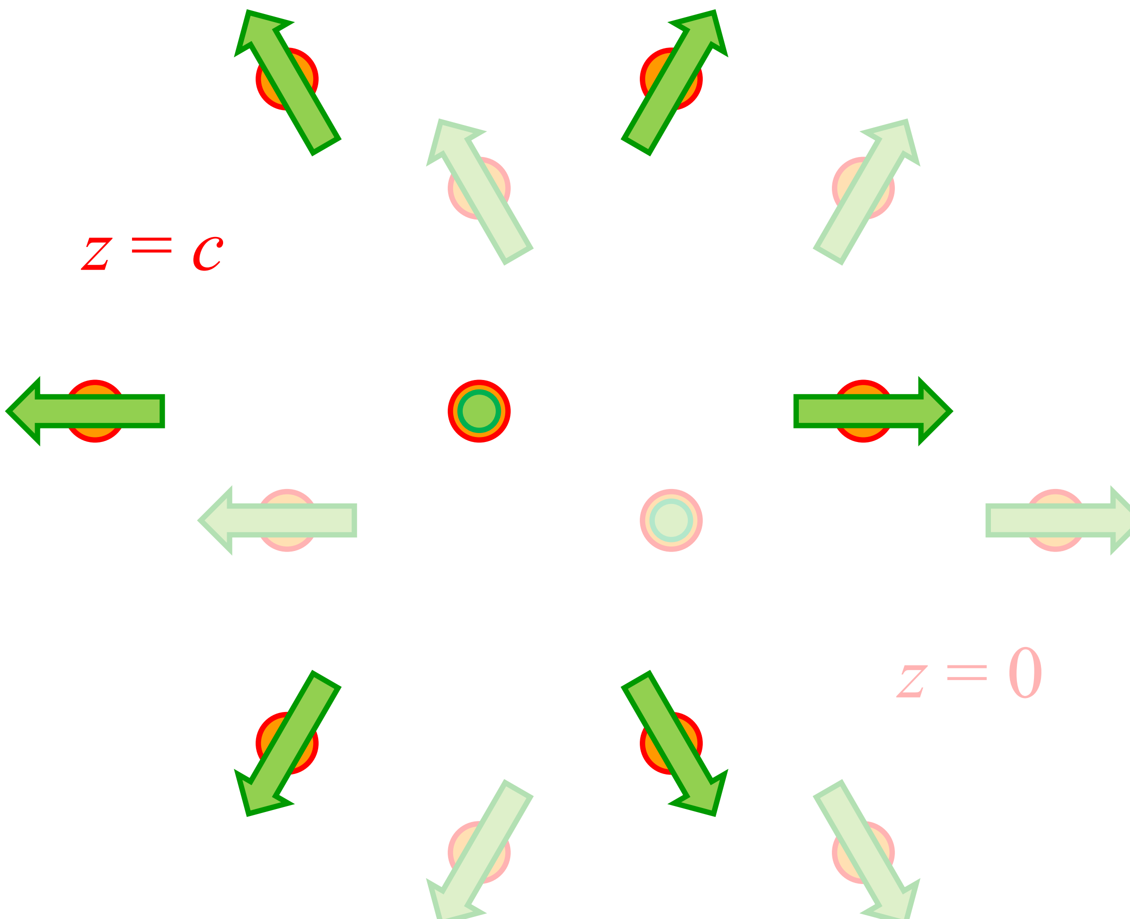

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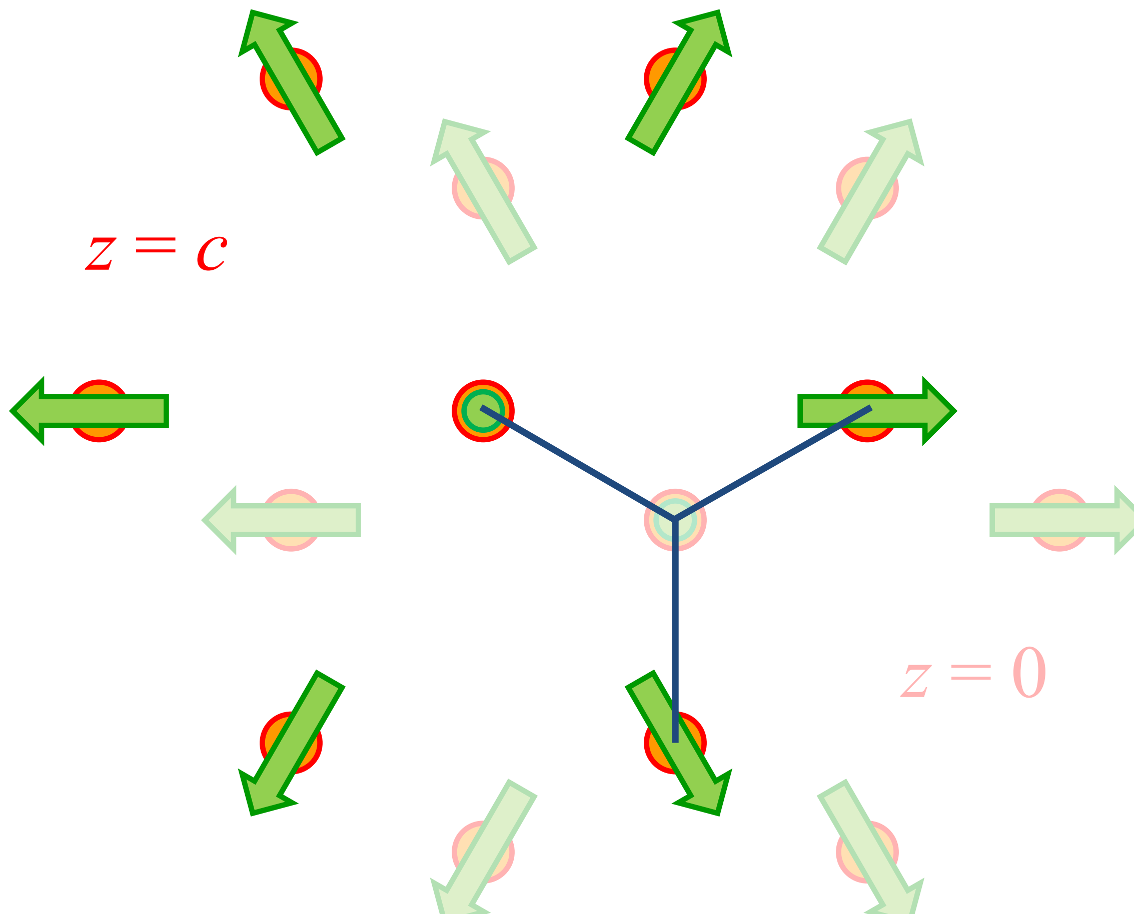
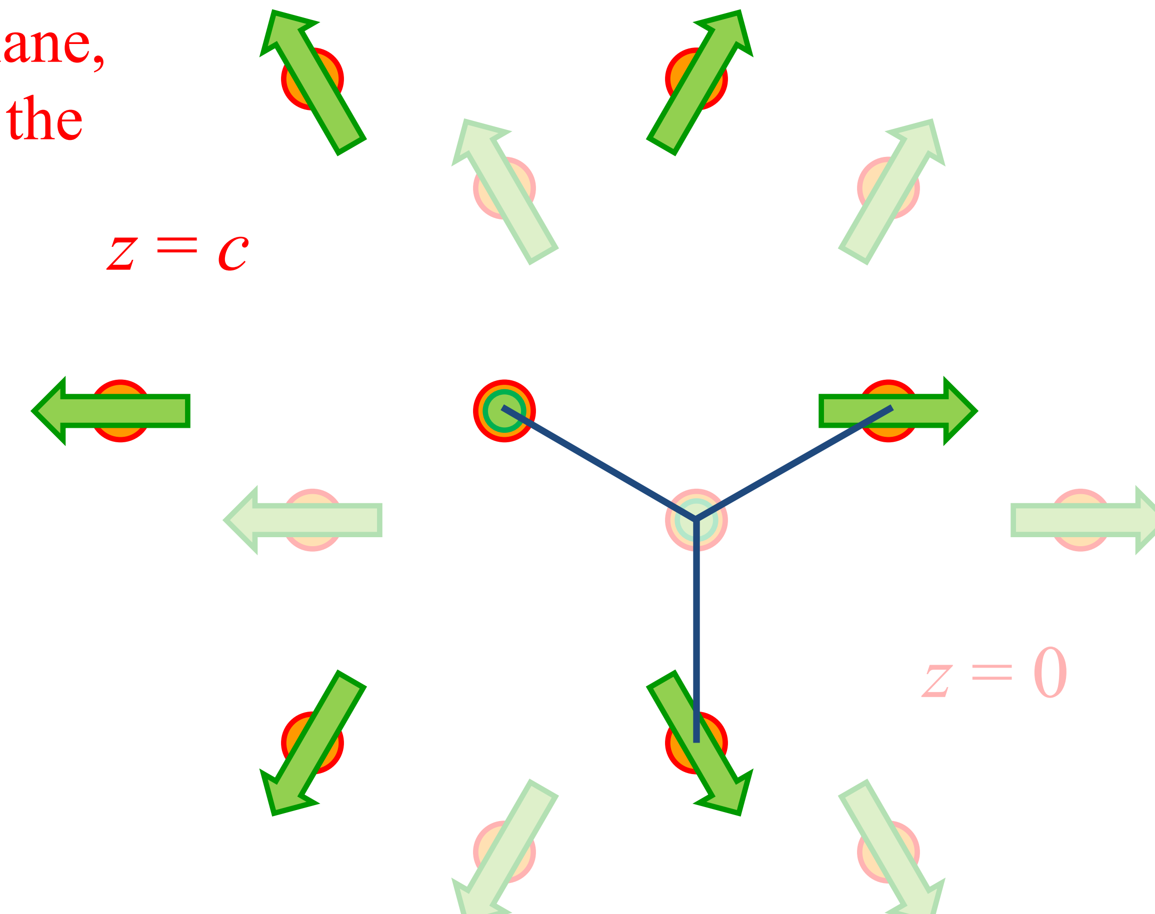


