Probing Quantum Magnetism in Spin-Orbit Entangled Materials

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DMR-1608760 & DMR-1905532

Acknowledgments

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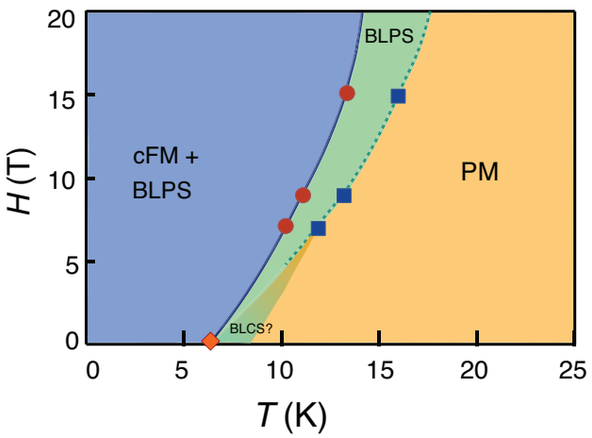
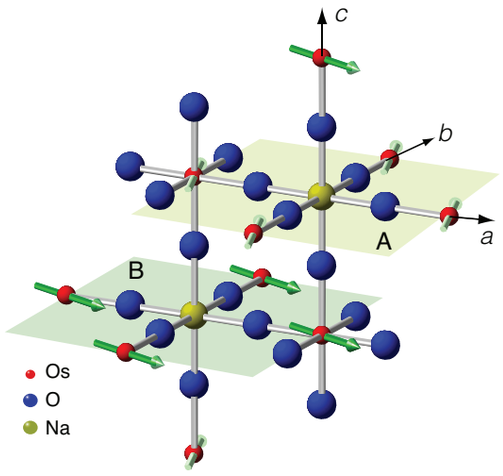
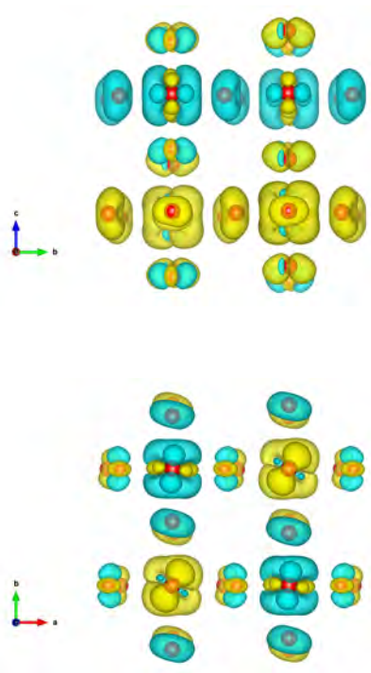
Brown: R. Cong, E. Garcia, L. Lu (magnetism), W. Liu (EFG), M. Song, R. Nanguneri, B. Rubenstein







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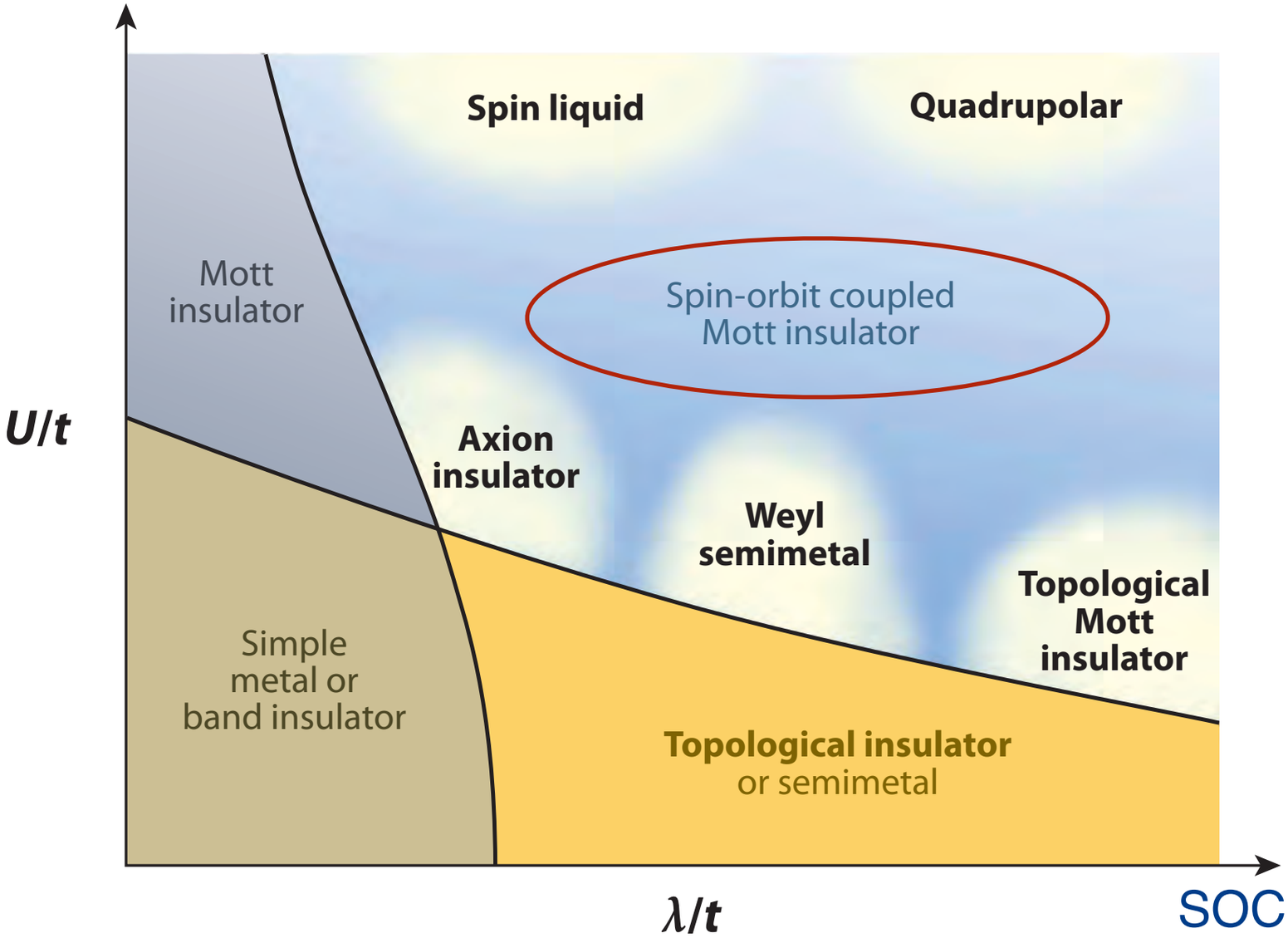
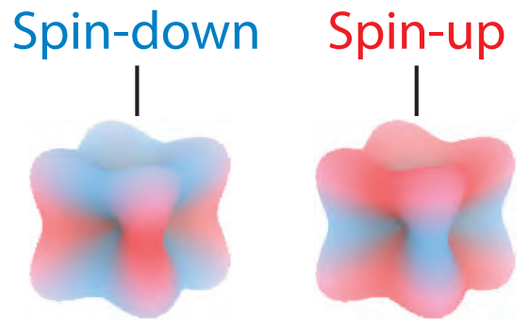
Correlations & Spin-Orbit

What happens when both correlations and SOC are present?



SOC ⇒ spin not a good quantum number

spin & orbital DOF entangled

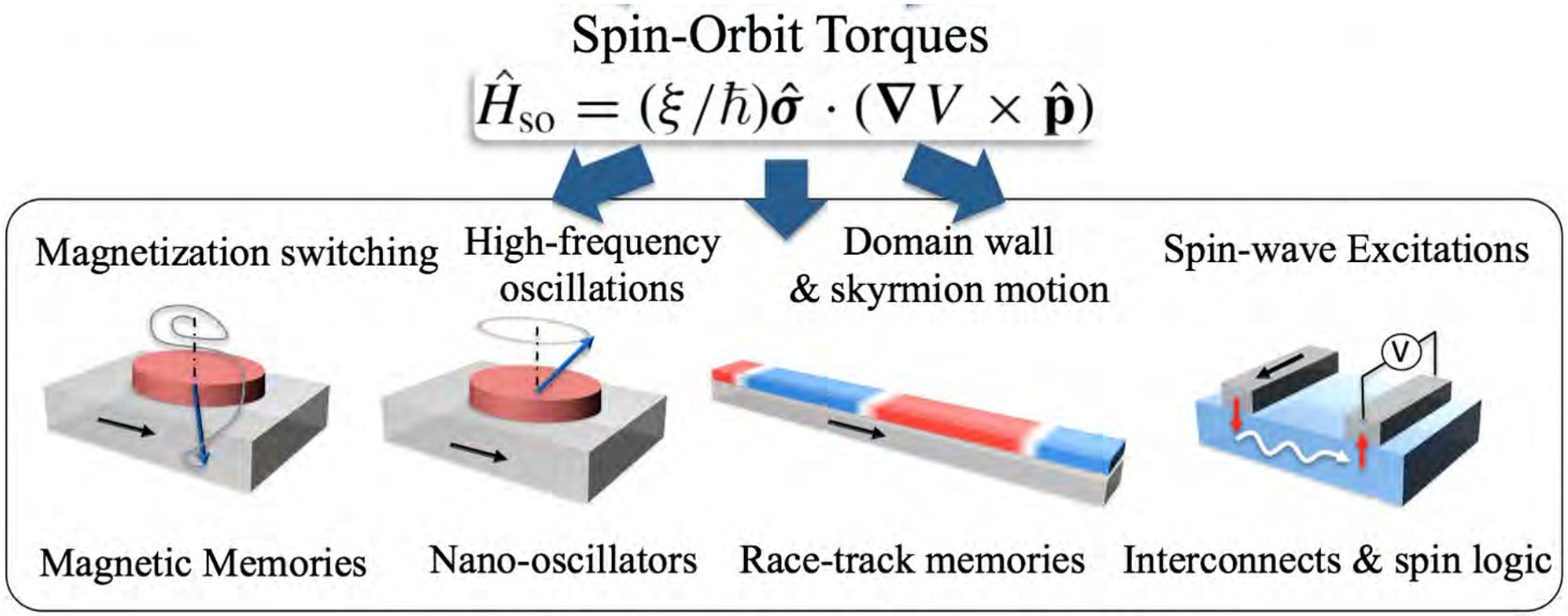


$$\mathcal{H}_{\rm spin} = J \sum_{\langle i,j \rangle} \hat{S}_i \cdot \hat{S}_j \, ?$$

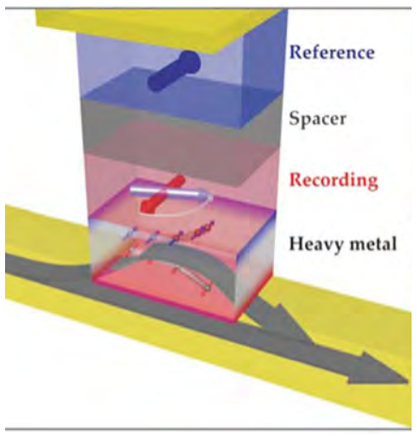
Test ⇒ need local probes

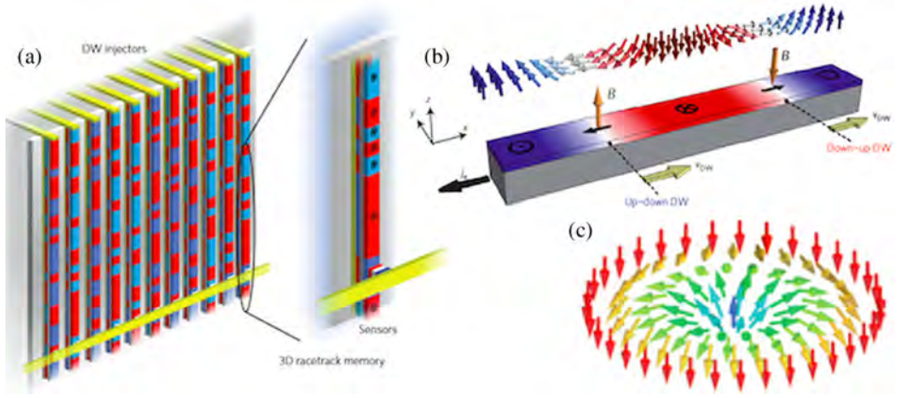
Witczak-Krempa *et al.*, Annu. Rev. Condens. Matter Phys. v5, 57 (2014)

