First principles calculations of the electric field gradient (EFG) tensors of Ba_2NaOsO_6, a Mott insulator with strong spin orbit coupling

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Abstract

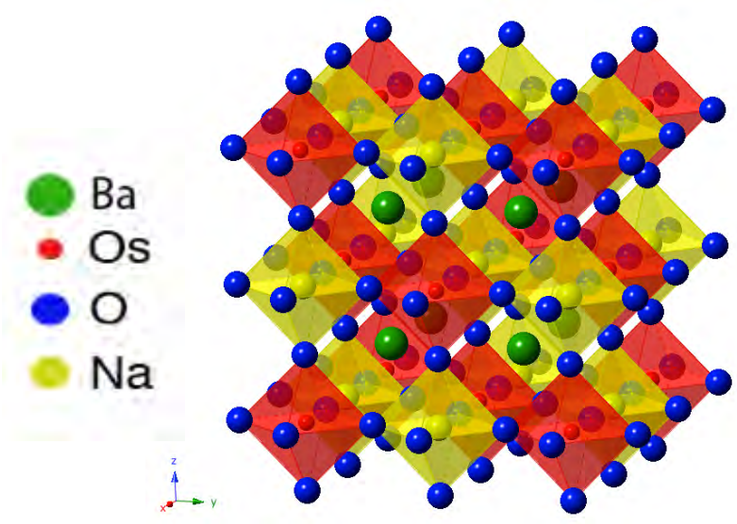
- We present a DFT+U calculation of the electronic and magnetic properties of Ba_2NaOsO_6, a magnetic Mott insulator with strong spin orbit coupling (SOC), **using electronic and magnetic results from NMR experiment**.

- We found that the breaking local point symmetry (BLPS) phase corresponds to an orthorhombic static distortion of Na-O octahedral.

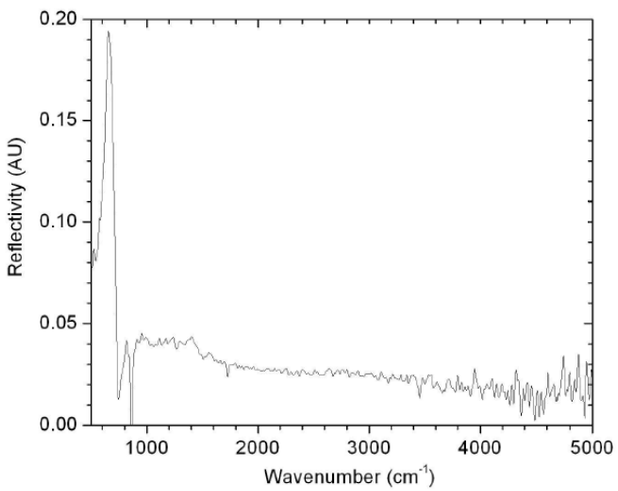
- We found a two-sublattice orbital ordering pattern revealed by distinct spin density and coexisting with canted ferromagnetic ordering.

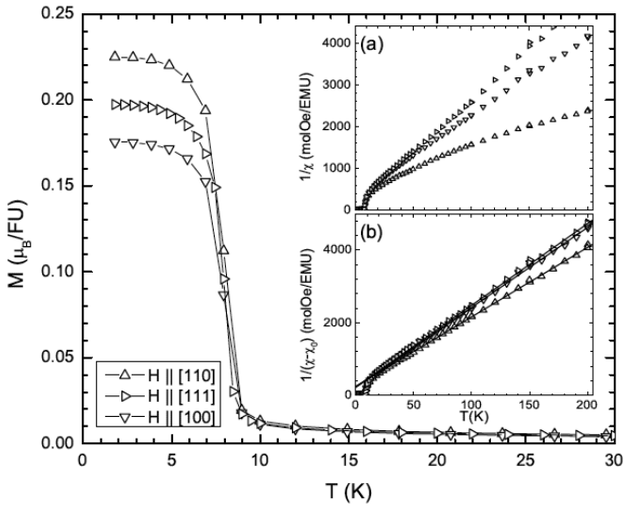
Ba_2NaOsO_6 bulk characterization

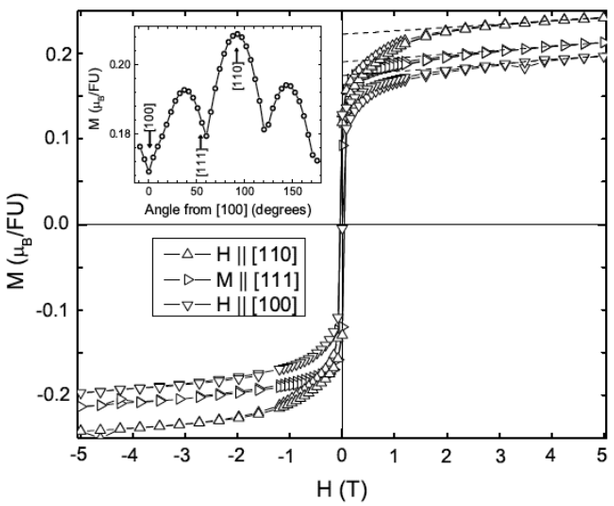
- Fcc double perovskite with $5d^1$ Os magnetic ion
- Magnetic mott insulator U ~ 3.3 eV t ~ 0.05 eV
- FM T_N ~ 6.8(3)K Θ_{CW} ~ -11K μ_{eff} ~0.6 μ_B
- FM[110] ~ 0.2 μ_B