$$\boldsymbol{P} = \sum_{\langle ij\rangle} \underbrace{\boxed{\boldsymbol{\epsilon}_{ji}}}_{\text{direction of bond}} \overbrace{\boxed{(\boldsymbol{e}_i \overleftrightarrow{\mathscr{P}}_{ij} \boldsymbol{e}_j)}}^{\text{spin-dependence}}$$

- $\boldsymbol{P}$ || direction of the bond
- only out-of-plane bonds contribute to P^z

not only the skyrmion plane, but also the stacking of the planes is important



$$\boldsymbol{P} = \sum_{\langle ij\rangle} \underbrace{\boxed{\epsilon_{ji}}}_{\text{direction of bond}} \overbrace{\boxed{(\boldsymbol{e}_i \overleftrightarrow{\mathscr{P}}_{ij} \boldsymbol{e}_j)}}^{\text{spin-dependence}}$$

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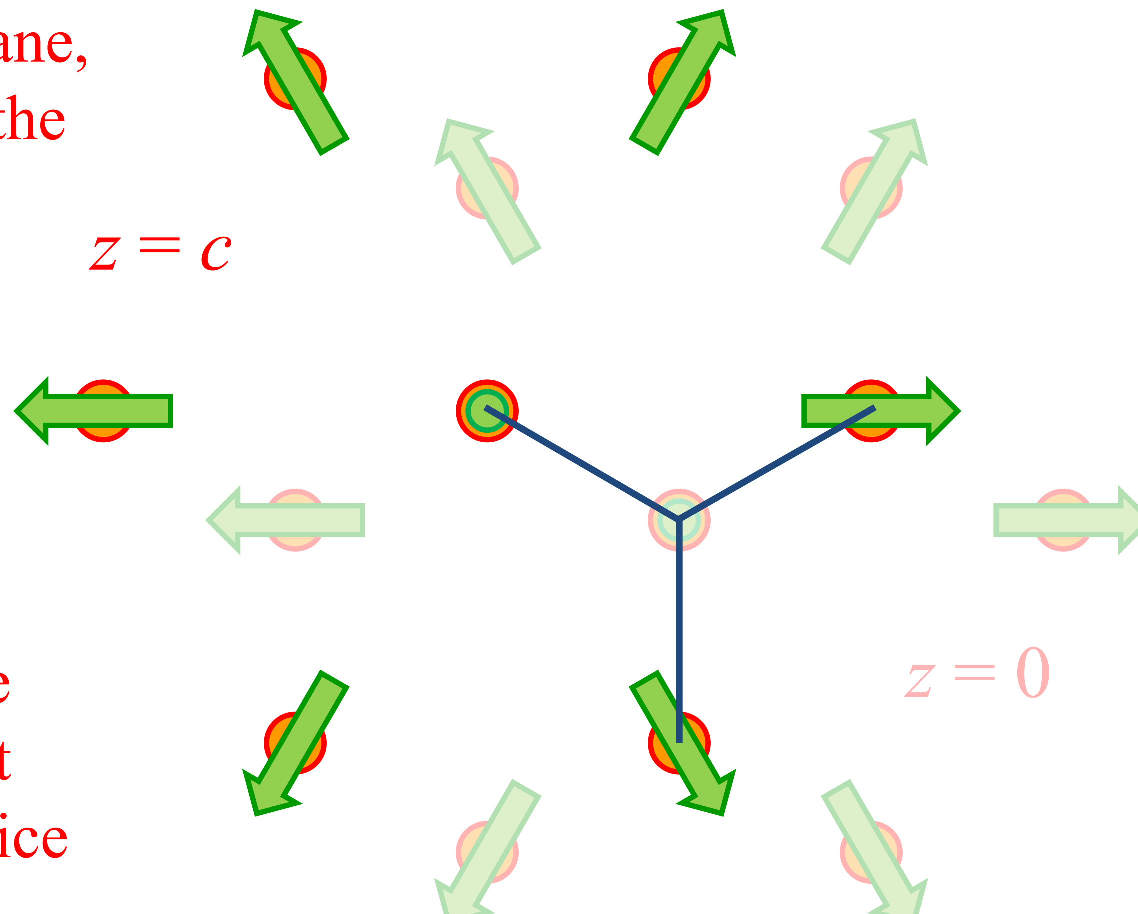
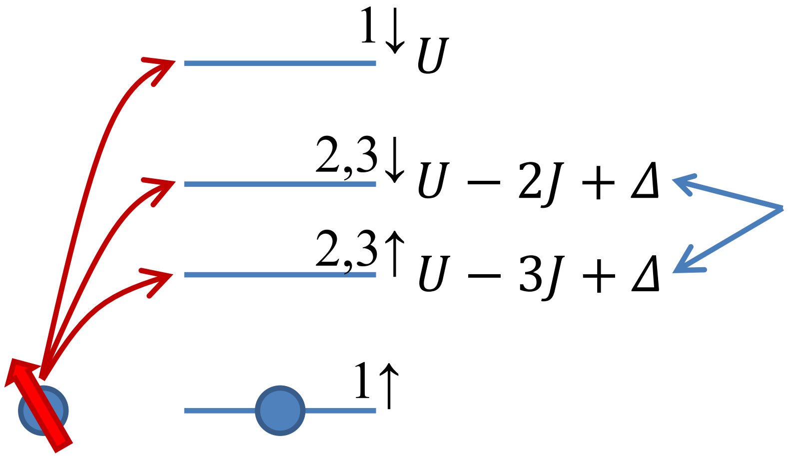