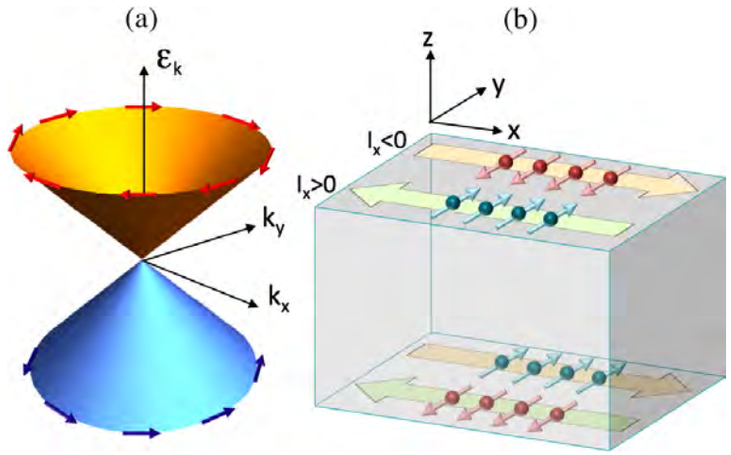
Importance of SOC to Applications



Functionalities & potential applications



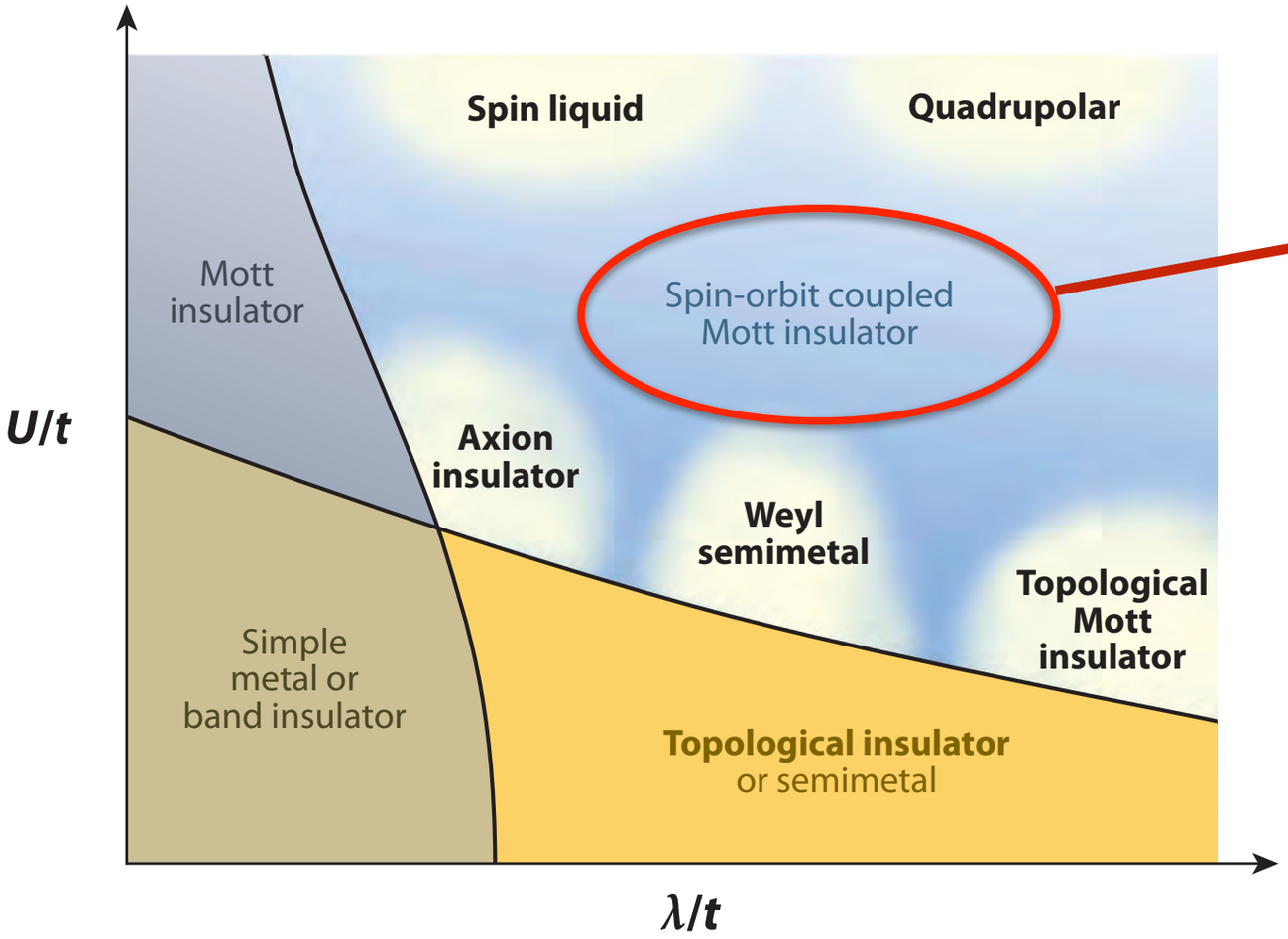




A. Manchon *et al.*: *Current-induced spin-orbit torques in ferromagnetic & antiferromagnetic systems*, RMP v**91**, 035004 (2019).

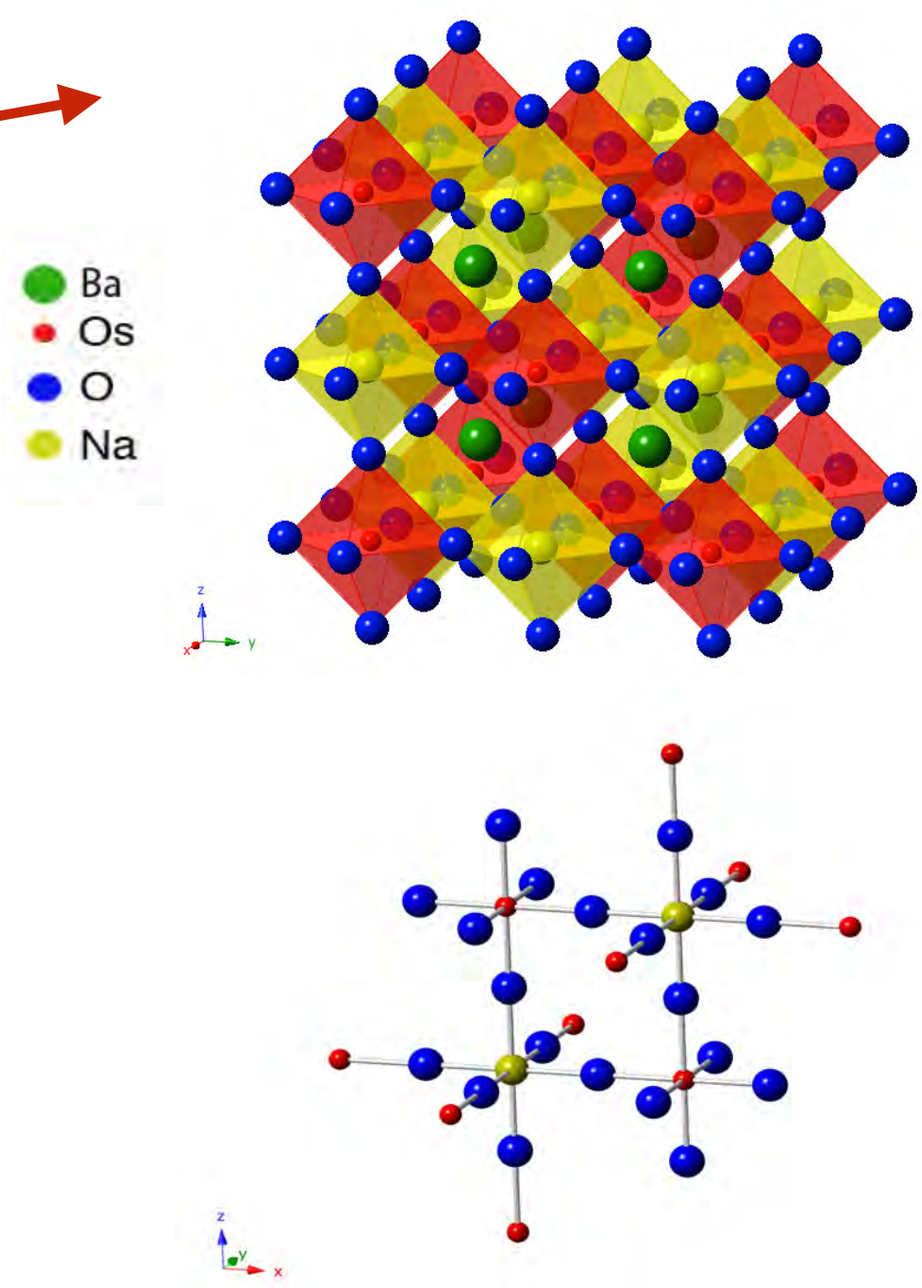
Double Perovskites - Mott insulators with SOC

What happens when both SOC and correlations are present?



Witczak-Krempa *et al.*, Annu. Rev. Condens. Matter Phys. v5, 57 (2014)

Ba_2NaOsO_6



- double perovskite structure
- unpaired $5d^1$ Os electron
- two sub-lattices of *fcc* symmetry
- large magnetic ion separation

Quantum Models of Multipolar Interactions

With strong SOC, spin or orbital is not longer good quantum number.

J = L + S

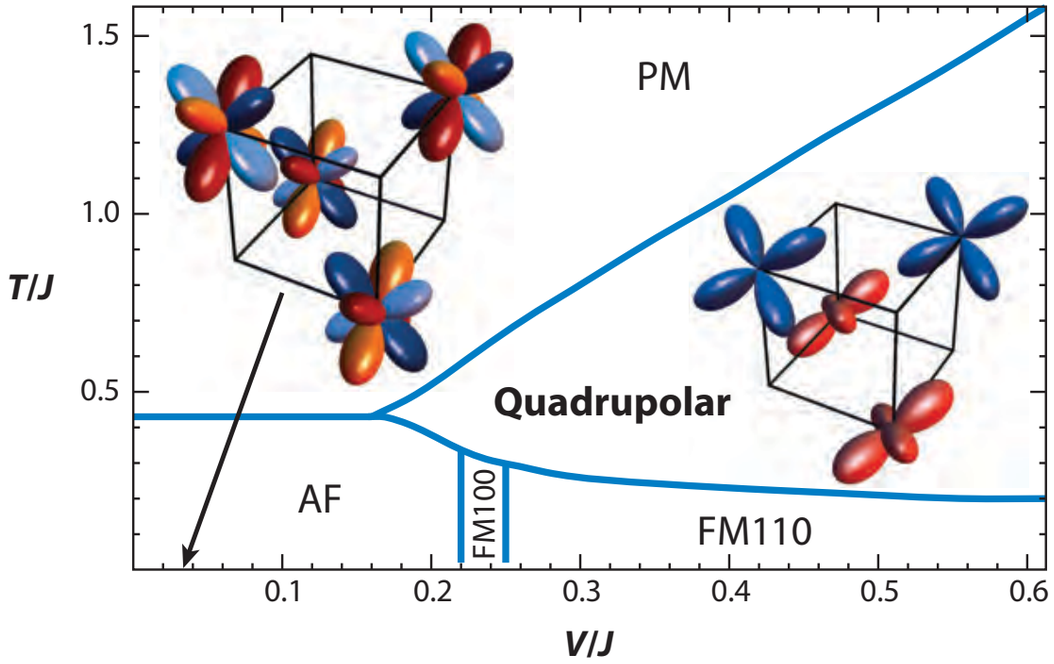
Projection of spin operators into the new |*j, m*$_j$> subspace introduces **multipolar spin coupling**.

$$\mathcal{H}_{AFM} = J \sum_{\alpha} \sum_{i,j} (\mathbf{S}_{i,\alpha} \cdot \mathbf{S}_{j,\alpha} - \frac{1}{4} n_{i,\alpha} n_{j,\alpha})$$

$$\tilde{S}_{i,xy} = \frac{1}{4} j_i^x - \frac{1}{3} j_i^z j_i^x j_i^z$$

$$\tilde{n}_{i,xy} = \frac{3}{4} - \frac{1}{3} (j_i^z)^2$$

Chen et al., Phys. Rev. B **82**, 174440 (2010)



Witczak-Krempa *et al.*, Annu. Rev. Condens. Matter Phys. v5, 57 (2014)