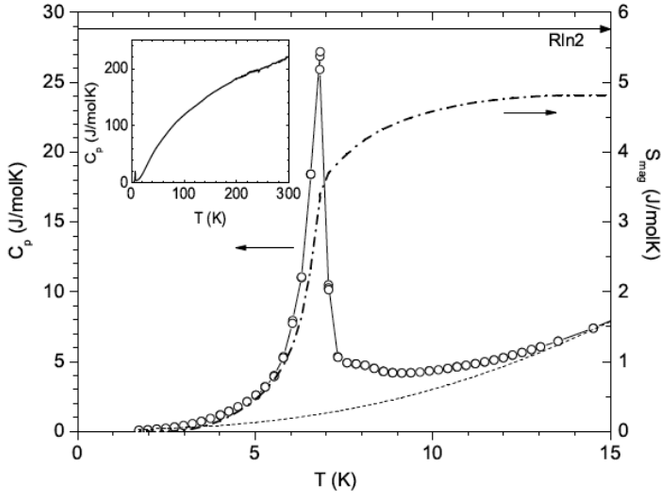


- J_{eff}= 3/2 entropy ~ *Rln2*



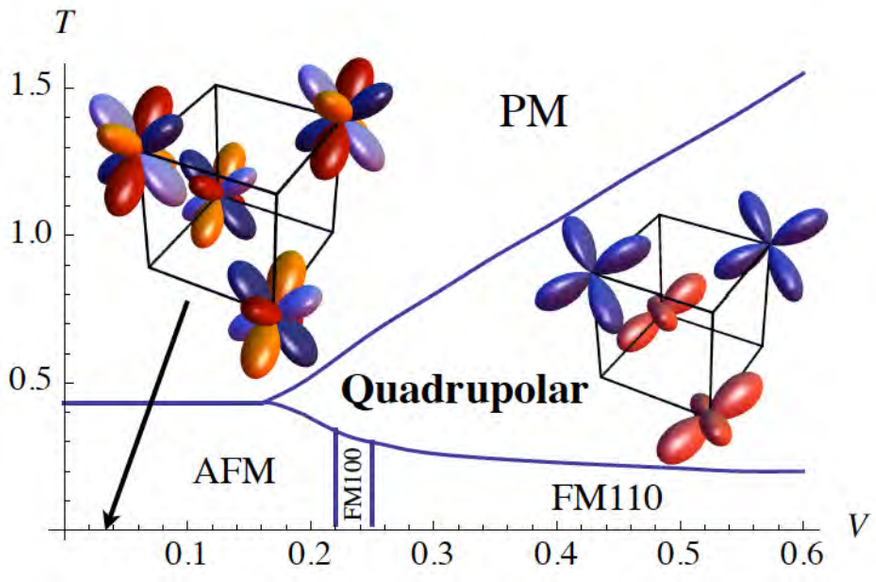






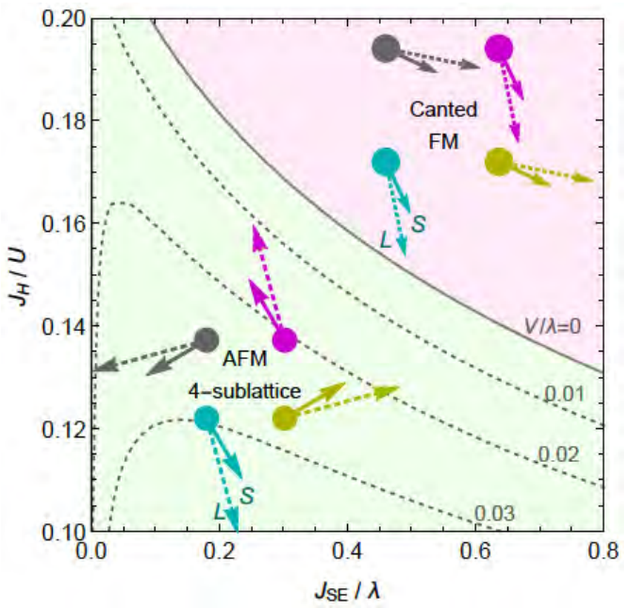
Erickson et al., PRL **99,** 016404 (2007).

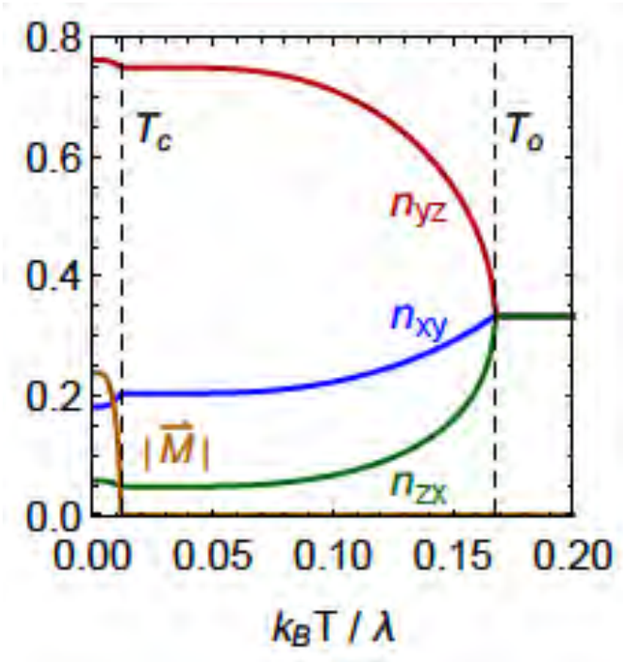
Spin-orbit coupled models

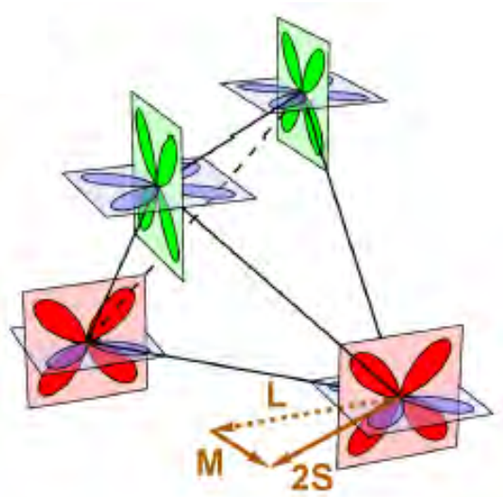


- NN antiferromagnetic exchange J
- NN ferromagnetic exchange J'
- NN electric quadrupole-quadrupole interaction V