important aspect is the stacking misalignment in the (distorted) fcc lattice

Isotropic part of the polarization



crystal-field splitting

superexchange paths

$$\boldsymbol{P}_{ij} = -\frac{e}{V}\boldsymbol{\tau}_{ji} \sum_{\alpha} (w_{ij}^{\alpha} - w_{ji}^{\alpha})$$

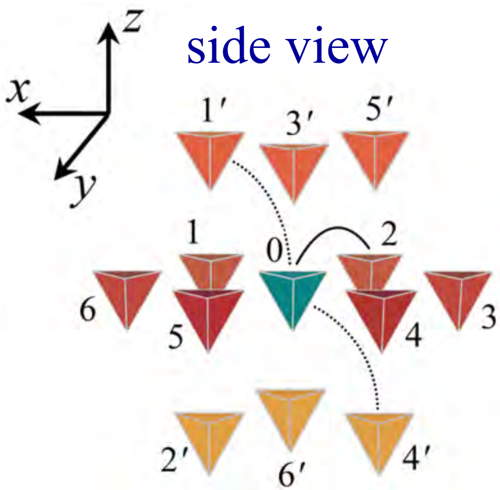
$$w_{ij} = |\xi_{ij}^{\uparrow\uparrow}|^2 \frac{(t_{ij}^{12})^2 + (t_{ij}^{13})^2}{(U - 3J + \Delta)^2} + |\xi_{ij}^{\uparrow\downarrow}|^2 \frac{(t_{ij}^{12})^2 + (t_{ij}^{13})^2}{(U - 2J + \Delta)^2} + |\xi_{ij}^{\uparrow\downarrow}|^2 \frac{(t_{ij}^{11})^2}{U^2}$$

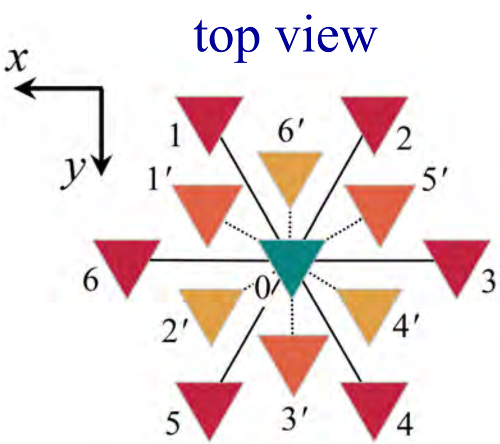
$$|\xi_{ij}^{\uparrow\uparrow}|^2 = |\xi_{ij}^{\downarrow\downarrow}|^2 = \frac{1}{2}(1 + \boldsymbol{e}_i \cdot \boldsymbol{e}_j) \qquad |\xi_{ij}^{\downarrow\uparrow}|^2 = |\xi_{ij}^{\uparrow\downarrow}|^2 = \frac{1}{2}(1 - \boldsymbol{e}_i \cdot \boldsymbol{e}_j)$$

$$\boldsymbol{P}_{ij} = -\frac{e\boldsymbol{\tau}_{ji}}{2V}\left(\frac{1}{(U - 3J + \Delta)^2} - \frac{1}{(U - 2J + \Delta)^2}\right)\left((t_{ij}^{12})^2 + (t_{ij}^{13})^2 - (t_{ji}^{12})^2 - (t_{ji}^{13})^2\right)\boldsymbol{e}_i \cdot \boldsymbol{e}_j$$

$t_{ij}^{ab} \neq t_{ji}^{ab}$ (no inversion!)

$P_{ij} \sim J/U$ $\Rightarrow$ *no J, no P!*





$$\boxed{\mathcal{H}^S = \sum_{\langle ij\rangle}(-J_{ij}\boldsymbol{e}_i\boldsymbol{e}_j + \boldsymbol{D}_{ij}\boldsymbol{e}_i \times \boldsymbol{e}_j + \boldsymbol{e}_i\overleftrightarrow{\Gamma}_{ij}\boldsymbol{e}_j)}$$

$$\boldsymbol{D}_{0j} = d_{\parallel}\left(\sin\frac{\pi j}{3}, \cos\frac{\pi j}{3}, (-1)^j\delta\right) \qquad j = 1 - 6$$

$$\boldsymbol{D}_{0j} = d_{\perp}(\cos\frac{\pi j}{3}, \sin\frac{\pi j}{3}, 0) \qquad j = 1' - 6'$$

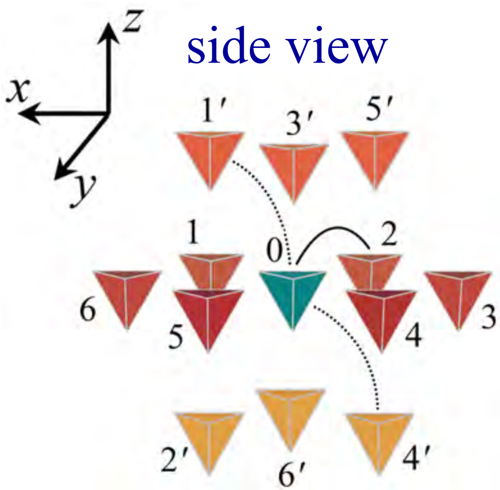
$$\overleftrightarrow{\Gamma}_{0j} = \begin{pmatrix} -\frac{1}{3}\Gamma + \Delta\Gamma\cos\frac{2\pi j}{3} & \pm\Delta\Gamma\sin\frac{2\pi j}{3} & \pm\Delta\Gamma'\sin\frac{2\pi j}{3} \\ \pm\Delta\Gamma\sin\frac{2\pi j}{3} & -\frac{1}{3}\Gamma - \Delta\Gamma\cos\frac{2\pi j}{3} & \Delta\Gamma'\cos\frac{2\pi j}{3} \\ \pm\Delta\Gamma'\sin\frac{2\pi j}{3} & \Delta\Gamma'\cos\frac{2\pi j}{3} & \frac{2}{3}\Gamma \end{pmatrix}$$