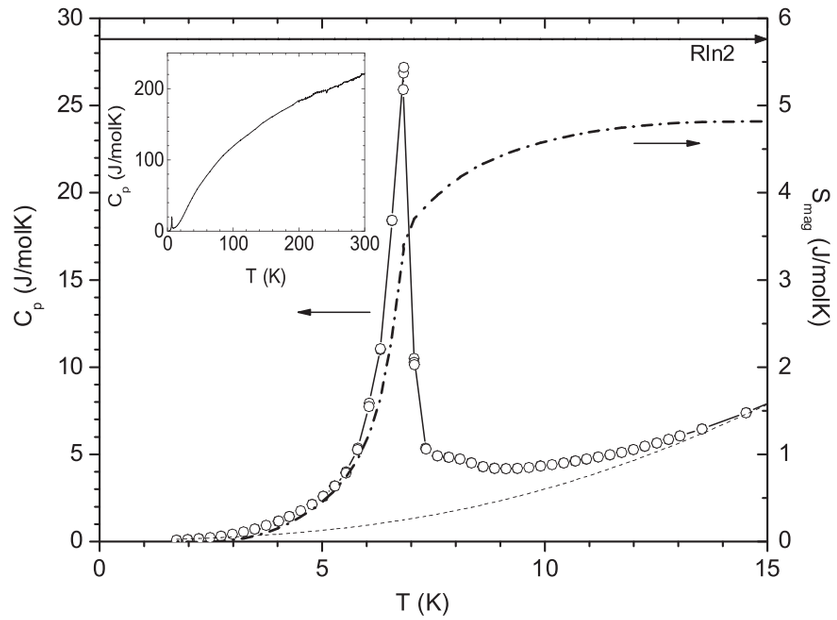
novel directional-dependent exchange coupling of spins

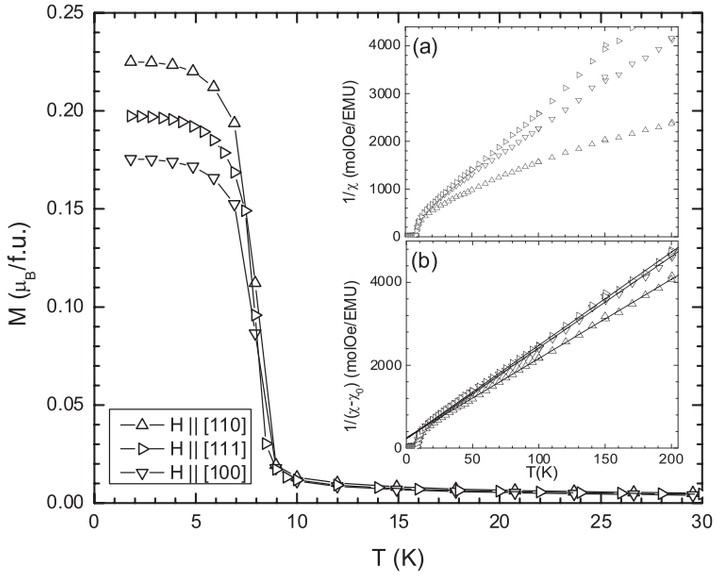
Distinct predictions of **the quantum models**:

- **Local spin expectation values** that differ from the average ones
- **Structural change associated** with quadrupolar ordering (i.e. local cubic symmetry breaking) drives the magnetism (**precedes** LRO)

Use **NMR** to concurrently probe **spin** and **orbital/lattice** degrees of freedom !

Ba_2NaOsO_6 bulk characterization





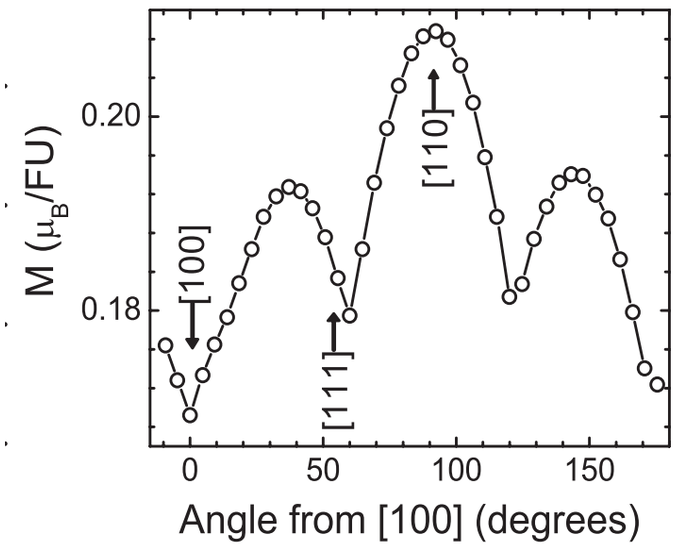


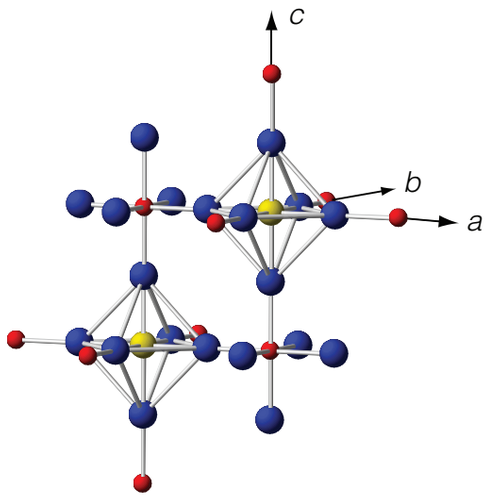
FIG. 3. Magnetization of Ba_2NaOsO_6 along high-symmetry directions as a function of applied field at 1.8 K for a full hysteresis loop. "f.u." refers to one formula unit. The inset shows magnetization as a function of angle in the $(01\bar{1})$ plane at a temperature of 1.8 K and a field of 2 T. A line is drawn between data points to guide the eye.

Erickson et al., PRL **99**, 016404 (2007).

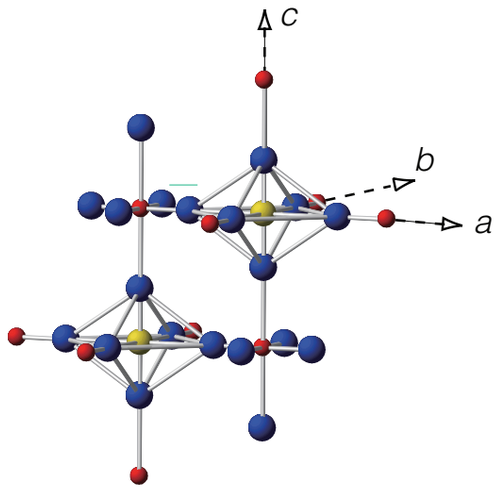
- S_{eff} = 3/2 but magnetic entropy ~ *R*ln2
- [110] FM

Compound	B'	Electron configuration	Θ_{CW} (K)	μ_{eff} (μ_B)	Magnetic transition
Ba_2NaOsO_6	Os^{7+}	$5d^1$	~ -10	~ 0.6	FM $T_c = 6.8$ K

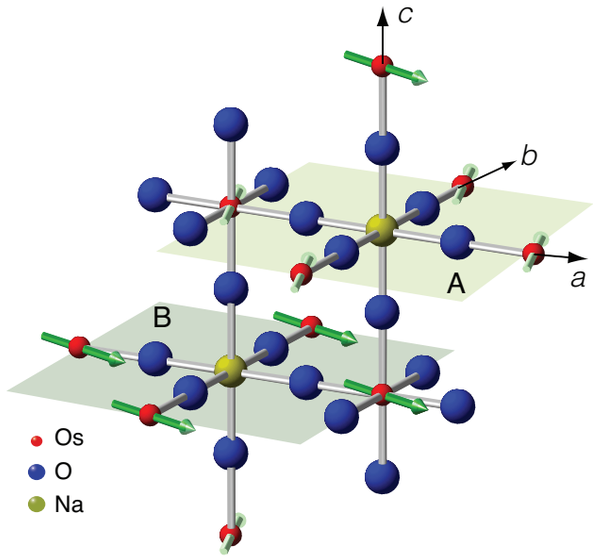
Ba_2NaOsO_6



cubic

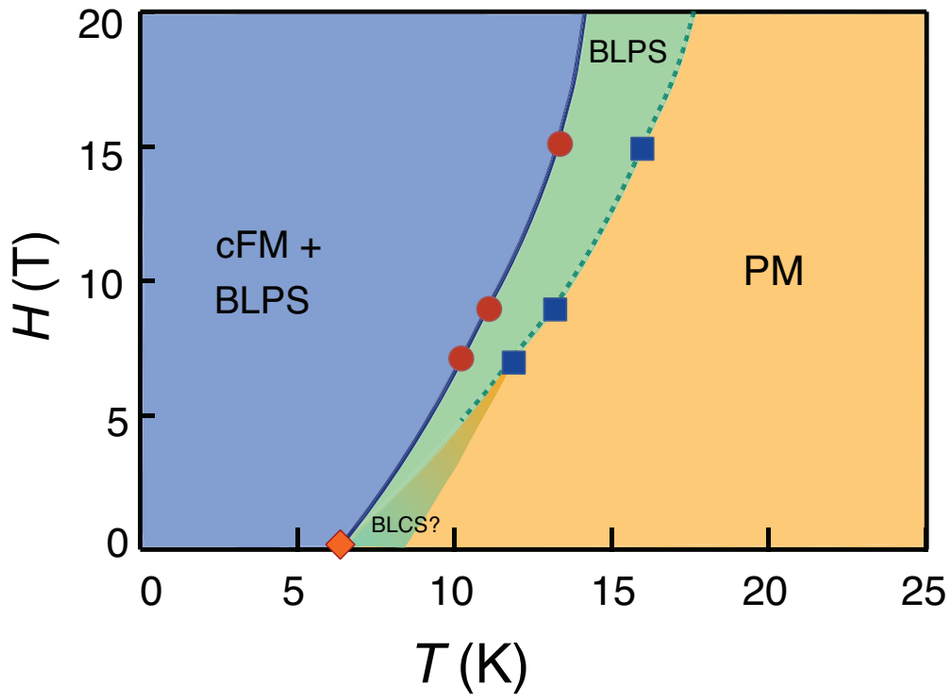


broaken local point symmetry (BLPS)



BLPS + FM

Temperature



NMR

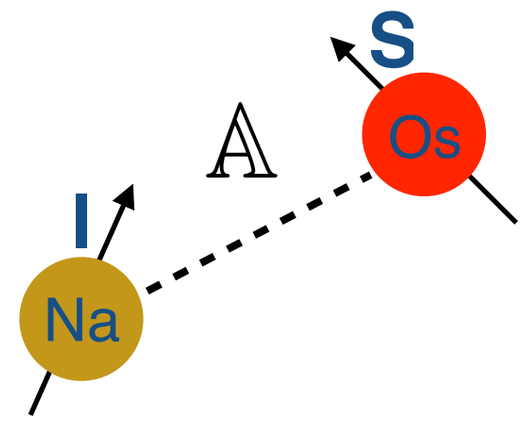
Static NMR Spectrum Measurements - $\omega_n = \gamma_n H_{\rm loc} \Rightarrow$

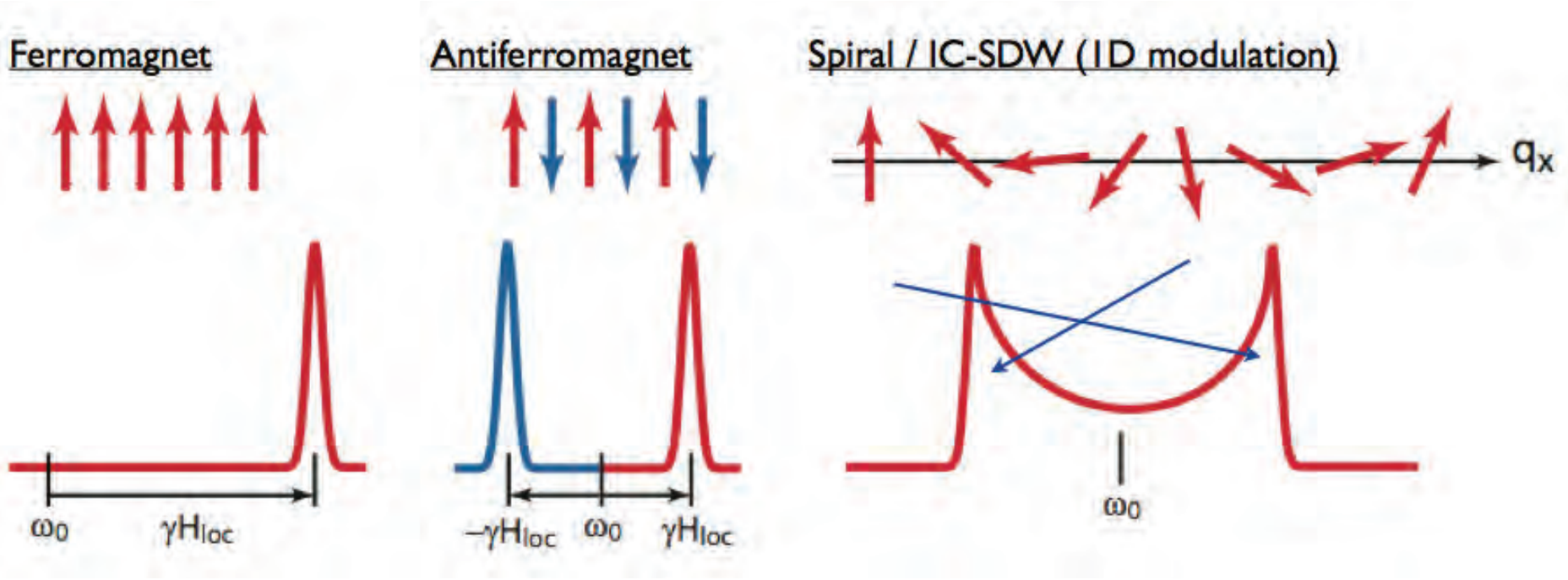
Image of Local Magnetic Field Probability Distribution