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

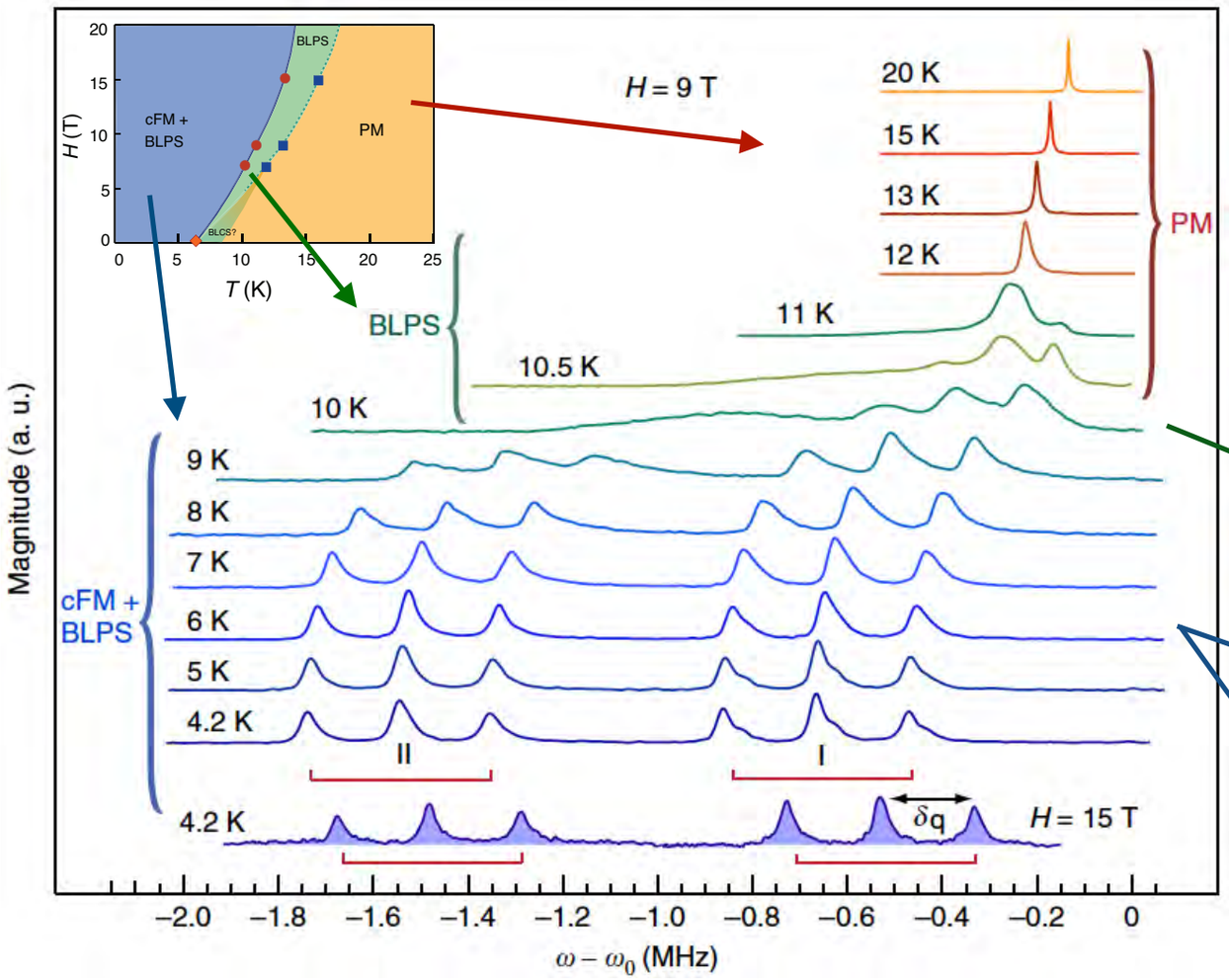


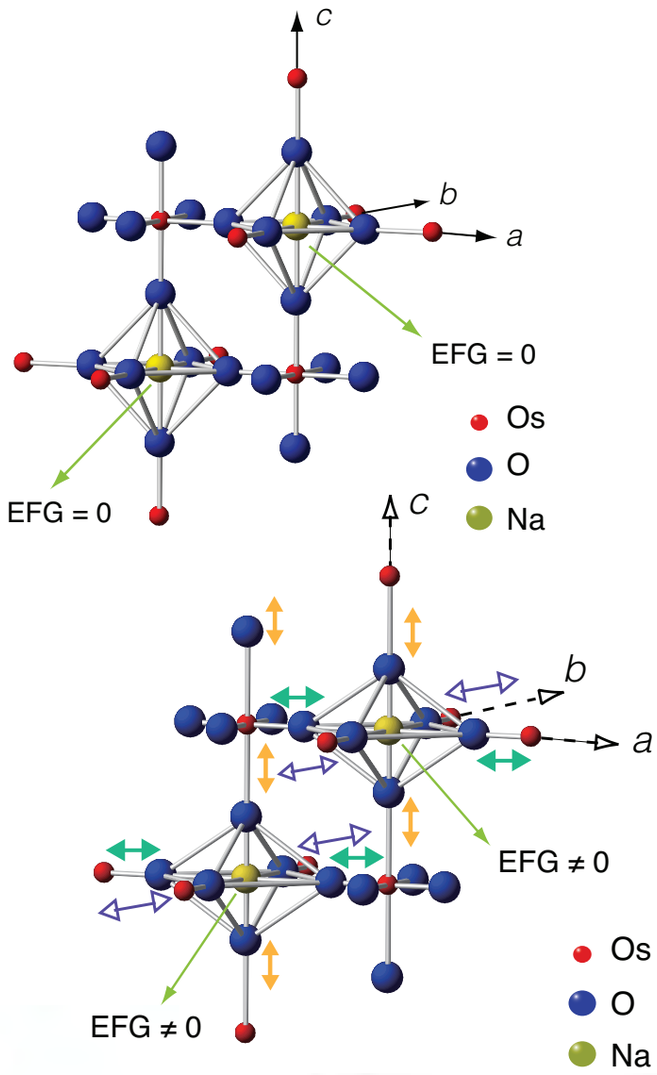


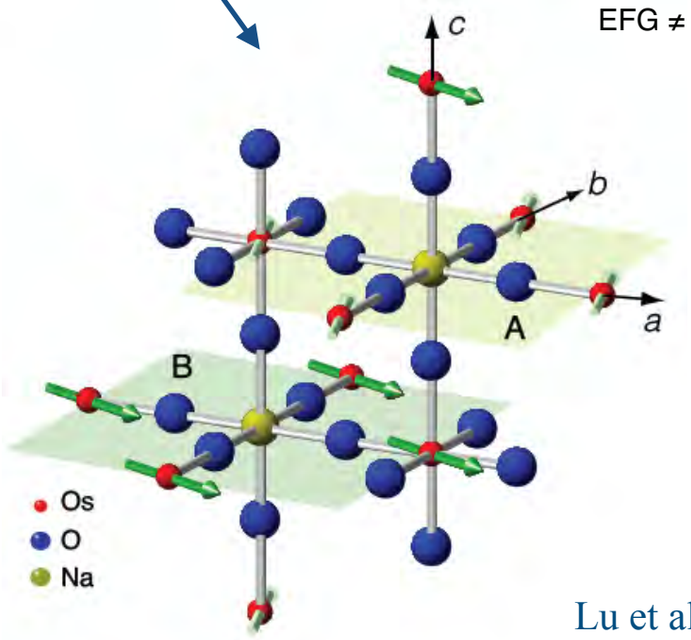


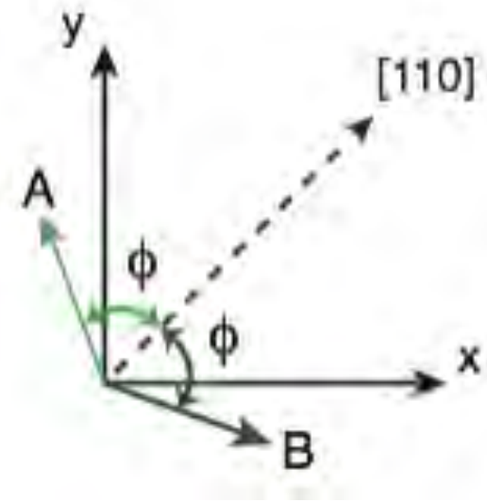
Svoboda et al., arXiv: 1702. 03199v1 [cond-mat-str-el] (2017).