$+$: $j = 1 - 6$ $\qquad$ $-$: $j = 1' - 6'$

(meV, except δ)

$J_{\parallel}$	$d_{\parallel}$	δ	$\Gamma_{\parallel}$	$\Delta\Gamma_{\parallel}$	$\Delta\Gamma'_{\parallel}$
0.180	0.073	0.137	−0.007	−0.022	0.003

$J_{\perp}$	$d_{\perp}$	$\Gamma_{\perp}$	$\Delta\Gamma_{\perp}$	$\Delta\Gamma'_{\perp}$
0.217	0.057	−0.022	0.029	0



$$\boxed{\mathcal{H}^S = \sum_{\langle ij \rangle} (-J_{ij}\boldsymbol{e}_i\boldsymbol{e}_j + \boldsymbol{D}_{ij}\boldsymbol{e}_i \times \boldsymbol{e}_j + \boldsymbol{e}_i\overleftrightarrow{\Gamma}_{ij}\boldsymbol{e}_j)}$$

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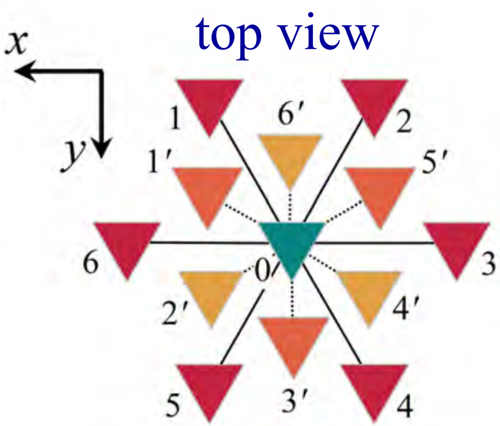


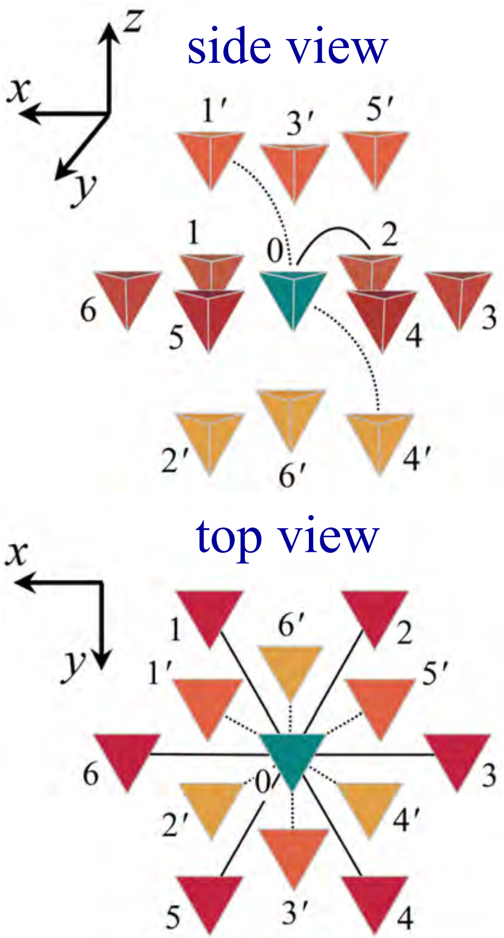
$$\overleftrightarrow{\Gamma}_{0j} = \begin{pmatrix} -\frac{1}{3}\Gamma + \Delta\Gamma\cos\frac{2\pi j}{3} & \pm\Delta\Gamma\sin\frac{2\pi j}{3} & \pm\Delta\Gamma'\sin\frac{2\pi j}{3} \\ \pm\Delta\Gamma\sin\frac{2\pi j}{3} & -\frac{1}{3}\Gamma - \Delta\Gamma\cos\frac{2\pi j}{3} & \Delta\Gamma'\cos\frac{2\pi j}{3} \\ \pm\Delta\Gamma'\sin\frac{2\pi j}{3} & \Delta\Gamma'\cos\frac{2\pi j}{3} & \frac{2}{3}\Gamma \end{pmatrix}$$

$+$: $j = 1-6$ $\quad$ $-$: $j = 1'-6'$

(meV, except δ)

$J_{\parallel}$	$d_{\parallel}$	δ	~~$\Gamma_{\parallel}$~~	~~$\Delta\Gamma_{\parallel}$~~	~~$\Delta\Gamma'_{\parallel}$~~
0.180	0.073	0.137	~~−0.007~~	~~−0.022~~	~~0.003~~

$J_{\perp}$	$d_{\perp}$	~~$\Gamma_{\perp}$~~	~~$\Delta\Gamma_{\perp}$~~	~~$\Delta\Gamma'_{\perp}$~~
0.217	0.057	~~−0.022~~	~~0.029~~	~~0~~



$$\boldsymbol{P} = \sum_{\langle ij \rangle} \epsilon_{ji} (P_{ij} \boldsymbol{e}_i \boldsymbol{e}_j + \boldsymbol{\mathcal{P}}_{ij} \boldsymbol{e}_i \times \boldsymbol{e}_j + \boldsymbol{e}_i \overleftrightarrow{\Pi}_{ij} \boldsymbol{e}_j)$$

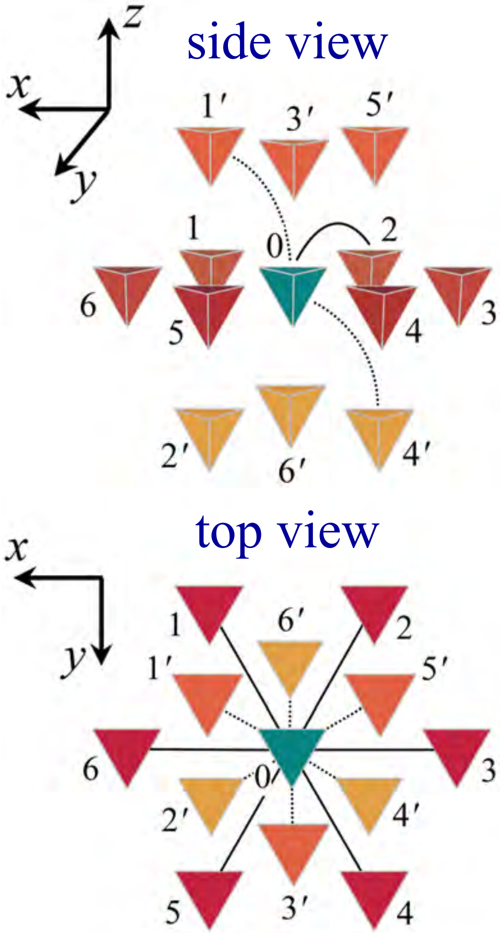
$$P_{0j} = (-1)^j P_\perp$$

$$\boldsymbol{\mathcal{P}}_{0j} = (-1)^j p_\perp (\cos\frac{\pi j}{3}, \sin\frac{\pi j}{3}, 0)$$

$$\overleftrightarrow{\Pi}_{0j} = (-1)^j \begin{pmatrix} -\frac{1}{3}\Pi + \Delta\Pi\cos\frac{2\pi j}{3} & -\Delta\Pi\sin\frac{2\pi j}{3} & -\Delta\Pi'\sin\frac{2\pi j}{3} \\ -\Delta\Pi\sin\frac{2\pi j}{3} & -\frac{1}{3}\Pi - \Delta\Pi\cos\frac{2\pi j}{3} & \Delta\Pi'\cos\frac{2\pi j}{3} \\ -\Delta\Pi'\sin\frac{2\pi j}{3} & \Delta\Pi'\cos\frac{2\pi j}{3} & \frac{2}{3}\Pi \end{pmatrix}$$