Local Magnetic Susceptibility (LDOS)

+ site-selective

$$H_{int}^{\parallel} = \hat{h} \cdot \sum_{\langle i \rangle} \mathbb{A}_i \cdot \boldsymbol{\mu}_i,$$

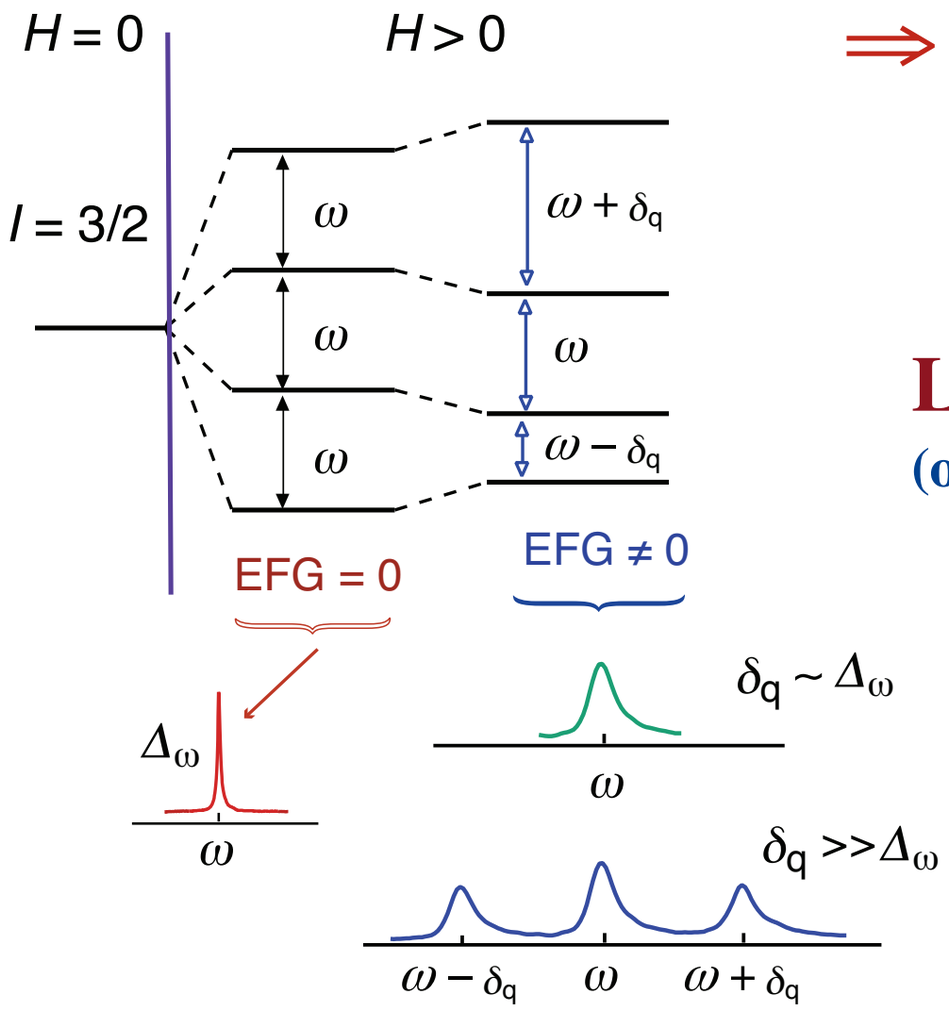




Quadrupolar Interactions

For $I > 1/2$ $\Rightarrow$ nuclei have nuclear **quadrupole moment *Q***

For $I > 1/2$ & non-cubic local symmetry (non-zero EFG) $\Rightarrow$



$\Rightarrow$ $H_0 \neq 0$ NMR line splits into ***2I*** lines

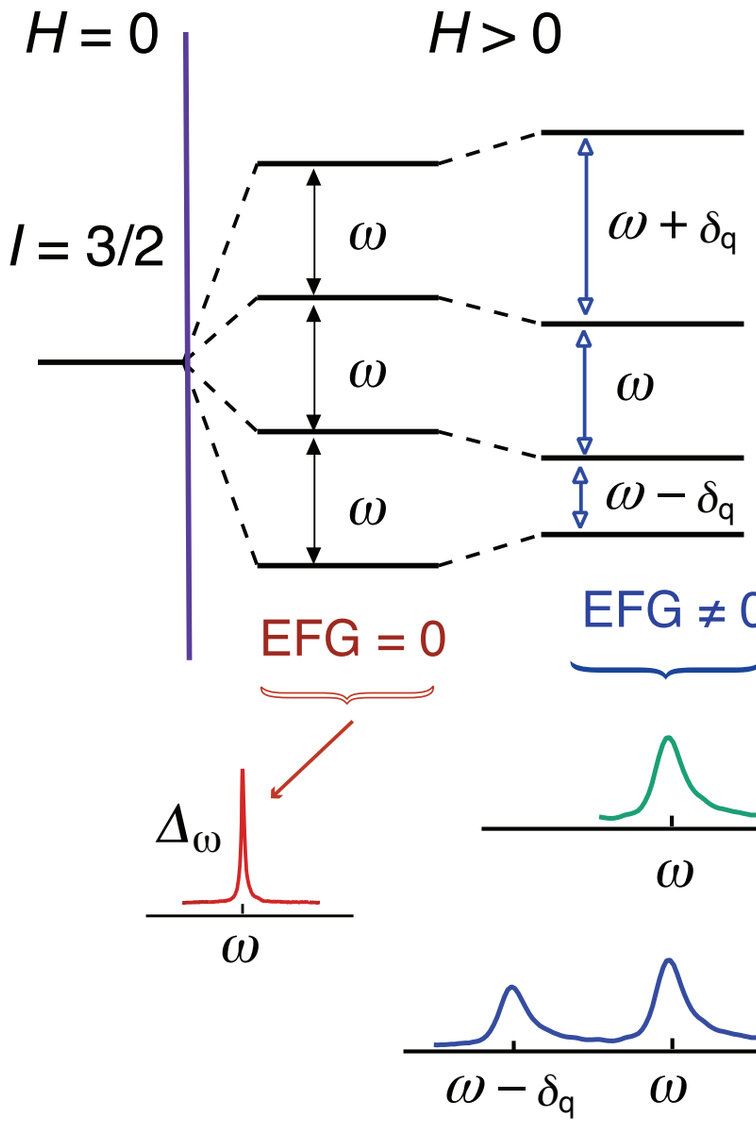
$H_0 = 0$ NQR lines with $\omega_Q \propto \nu_Q$

Local lattice/charge distribution deformations

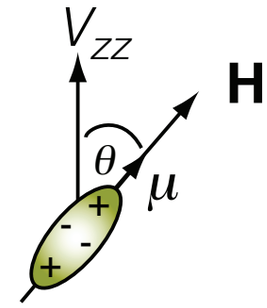
(often with sensibility far superior to x-rays)....

Quadrupolar Interactions

For $I > 1/2$ $\Rightarrow$ nuclei have nuclear **quadrupole moment Q interacts** with the **EFG**



$$\mathcal{H}_{\mathrm{Q}} = \frac{(eQ)(eq)}{4I(2I-1)}[3I_z^2 - I(I+1)]$$



$$\Downarrow$$

$$E = \frac{(eQ)(eq)}{4I(2I-1)}\,[3m^2 - I(I+1)]$$

$$\omega_{\mathrm{m}\to\mathrm{m}-1} = \frac{(eQ)(eq)}{h\,4I(2I-1)}\,[3(2m-1)] = \frac{(eQ)(eq)}{h} \times \Omega$$

$$\Omega \equiv \begin{cases} \frac{1}{2}, & \text{for} \quad |+3/2\rangle \to |+1/2\rangle \\ 0, & \text{for} \quad |+1/2\rangle \to |-1/2\rangle \\ -\frac{1}{2}, & \text{for} \quad |-1/2\rangle \to |-3/2\rangle \end{cases}$$

for $I = 3/2$

$$\delta_{\mathrm{q}} = \frac{1}{2h}(eQ)(eq) \Rightarrow$$

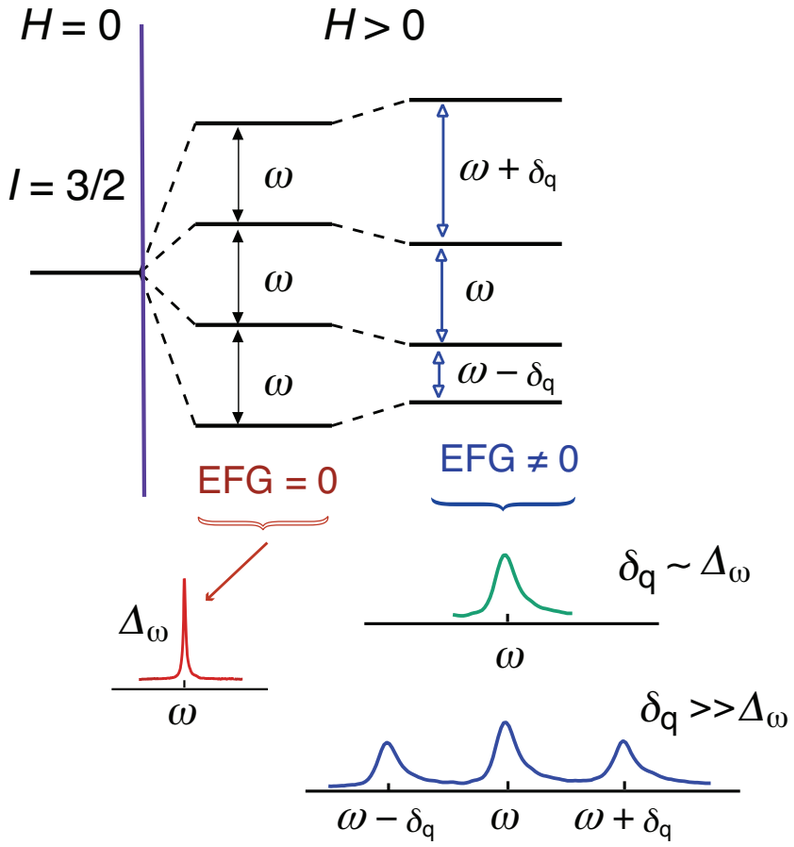
$$\boxed{\delta_{\mathrm{q}} = \frac{1}{2h}(\text{Quadrupole moment}) \times (\text{EFG})}$$

Quadrupolar Interactions

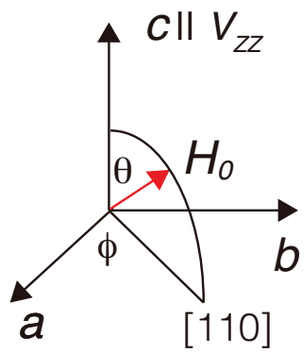
For anisotropic charge distributions, quadrupole Hamiltonian expressed in the coordinate system define by the principal axes of the EFG ⇒

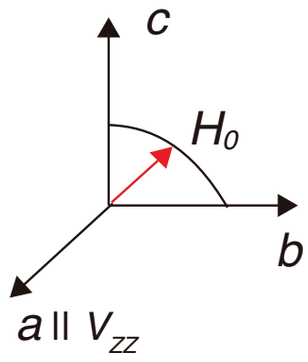
$$\mathcal{H}_{\mathrm{Q}}(x,y) = \frac{eQV_{zz}}{4I(2I-1)}\left[(3\hat{I}_z^2 - \hat{I}^2) + \eta(\hat{I}_x^2 - \hat{I}_y^2)\right],$$

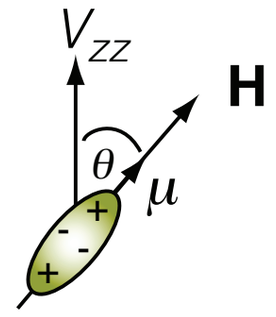
$$\eta \equiv |V_{xx} - V_{yy}| / V_{zz}$$