^{23}Na NMR Spectrum - Temperature evolution







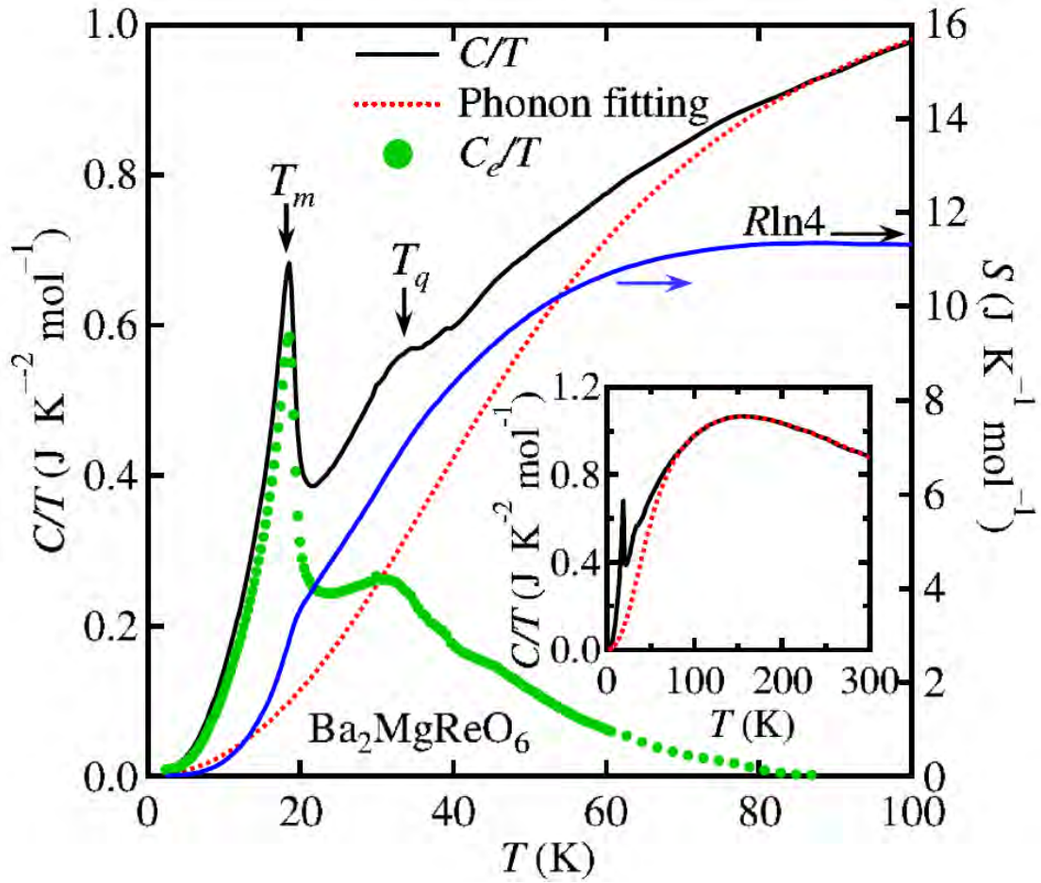


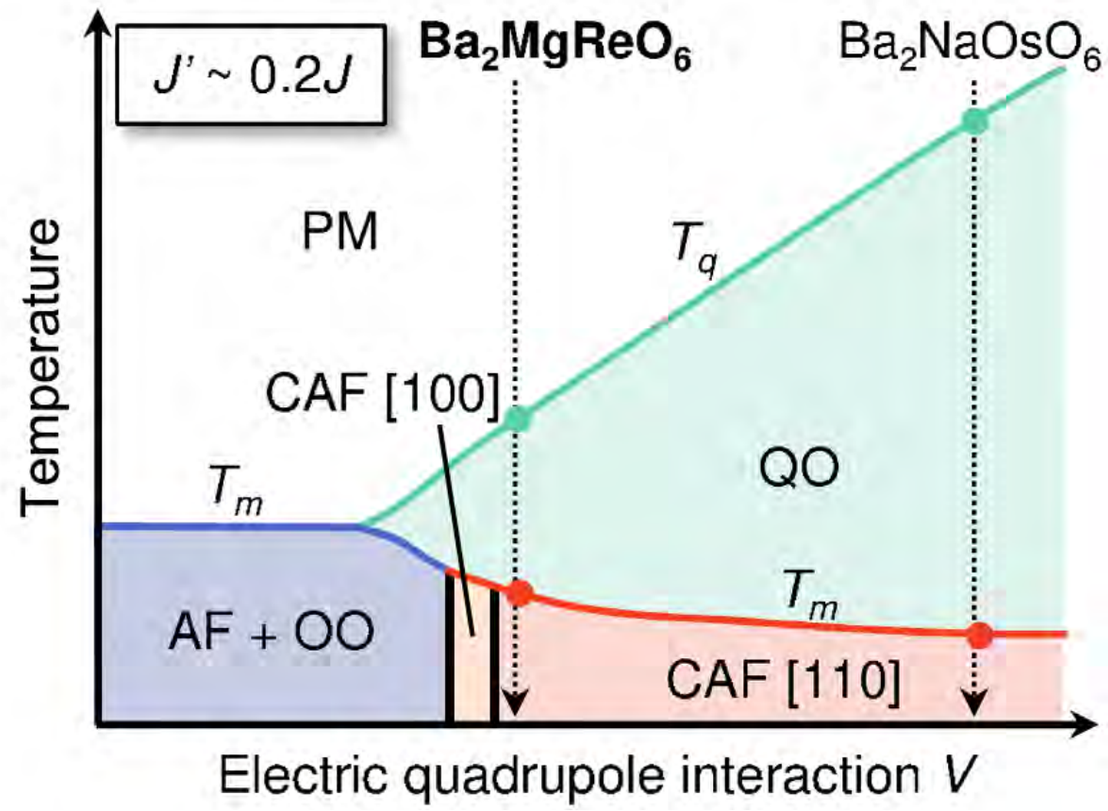
- **I and II :** 2 magnetically distinct Na sites - canted ferromagnetic order

- **Triplets of I and II :** non-zero electric field gradient - breaking local cubic symmetry

Lu et al., Nat. Commun. **8** (2017): 14407

Similar successive symmetry breaking in related materials





Hirai et al., JPSJ. **88,** 064712 (2019)

- Ba_2MgReO_6 : fcc double perovskite with $5d^1$ Re^{6+} magnetic ion
- FM $T_M \sim 18$K, $T_q \sim 33$K $\Theta_{CW} \sim -13.7$ K $\mu_{eff} \sim 0.68\ \mu_B$
- FM[110] $\sim 0.3\mu_B$
- $J_{eff} = 3/2$ entropy ~ *Rln4*

Electric field gradient (EFG) tensor $\nabla \vec{E}$

- Symmetric $\nabla \times \vec{E} = 0$
- Traceless $\nabla \cdot \vec{E} = 0$
- Eigenvalues : $|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$
- Asymmetry factor : $\eta = (V_{XX} - V_{YY})/V_{ZZ}$ $0 \leq \eta \leq 1$
- Eigenvectors : principal axes XYZ
- Diagonalization

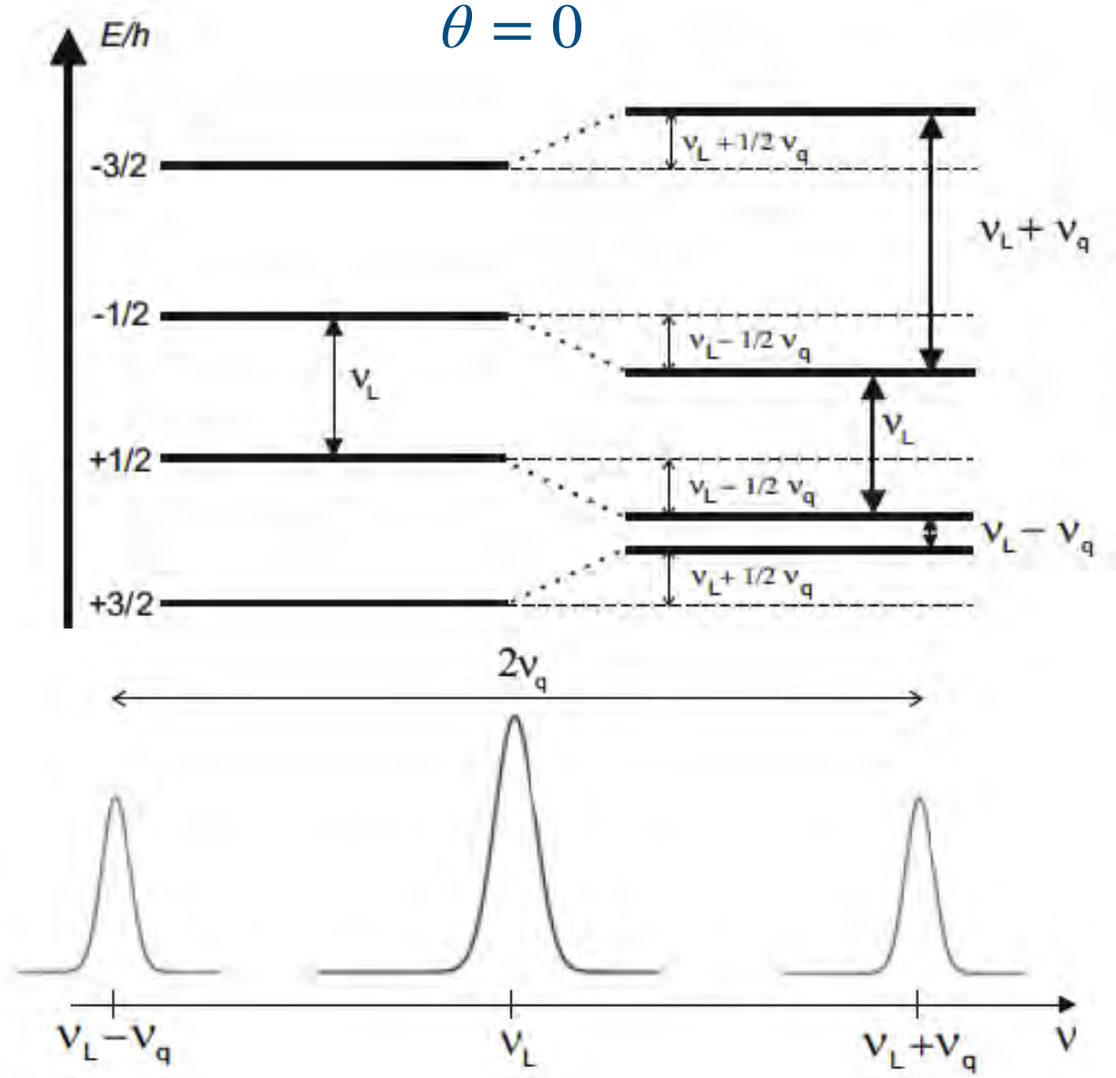
$$\begin{pmatrix} -V_{ZZ}(1-\eta)/2 & 0 & 0 \\ 0 & -V_{ZZ}(1+\eta)/2 & 0 \\ 0 & 0 & V_{ZZ} \end{pmatrix}$$