(in μC/m²)

$P_\perp$	$p_\perp$	$\Pi_\perp$	$\Delta\Pi_\perp$	$\Delta\Pi'_\perp$
-362	41	1	7	1



$$\boxed{\boldsymbol{P} = \sum_{\langle ij\rangle} \epsilon_{ji}\left(P_{ij}\boldsymbol{e}_i\boldsymbol{e}_j + \boldsymbol{\mathcal{P}}_{ij}\boldsymbol{e}_i \times \boldsymbol{e}_j + \boldsymbol{e}_i \overleftrightarrow{\Pi}_{ij}\boldsymbol{e}_j\right)}$$

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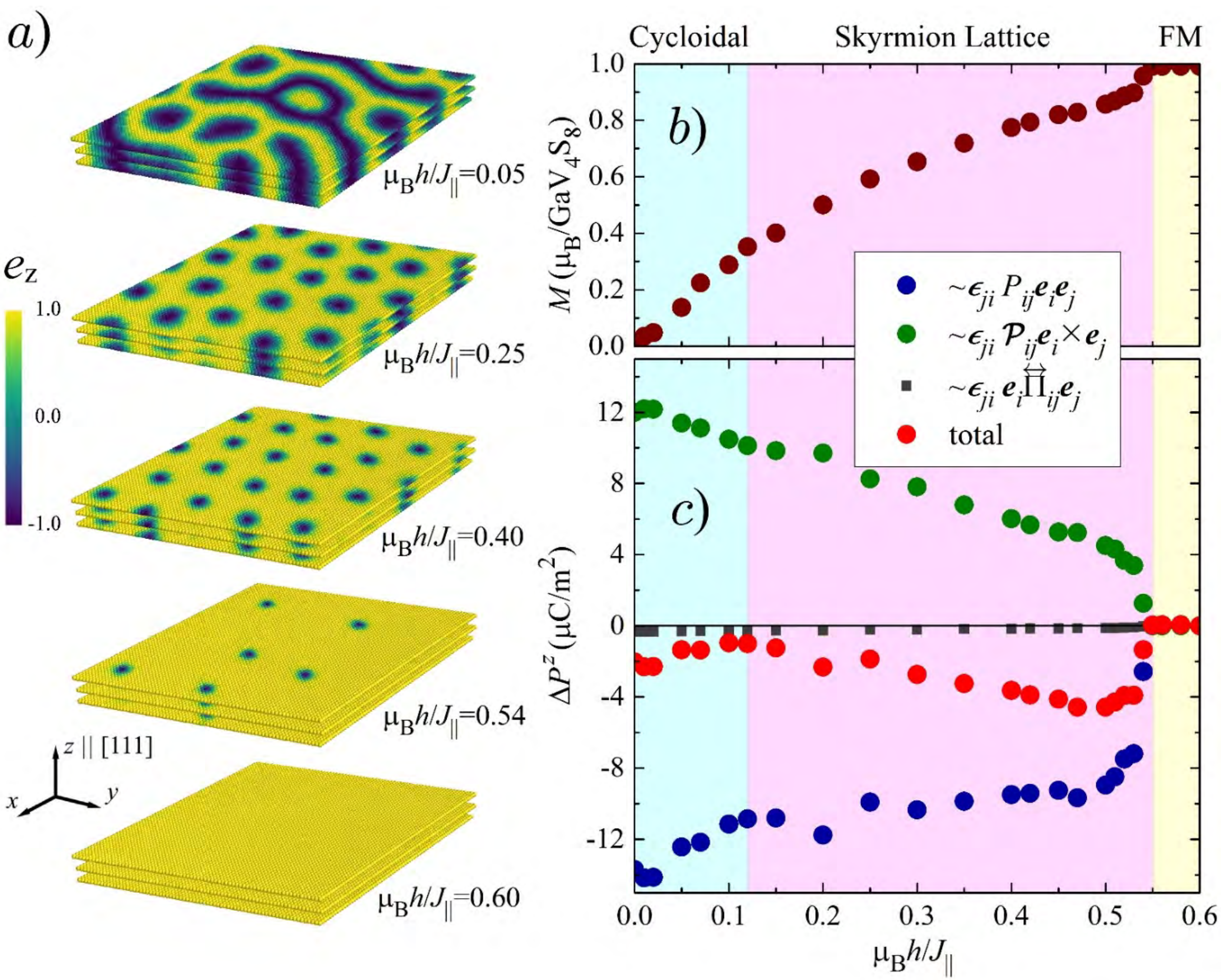
(in $\mu C/m^2$)