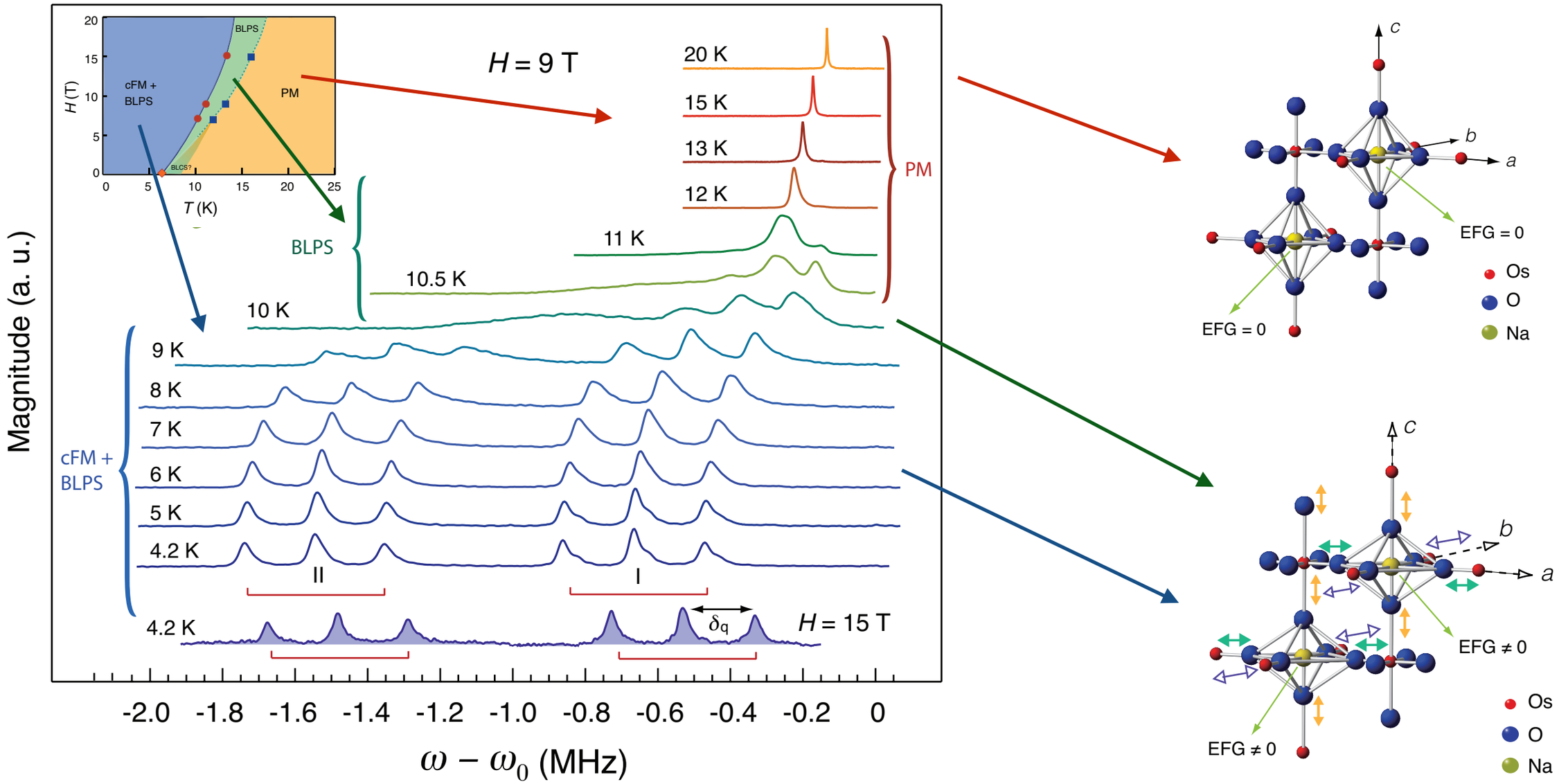
$$\delta_{\mathrm{q}} = \frac{(eQ)(V_{\mathrm{zz}})}{2h}\left(1 + \frac{\eta^2}{3}\right)^{1/2} \quad \textit{for } I = 3/2$$







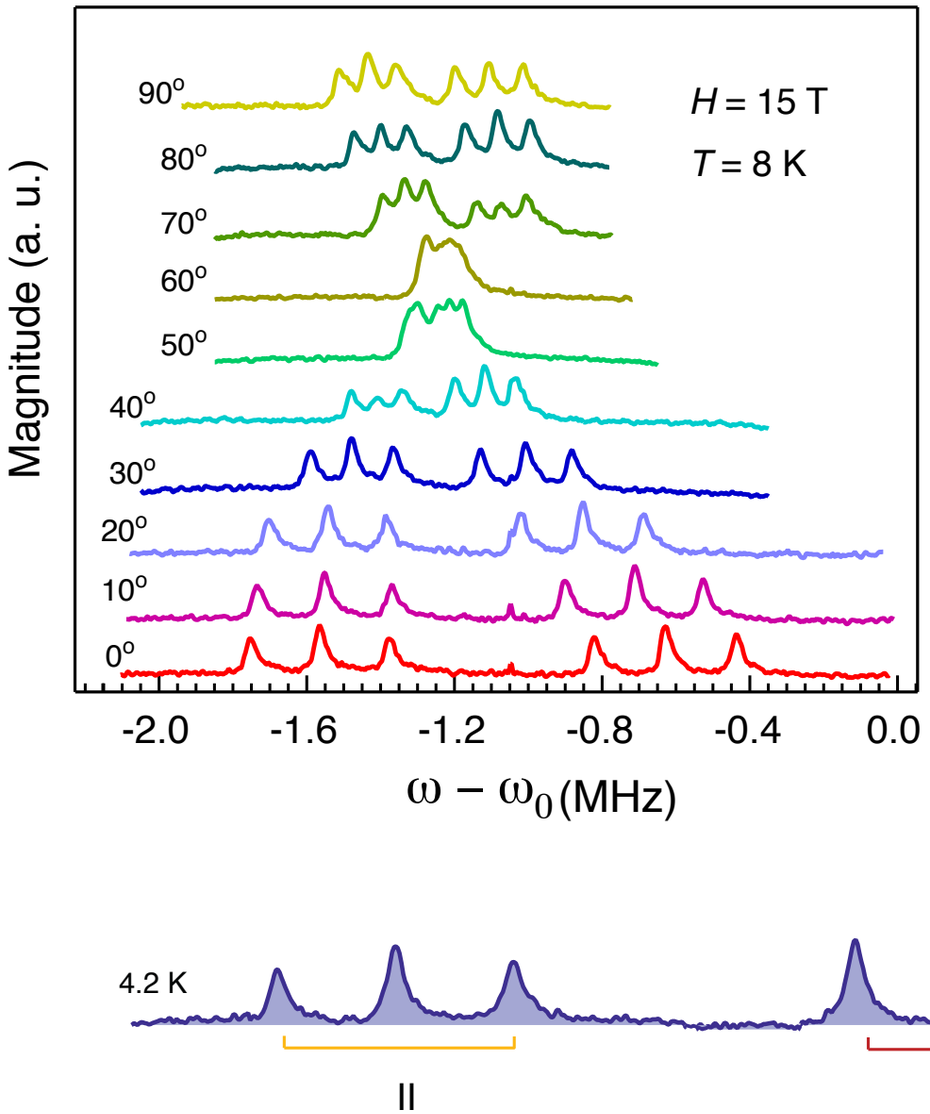
^{23}Na NMR Spectra - Temperature Evolution

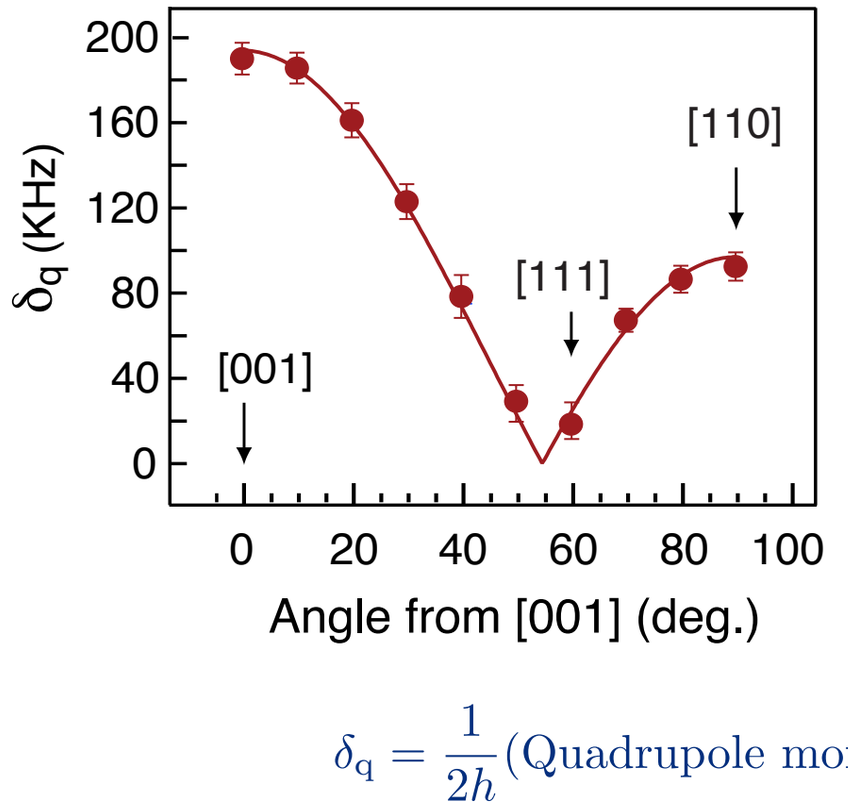


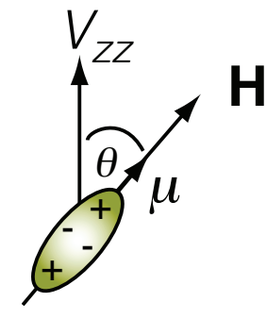
- **2 magnetically** distinct Na sites - I and II
- LRO magnetism - **Commensurate & FM**
- **triplets I and II - local cubic symmetry breaking**

Triplets I & II - Origin?

Examine δ_q as a function of strength (H) and orientation ($\mathbf{H}$)







$$\delta_q = \frac{1}{2h}(\text{Quadrupole moment}) \times (\text{EFG})$$

$$\mathcal{H}_Q = \frac{(eQ)(eq)}{4I(2I-1)}[3I_z^2 - I(I+1)]$$

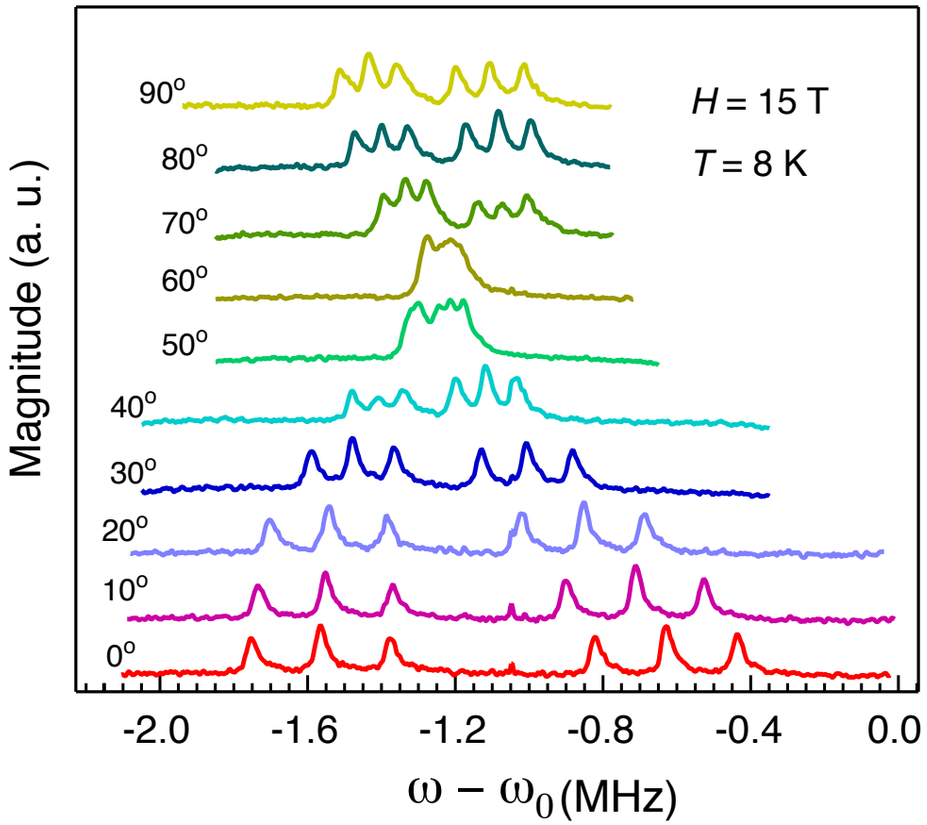
$$\delta_q = \frac{\Delta_q}{2}(3\cos^2\theta - 1)$$