- **Five irreducible elements :** V_{ZZ}, η, **principle axes**

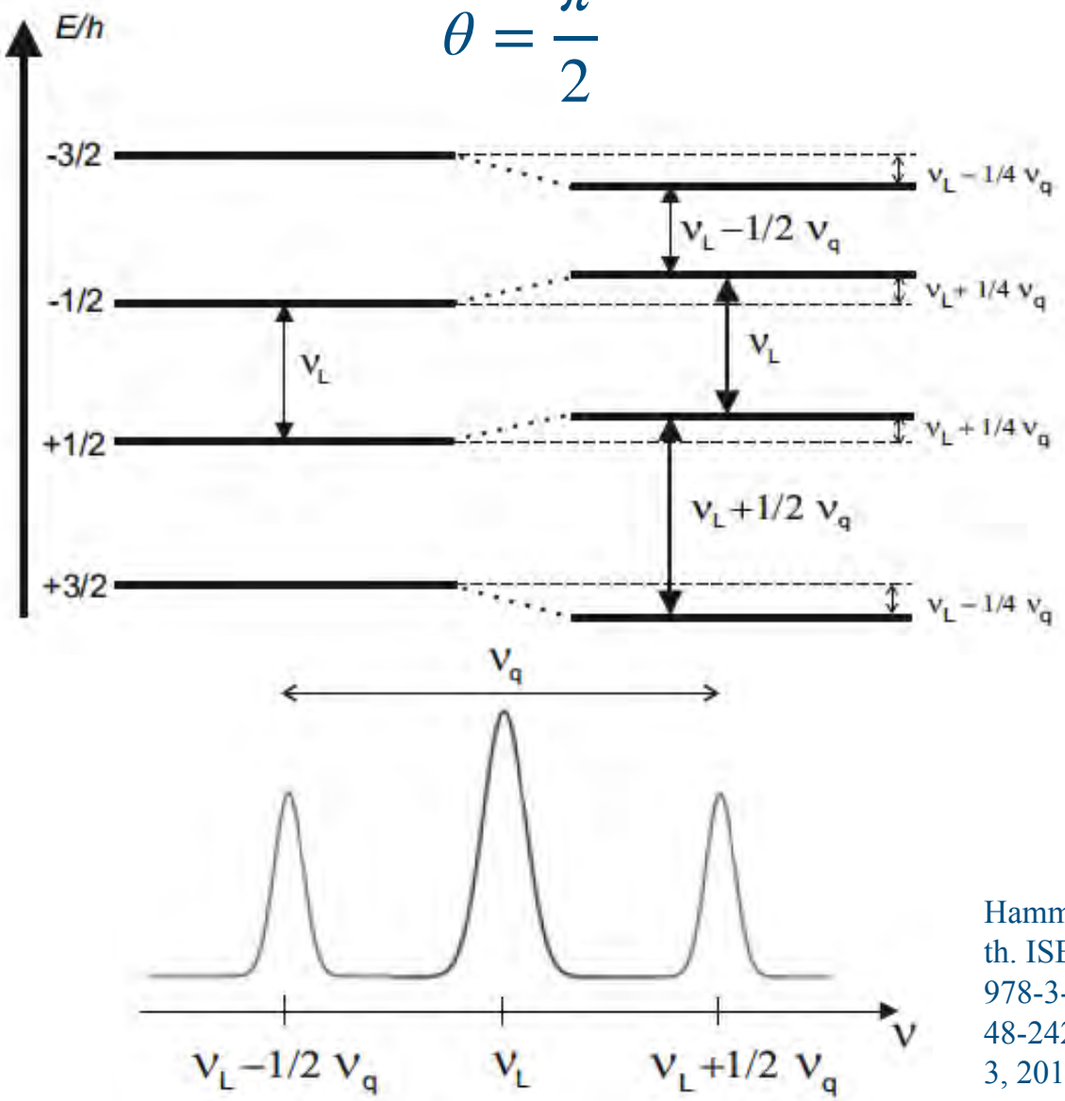
Electric quadrupolar interactions

- Hamiltonian $H_Q = \frac{h\nu_q}{2}\left(I_Z^2 - \frac{I(I+1)}{3} + \frac{\eta}{6}\left(I_+^2 + I_-^2\right)\right)$ $\nu_q = \frac{(eQ)V_{ZZ}}{2h}$
- Quadrupolar splitting $\delta_q = \frac{1}{2}\nu_q(3cos^2\theta - 1 + \eta sin^2\theta cos2\phi)$
- For nuclei with I=3/2 and $\eta = 0$