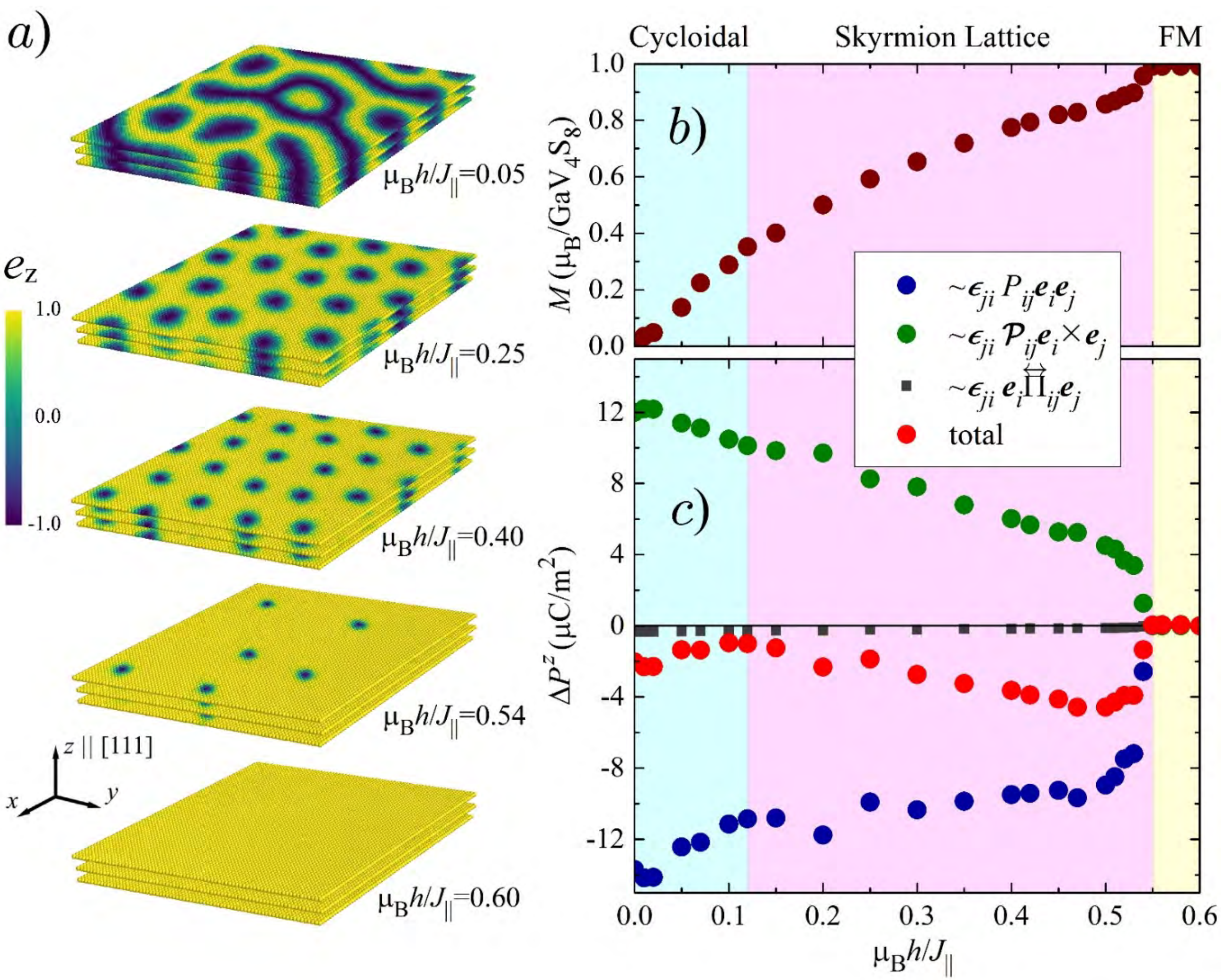
$P_\perp$	$p_\perp$	$\cancel{\Pi_\perp}$	$\cancel{\Delta\Pi_\perp}$	$\cancel{\Delta\Pi'_\perp}$
-362	41	$\cancel{1}$	$\cancel{7}$	$\cancel{1}$

Monte Carlo for the spin model



S. A. Nikolaev and IVS, Phys. Rev. B **99**, 100401(R) (2019)

Monte Carlo for the spin model

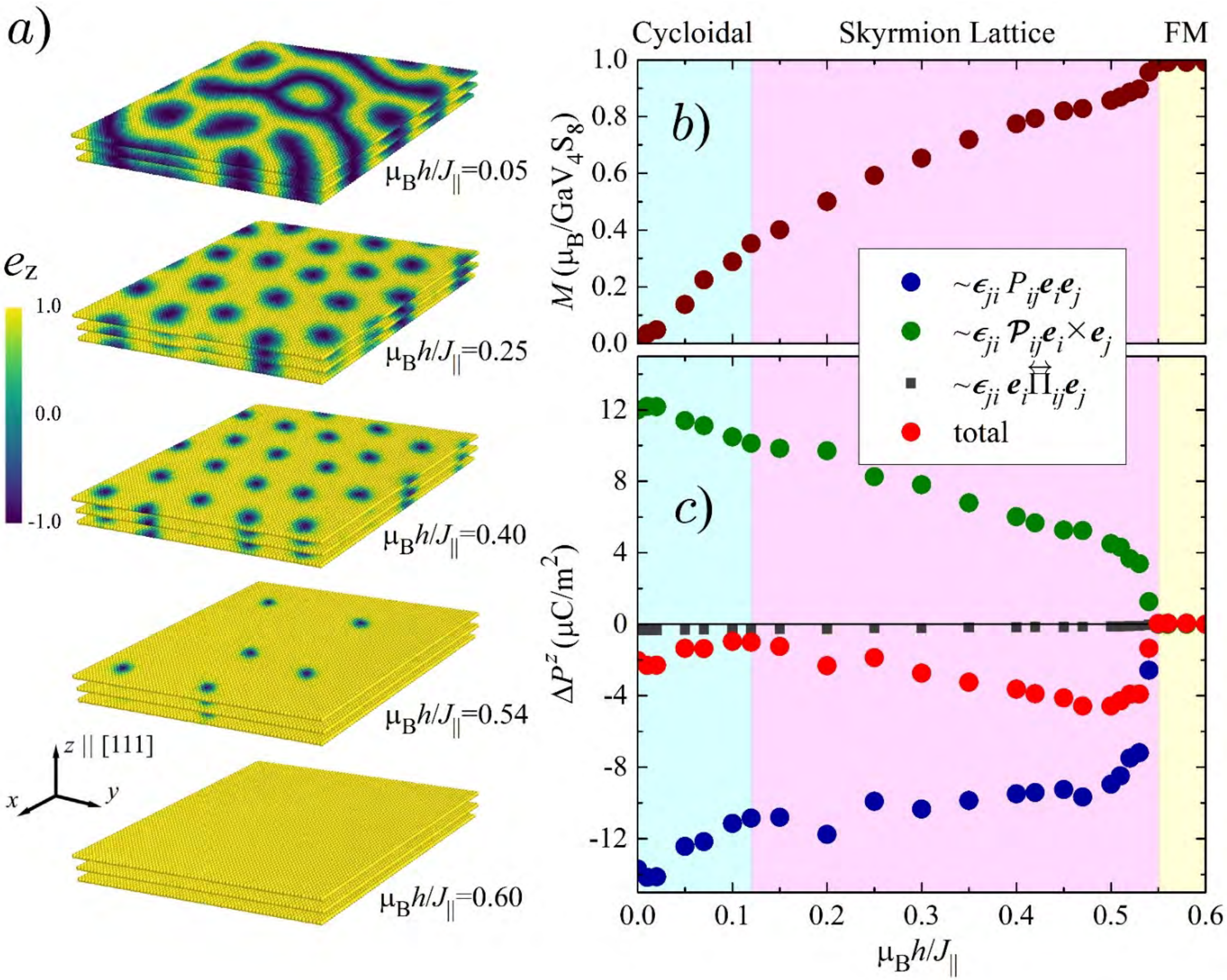


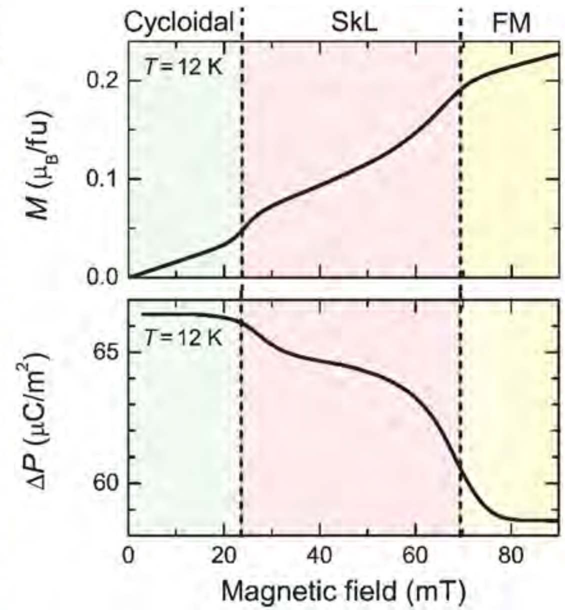
strong competition of isotropic and antisymmetric contributions!