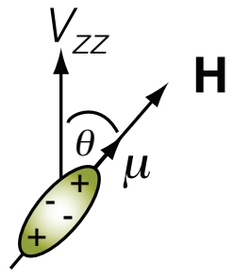
Origin of triplets I & II ⇒ **Quadrupolar interaction** of Na nuclei with an EFG

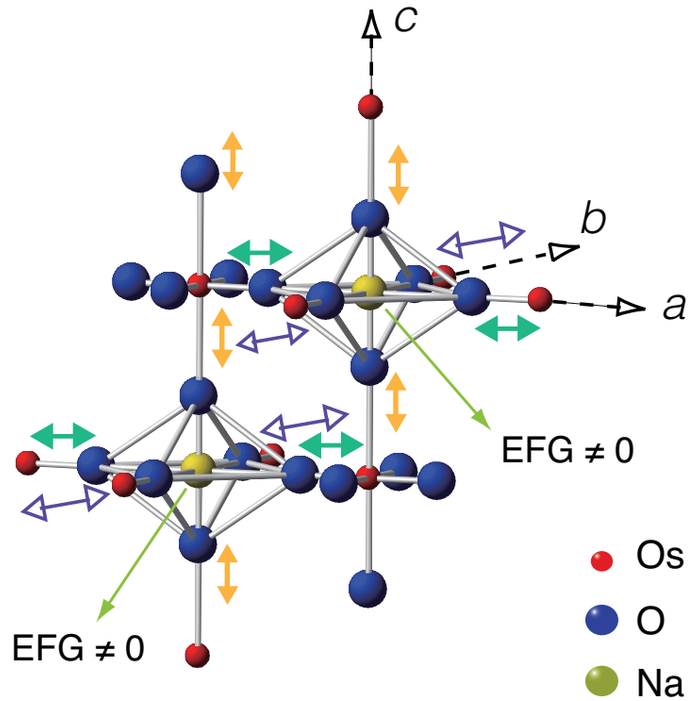
In **cubic symmetry EFG = 0**

⇒ **Broken local cubic symmetry at low *T***

Triplets ⇒ Broken local cubic symmetry







Regardless of θ 3 lines observed per site

⇓

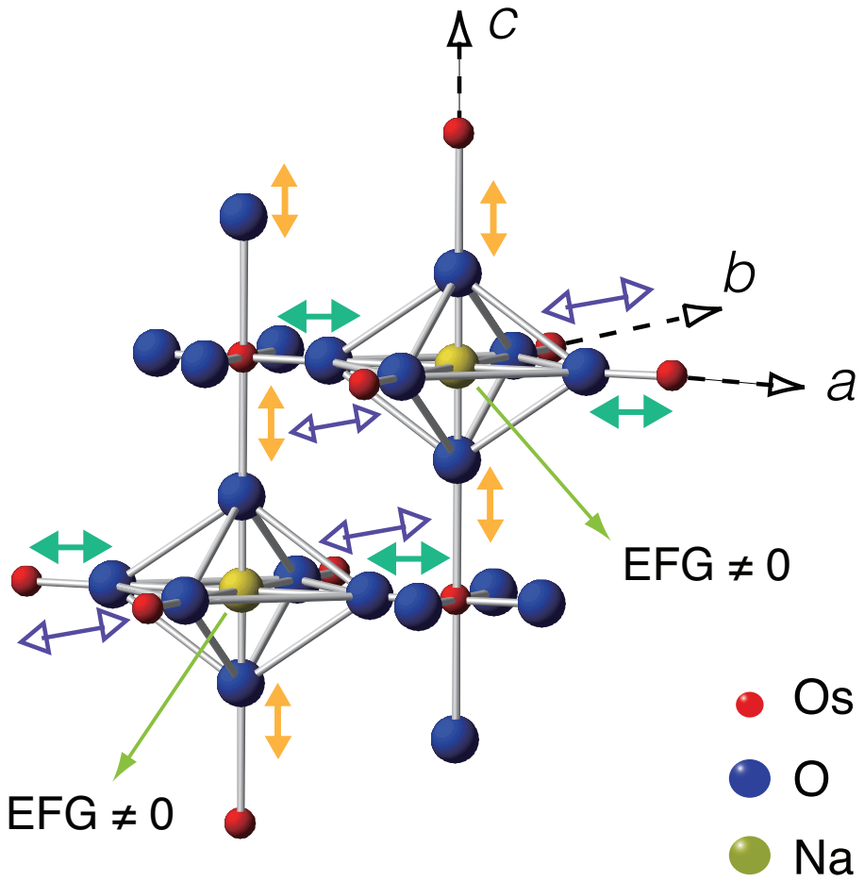
The principal axes of the EFG coincide with those of the crystal.

Broken local cubic symmetry - Nature of distortions

The principal axes of the EFG coincide with those of the crystal.

$$\delta_{\mathrm{q}} = \frac{(eQ)(V_{\mathrm{zz}})}{2h}\left(1+\frac{\eta^2}{3}\right)^{1/2}$$

Examine δ_{q} as a function of orientation of $\mathbf{H}$



Low *T* LRO phase: **Orthorhombic distortions**

Intermediate T (BLPS) phase:

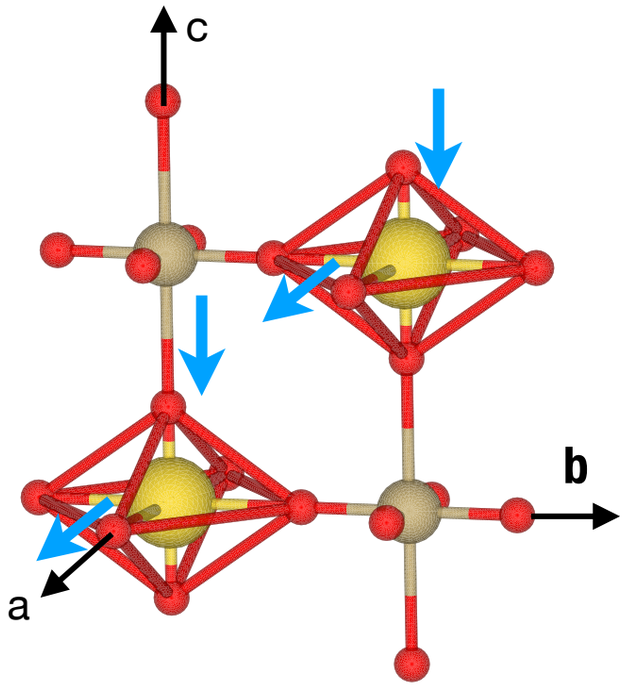
Tetragonal distortions possible

Broken local cubic symmetry - Nature of distortions

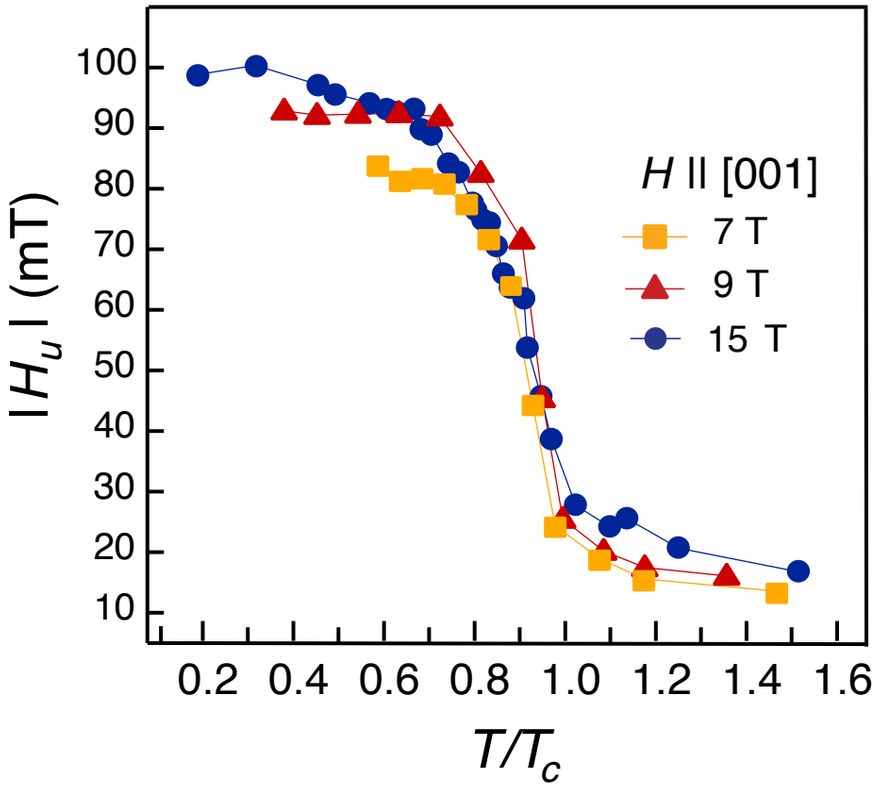
1. Point Charge Calculations (W. Liu *et al.* PRB **97**, 224103 (2018))
2. DFT+U - Rong Cong (arXiv:1908.09014)

- DFT+U calculation of the electronic properties of Ba_2NaOsO_6, a magnetic Mott insulator with strong spin orbit coupling (SOC), using electronic and magnetic results from NMR experiment.

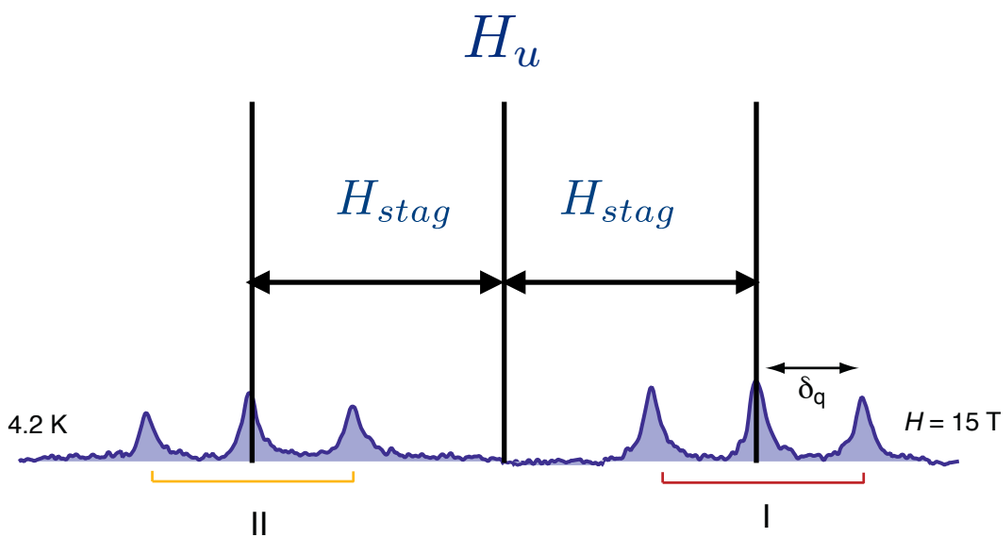
- The breaking local point symmetry (BLPS) phase is an orthorhombic Jahn-Teller distortion in the presence of strong SOC (*i.e.,* **a Q2 distortion mode of the Na-O octahedra**). => **This distortion is insensitive to the type of underlying magnetic order** and lifts the *J*=3/2 quartet to two Kramer doublets before the onset of cFM order.