$\theta = 0$

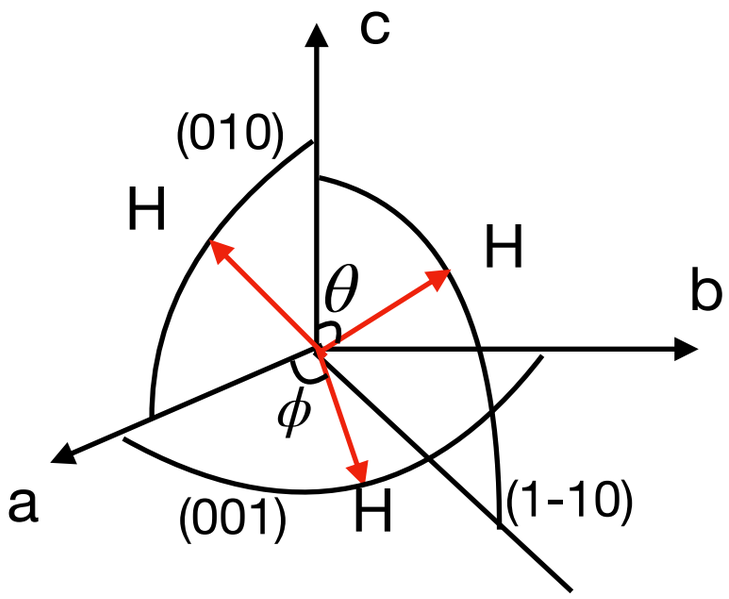


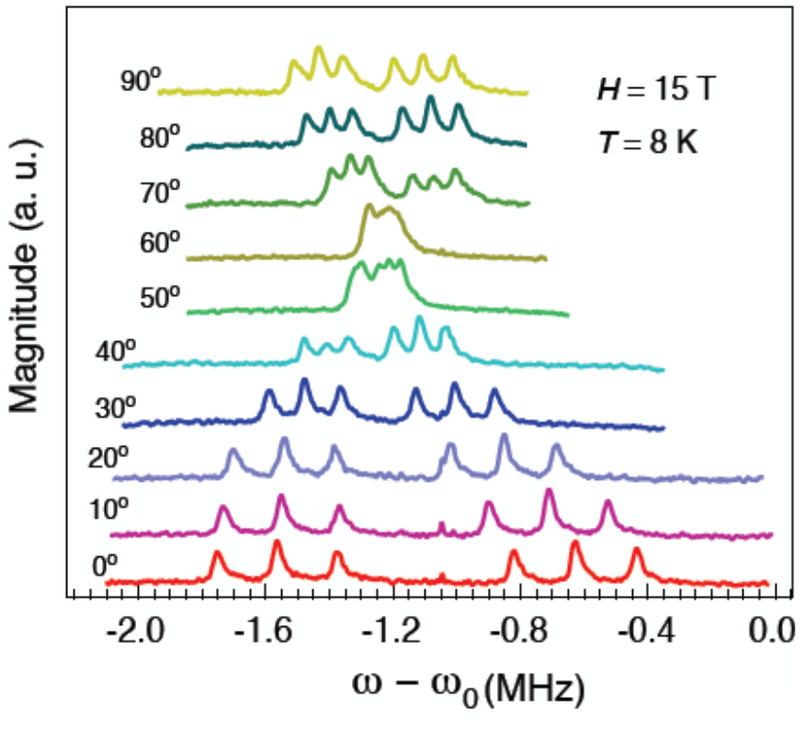
$\theta = \frac{\pi}{2}$

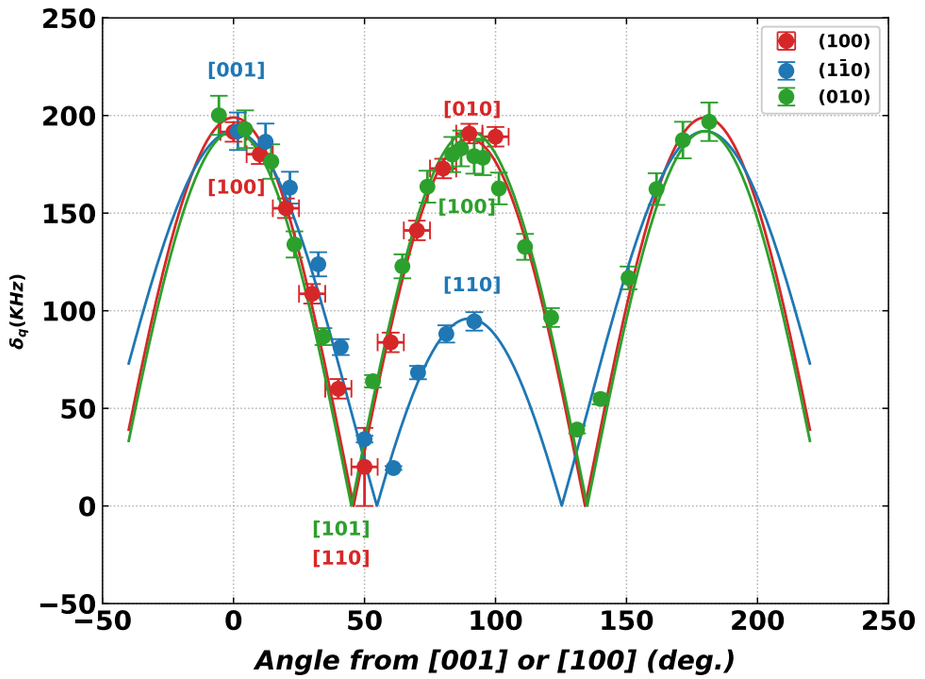


Hammerath. ISBN 978-3-8348-2423-3, 2012.

Rotation pattern





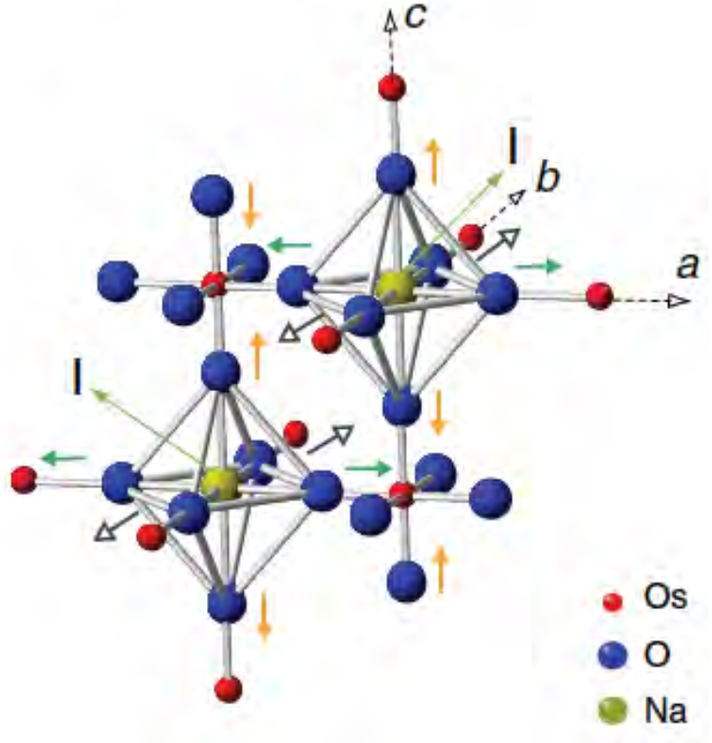


$$\delta_q = \frac{1}{2}\nu_Q(3cos^2\theta - 1 + \eta sin^2\theta cos2\phi) \qquad \nu_Q = \frac{(eQ)V_{ZZ}}{2h}$$

- EFG parameters :

$$V_{ZZ}||a, V_{YY}||c, V_{XX}||b \quad \text{or} \quad V_{ZZ}||c, V_{YY}||a, V_{XX}||b$$

$$\nu_q \approx \pm 186 - 200kHz, \eta \approx 0.86 - 1$$



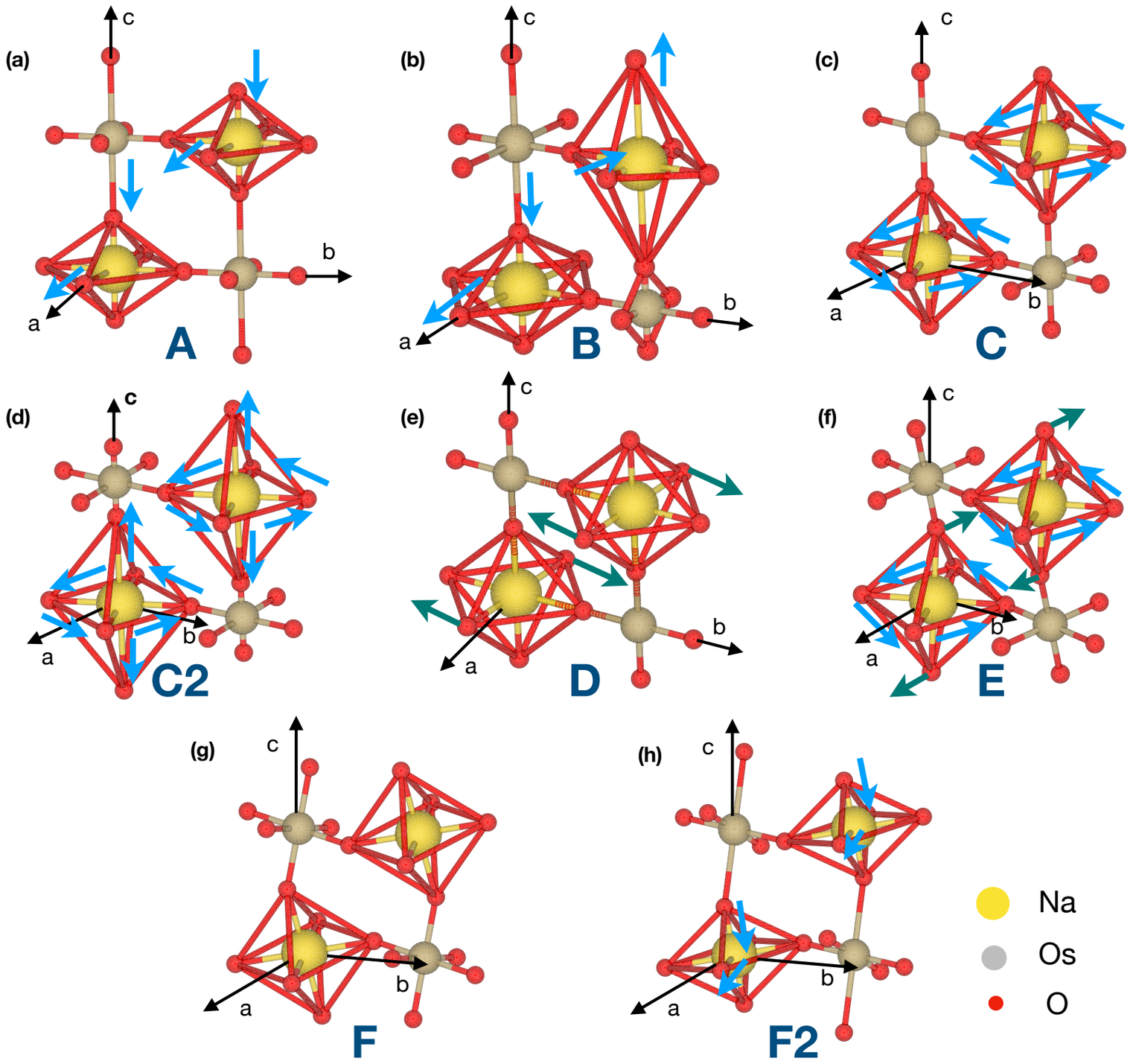
Liu et al., PRB **97.22,** (2018): 224103