S. A. Nikolaev and IVS, Phys. Rev. B **99**, 100401(R) (2019)

Monte Carlo for the spin model

experiment:
E. Ruff *et al.*, Sci. Adv. **1**, e1500916 (2015)



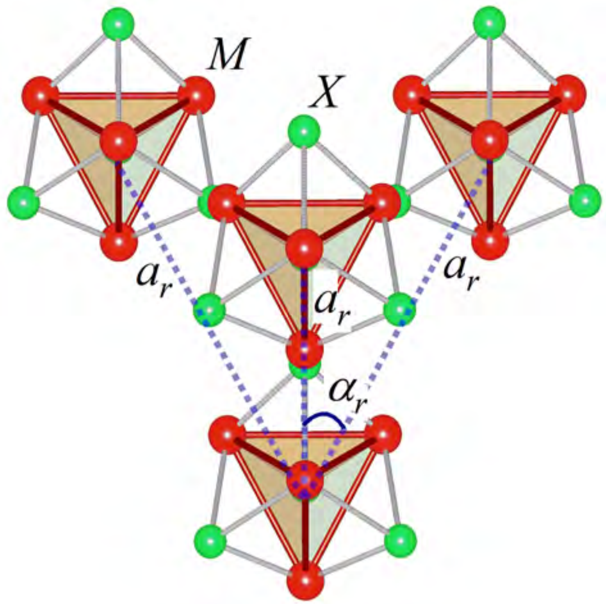


strong competition of isotropic and antisymmetric contributions!

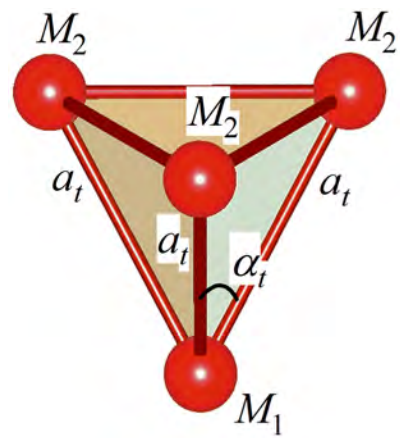
S. A. Nikolaev and IVS, Phys. Rev. B **99**, 100401(R) (2019)

So far so good…

What about other systems?



Other Systems: Structure



S. A. Nikolaev and IVS, to be published

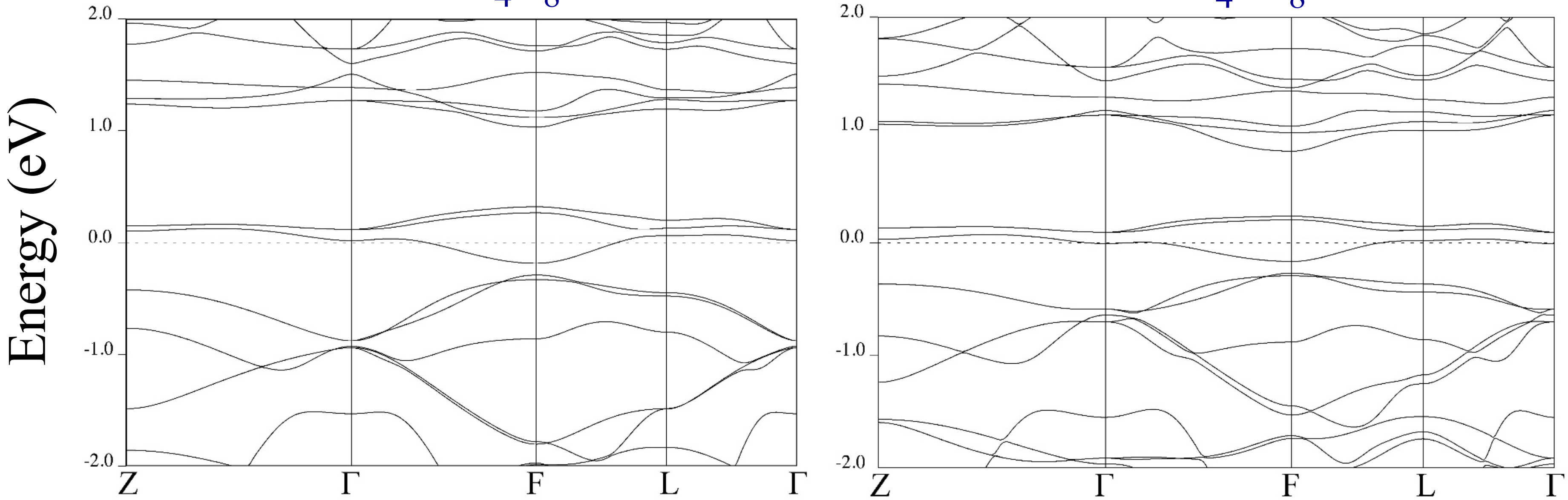
Crystal-structure parameters of GaM_4X_8 in the low-temperature $R3m$ phase (see Fig. 1): rhombohedral lattice parameter a_r (in Å), rhombohedral angle α_r (in °), and the unit cell volume V (in Å^3). The parameters of the single M_4 tetrahedron (the M_1-M_2 distance, a_t, the M_2-M_1-M_2 angle, α_t, and the volume, V_t) are given for comparison in parentheses.

	a_r (a_t)	α_r (α_t)	V (V_t)
GaV_4S_8	6.834 (2.898)	59.66 (58.36)	223.95 (2.76)
GaV_4Se_8	7.184 (3.033)	59.56 (57.72)	259.58 (3.12)
$GaMo_4S_8$	6.851 (2.823)	60.53 (61.51)	230.08 (2.74)