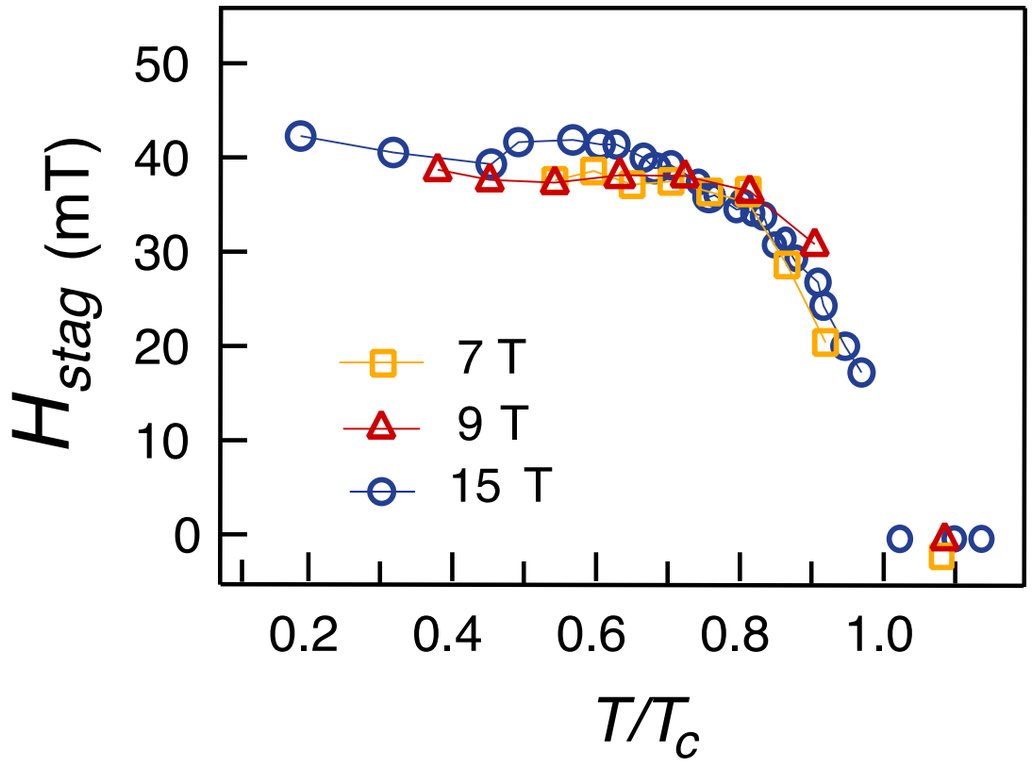


LRO Magnetism ?



$$H_u = \frac{1}{2}\left(\langle H_I \rangle + \langle H_{II} \rangle\right)$$

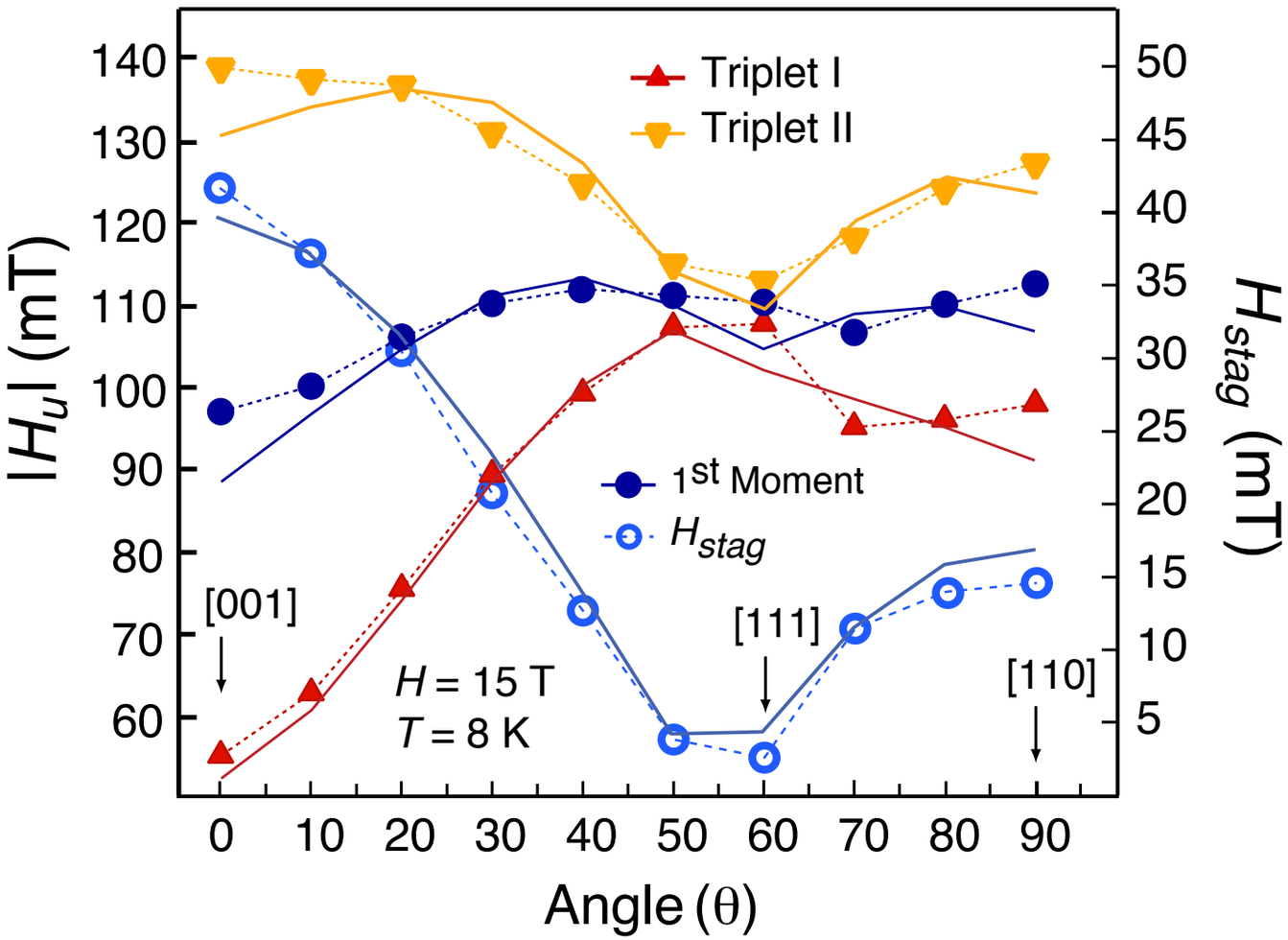




$$H_{stag} = \frac{1}{2}\left(\langle H_I \rangle - \langle H_{II} \rangle\right)$$

- uniform field increase with H_0, while staggered field stays constant
- uniform and staggered fields are of the same order: **non-uniform spin order**

Angular Dependence of Internal Fields

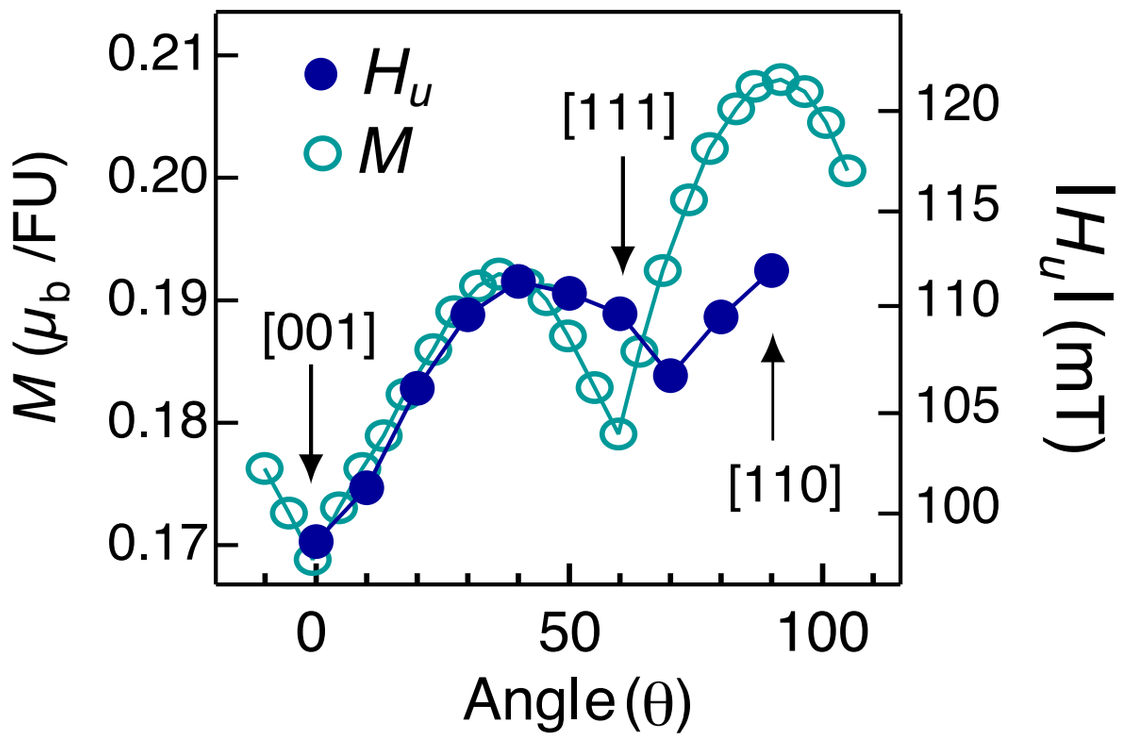


$$H_u = \frac{1}{2}\left(\langle H_I \rangle + \langle H_{II} \rangle\right)$$

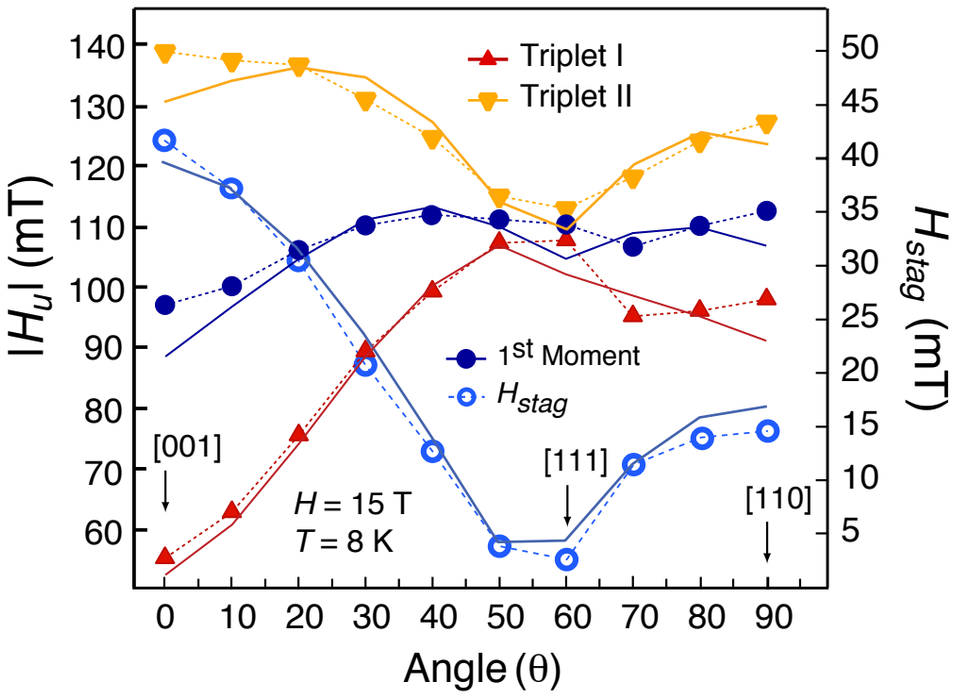
$$H_{stag} = \frac{1}{2}\left(\langle H_I \rangle - \langle H_{II} \rangle\right)$$