Undistorted case

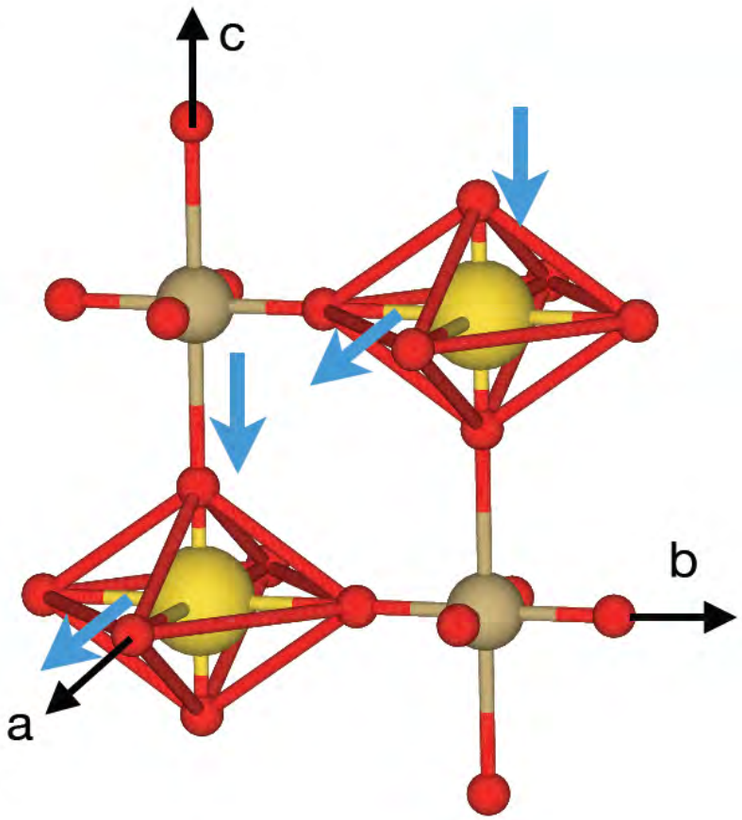
Condition	V_{zz}	η	ν_q(kHz)
GGA	n/a	n/a	0
GGA+U	n/a	n/a	0
GGA+SOC+cFM	a	0.81	-0.5
GGA+SOC+cFM+U	a	0.30	-25

- SOC and cFM order is not enough to give rise to the EFG parameters. There has to be other sources (such as structural distortions) to create the non-zero EFG.

Distortion models



Orthorhombic distortion



6 pseudopotentials (PP):

PP1: Ba_{sv}+Na+Os+O
PP2: Ba_{sv}+Na_{pv}+Os_{pv}+O_s
PP3: Ba_{sv}+Na_{pv}+Os+O
PP4: $Ba_{\mathbf{sv}}$+Na+$Os_{\mathbf{pv}}$+O
PP5: Ba_{sv}+Na+Os+O_s
PP6: $Ba_{\mathbf{sv}}$+Na+$Os_{\mathbf{pv}}$+O_s

Na-O bond

a ⟶ a+ δ
b ⟶ b
c ⟶ c- δ

Q_2 distortion mode

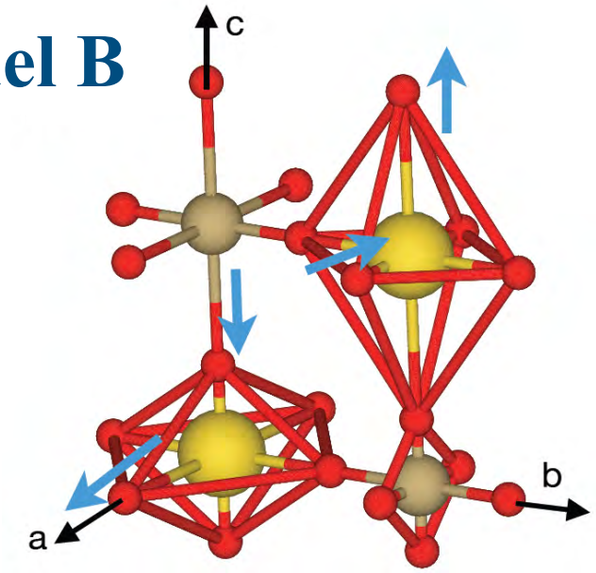
- GGA+cFM+SOC+U

δ_a (%)	δ_b(%)	δ_c (%)	Vzz	η	ν_q(kHz)
-0.54	0	0.55	c	1	-190
			c	0.991	-190.5
			a	0.818	209.5
			a	0.813	209.5
-0.525	0	0.52	a	0.981	183
			a	0.991	183
			a	0.795	202
			a	0.790	203

Method	Vzz	η	δ_q (kHz)
GGA+cFM+U	c	0.950	-211
	a	0.852	205
	-a	0.905	217
	a	0.768	209
GGA+U	c	0.984	186
	c	0.984	186
	c	0.984	186
	c	0.984	186

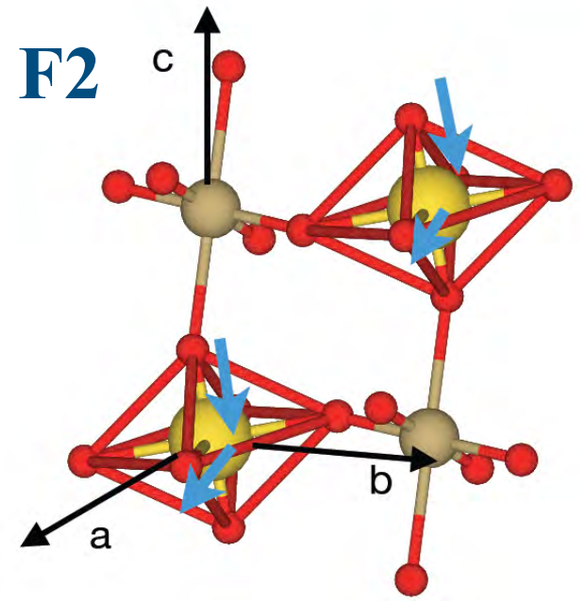
Other possibilities

Model B



δ_a (%)	δ_b (%)	δ_c (%)	Vzz	η	ν_q(kHz)
-0.53	0	0.55	c	0.974	-189.5
			c	0.982	-188.5
-0.55	0	0.53	c	0.778	209
			a	0.783	209.5
-0.56	0	0.56	-a	0.740	183
			-a	0.725	183
0.56	0	-0.56	a	0.853	-200
			a	0.847	-200
-0.52	0	0.52	a	0.768	165.5
			a	0.760	166.5
0.52	0	-0.52	a	0.913	-182.5
			a	0.911	-182