GaV_4Se_8 is the most distorted, has largest volume

Other Systems: Electronic Structure

GaV_4S_8 GaV_4Se_8

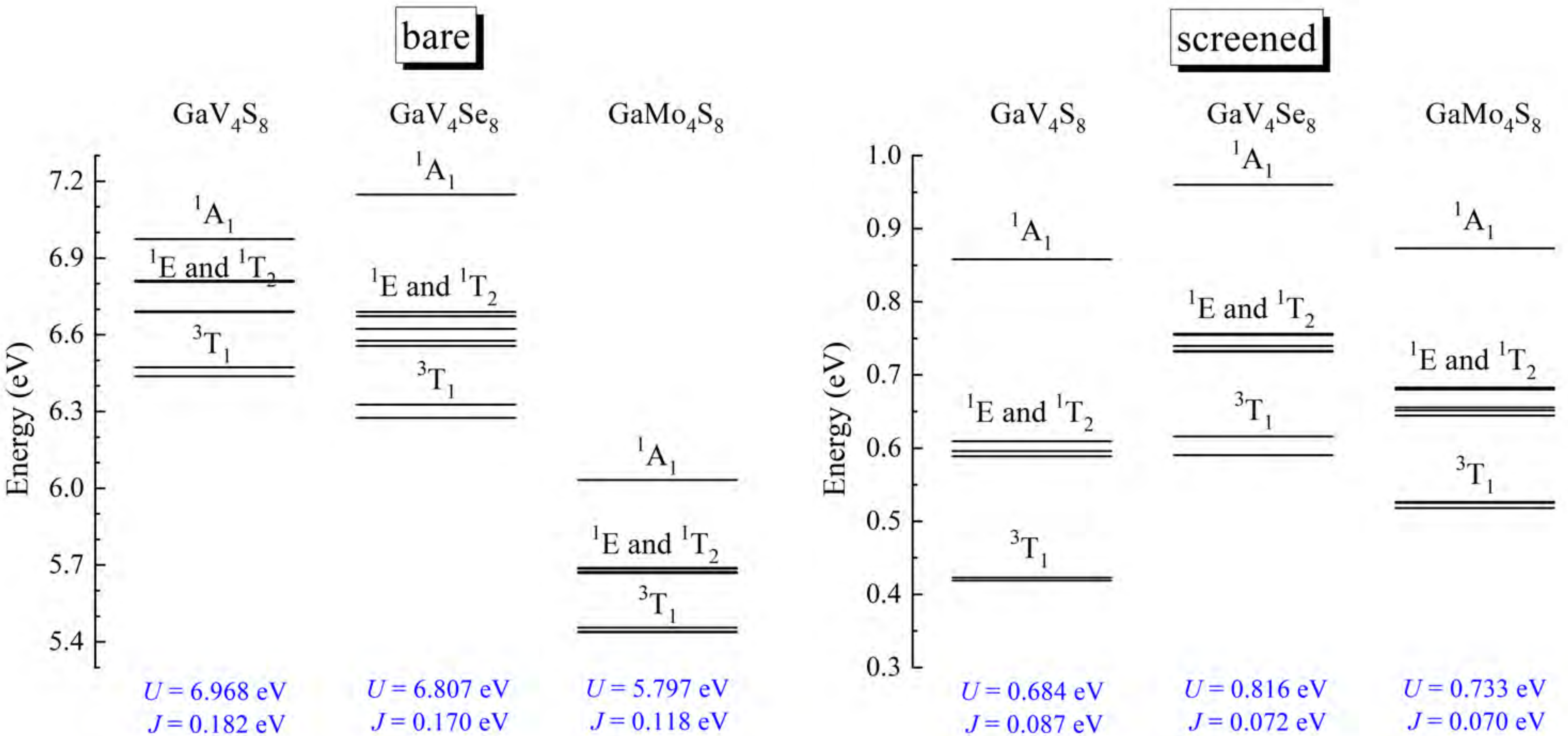


GaV_4Se_8: the bands are narrower (because the volume is larger)

S. A. Nikolaev and IVS, to be published

Other Systems: Coulomb interactions

(excited) two-electron states



controlled by the extension of the Wannier functions

controlled by the electronic structure and relative position of bands

U is less screened in GaV_4Se_8
(because of large volume and weaker hybridization)

Other Systems: Magnetic interactions

$$\boldsymbol{D}_{0j} = d_{\parallel}\left(\sin\frac{\pi j}{3}, \cos\frac{\pi j}{3}, (-1)^j\delta\right)$$

in-plane

		DM		anisotropy		
	$J_{\parallel}$	$d_{\parallel}$	δ	$\Gamma_{\parallel}$	$\Delta\Gamma_{\parallel}$	$\Delta\Gamma'_{\parallel}$
GaV_4S_8	0.180	0.073	0.137	−0.007	−0.022	0.003
GaV_4Se_8	0.036	0.029	0.244	0	−0.008	0.002
$GaMo_4S_8$	0.110	0.179	−0.399	0.004	−0.098	−0.054

out-of-plane

		DM	anisotropy		
	$J_{\perp}$	$d_{\perp}$	$\Gamma_{\perp}$	$\Delta\Gamma_{\perp}$	$\Delta\Gamma'_{\perp}$
GaV_4S_8	0.217	0.057	−0.022	0.029	0
GaV_4Se_8	0.103	0.045	−0.034	0.038	−0.001
$GaMo_4S_8$	0.157	0.136	−0.174	0.203	0.009

Other Systems: Magnetic interactions

$$\boldsymbol{D}_{0j} = d_{\parallel}\left(\sin\frac{\pi j}{3}, \cos\frac{\pi j}{3}, (-1)^j\delta\right)$$

in-plane

		DM		anisotropy		
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$GaMo_4S_8$	0.110	0.179	−0.399	0.004	−0.098	−0.054

main problem is here

out-of-plane

		DM	anisotropy		
	$J_{\perp}$	$d_{\perp}$	$\Gamma_{\perp}$	$\Delta\Gamma_{\perp}$	$\Delta\Gamma'_{\perp}$
GaV_4S_8	0.217	0.057	−0.022	0.029	0
GaV_4Se_8	0.103	0.045	−0.034	0.038	−0.001
$GaMo_4S_8$	0.157	0.136	−0.174	0.203	0.009

problem in GaV_4Se_8: small $J_{\parallel}$, large $J_{\perp}$ and $\Gamma_{\perp}$ destroy skyrmions…

inconsistency with the experiment…

SCIENTIFIC REPORTS

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Equilibrium Skyrmion Lattice Ground State in a Polar Easy-plane Magnet

Received: 20 June 2017
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S. Bordács[1], A. Butykai[1], B. G. Szigeti[1], J. S. White[2], R. Cubitt[3], A. O. Leonov[4,5], S. Widmann[6], D. Ehlers[6], H.-A. Krug von Nidda[6], V. Tsurkan[6,7], A. Loidl[6] & I. Kézsmárki[1,6]

The skyrmion lattice state (SkL), a crystal built of mesoscopic spin vortices, gains its stability via thermal fluctuations in all bulk skyrmion host materials known to date. Therefore, its existence is limited to a narrow temperature region below the paramagnetic state. This stability range can drastically increase in systems with restricted geometries, such as thin films, interfaces and nanowires. Thermal quenching can also promote the SkL as a metastable state over extended temperature ranges. Here, we demonstrate more generally that a proper choice of material parameters alone guarantees the thermodynamic stability of the SkL over the full temperature range below the paramagnetic state down to zero kelvin. We found that GaV_4Se_8, a polar magnet with easy-plane anisotropy, hosts a robust Néel-type SkL even in its ground state. Our supporting theory confirms that polar magnets with weak uniaxial anisotropy are ideal candidates to realize SkLs with wide stability ranges.

SCIENTIFIC REPORTS | 7: 7584 | DOI:10.1038/s41598-017-07996-x

Conclusions

Microscopic understanding of magnetic properties and magnetoelectric couling in GaV_4S_8

- Minimal model in the basis of molecular orbitals
- Superexchange theory for electric polarization
- Importance of stacking misalignment
- Competition of isotropic and antisymmetric contributions

Thank you!