Local spin values ≠ average spin values

Presence of significant staggered fields



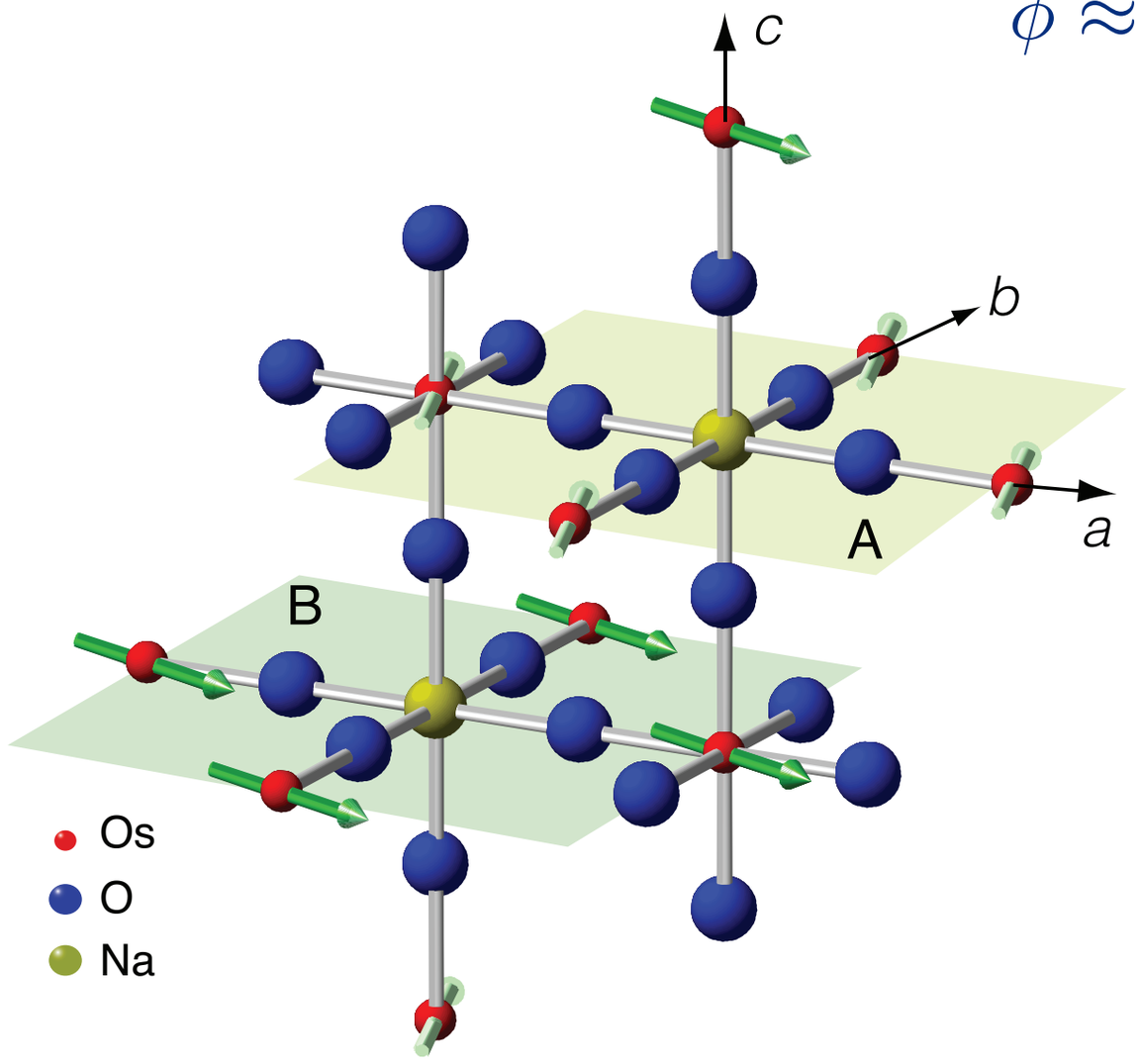
Exotic Canted FM



$$H_{int}^{\parallel} = \hat{h} \cdot \sum_{\langle i \rangle} \mathbb{A}_i \cdot \boldsymbol{\mu}_i,$$

$$\mu_i \approx 0.6\mu_B$$

$$\phi \approx 65^\circ$$



Exotic Canted FM - Multipolar exchange

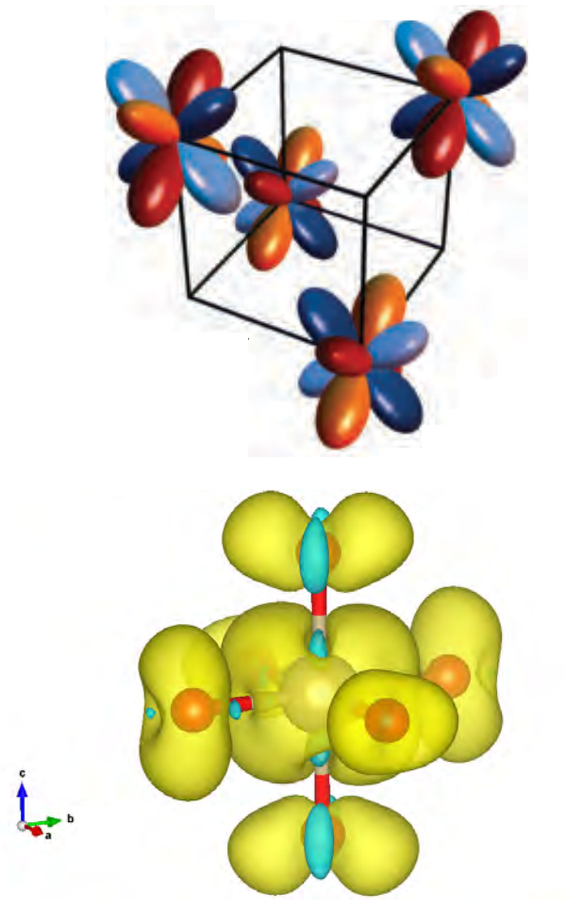
$$H_{int}^{\parallel} = \hat{h} \cdot \sum_{\langle i \rangle} \mathbb{A}_i \cdot \boldsymbol{\mu}_i,$$

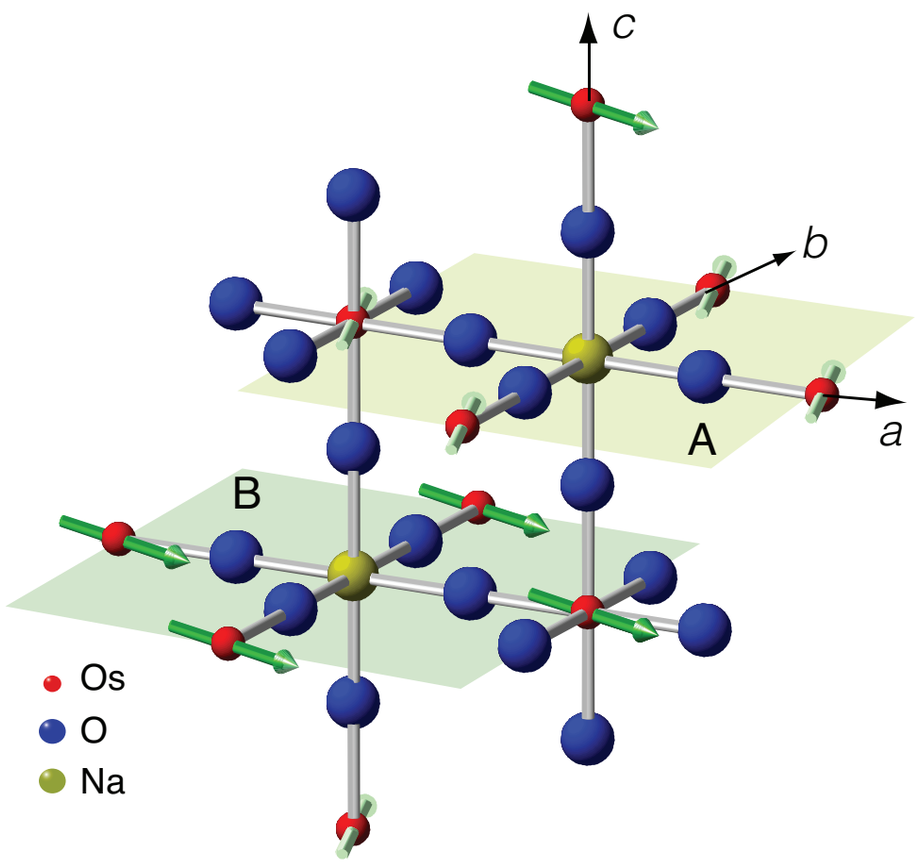
A_{LRO} Symmetry lower than tetragonal =>

Highly anisotropic complex spin exchange path

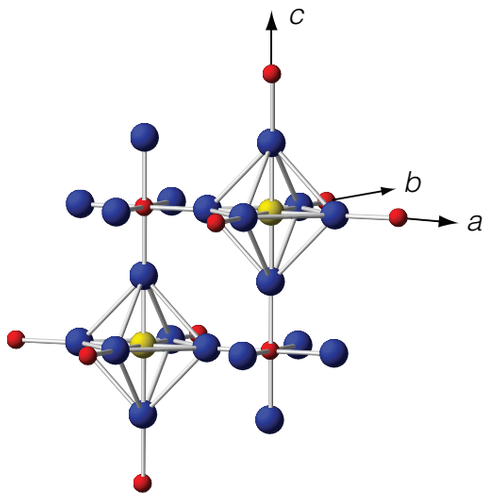
$$\mathbb{A}_{\mathrm{LRO}} \approx \begin{bmatrix} 0.45 & -0.13 & -0.14 \\ 0.13 & 0.45 & 0.16 \\ -0.14 & 0.16 & 0.48 \end{bmatrix}$$

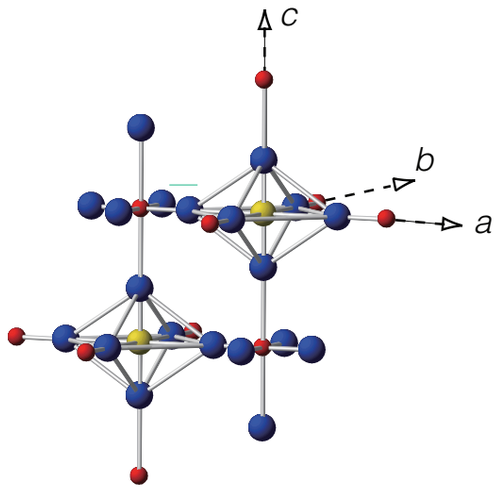
$$\mathbb{A}_{\mathrm{PM}} \approx \begin{bmatrix} 0.45 & 0 & 0 \\ 0 & 0.45 & 0 \\ 0 & 0 & 0.48 \end{bmatrix}$$



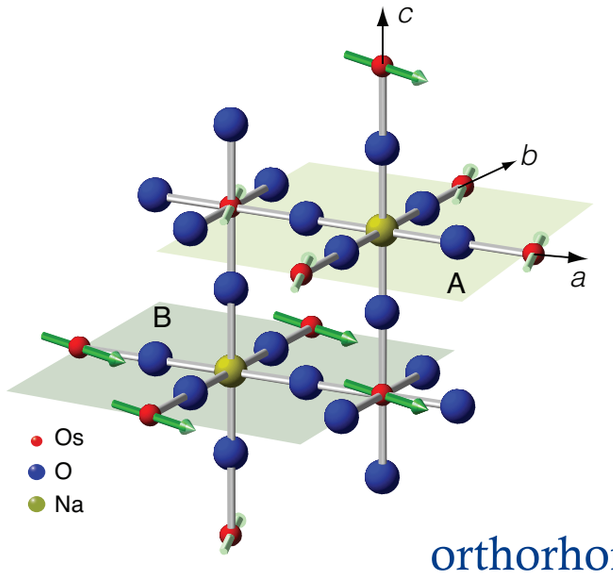


Ba_2NaOsO_6





tetragonal



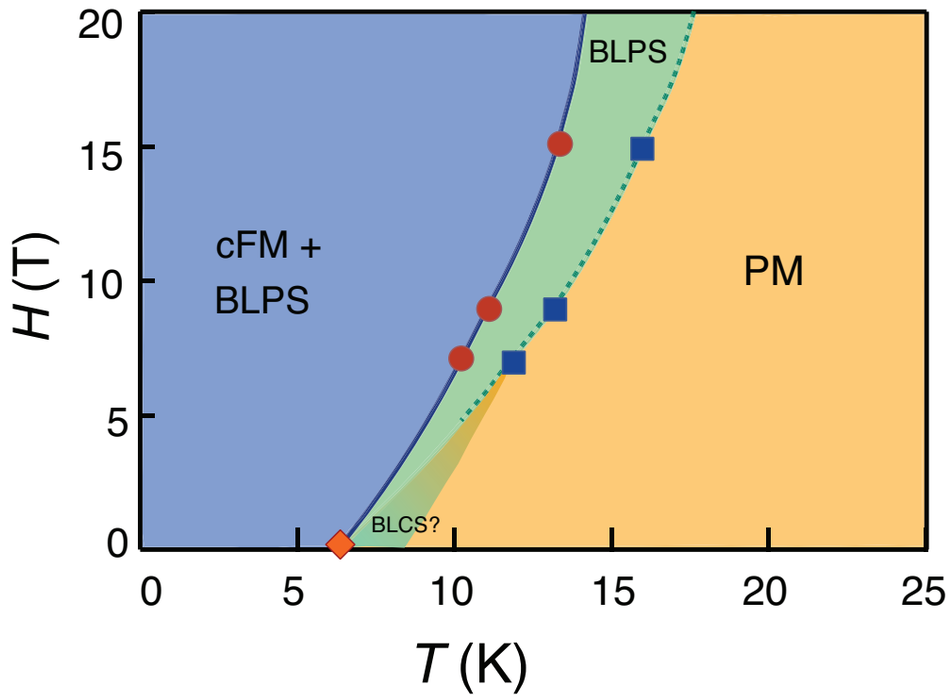
orthorhombic

cubic

broaken local point symmetry (BLPS)

BLPS + FM

Temperature



Conclusions

Low *T* LRO phase:

- **Broken local cubic symmetry (BLPS) precedes FM**
- **Exotic canted FM (with local orthorhombic distortions)**