Model F2

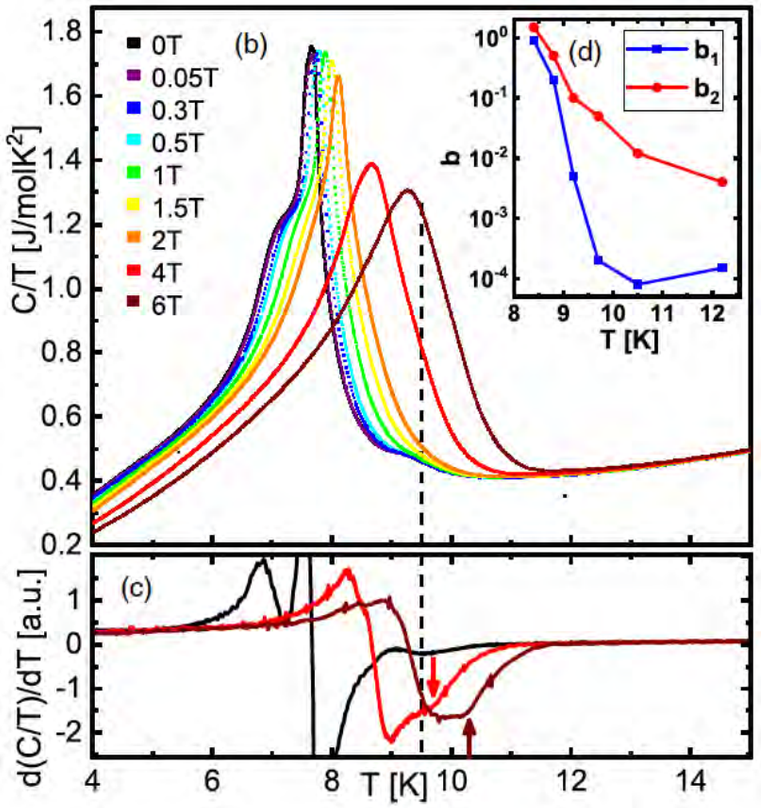


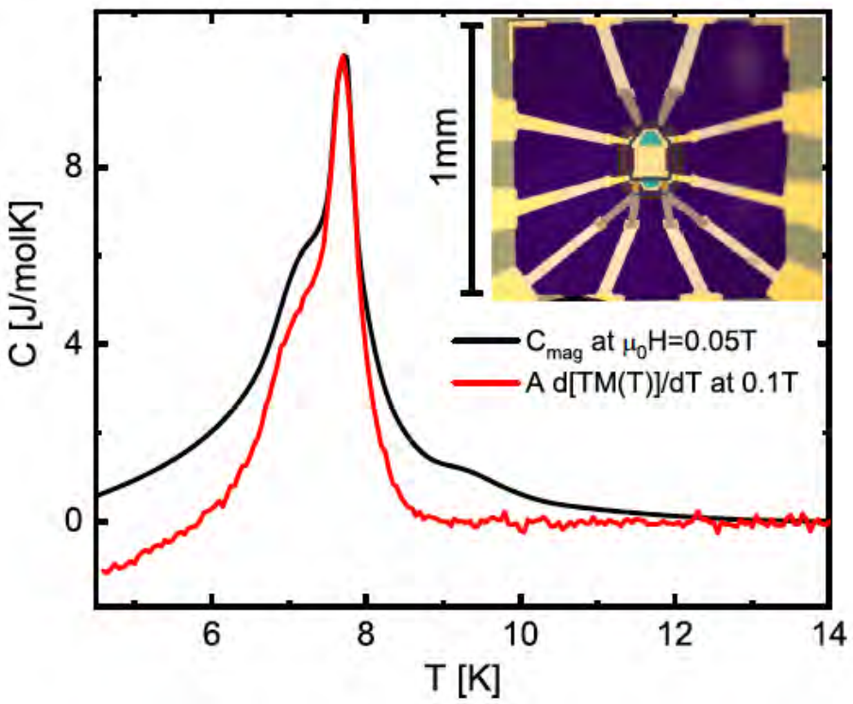
	Vzz	η	ν_q(kHz)
F	≈ (-a,-b) dia	0.359	22
	≈ (-a,-b) dia	0.349	23
	≈ [111] dia	0.340	15
	≈ [111] dia	0.346	15
F2	c	0.954	186
	c	0.954	186
	-a	0.948	191
	-a	0.948	191

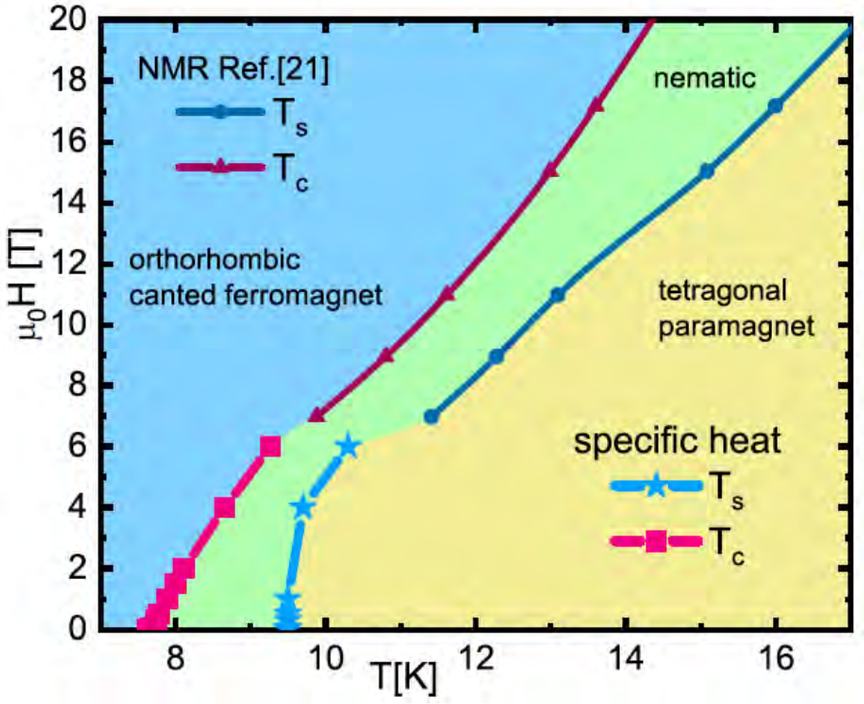
Sensitivity to distinct magnetic order

FM110	ν_Q (kHz)	η	V_{zz}
A	185	0.853	a
B Os1	190	0.750	a
B Os2	-213	0.899	a
F2 Os	-210	0.893	c
Cubic Os	58	0.62	[110]

- EFG is insensitive to the precise nature of the magnetic order
- Evidence for the structural origin of a high-temperature shoulder observed in specific heat.





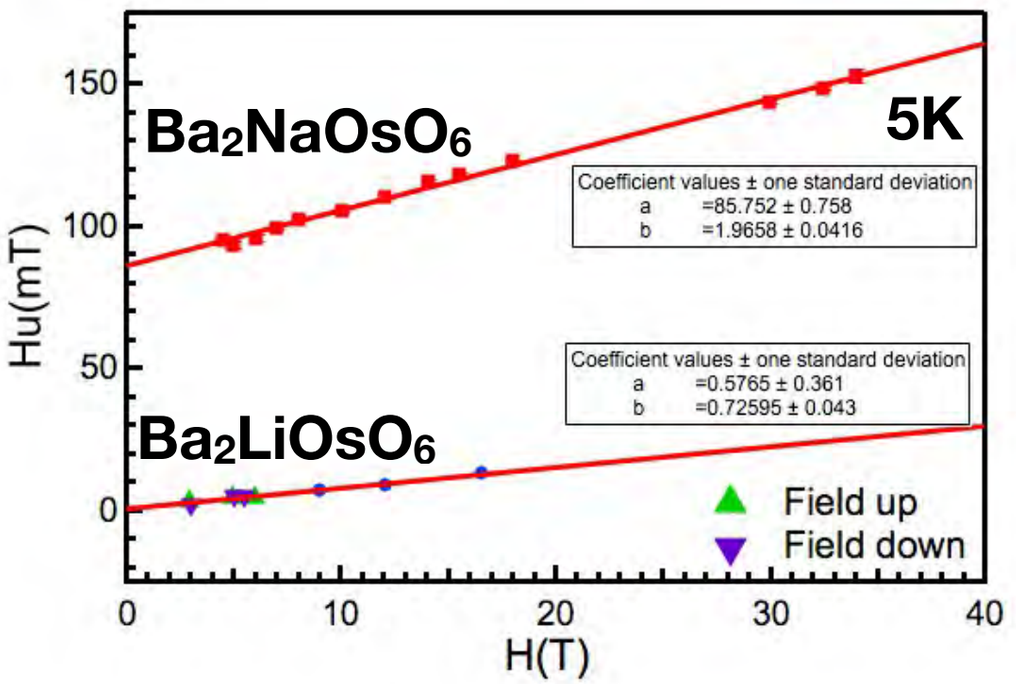


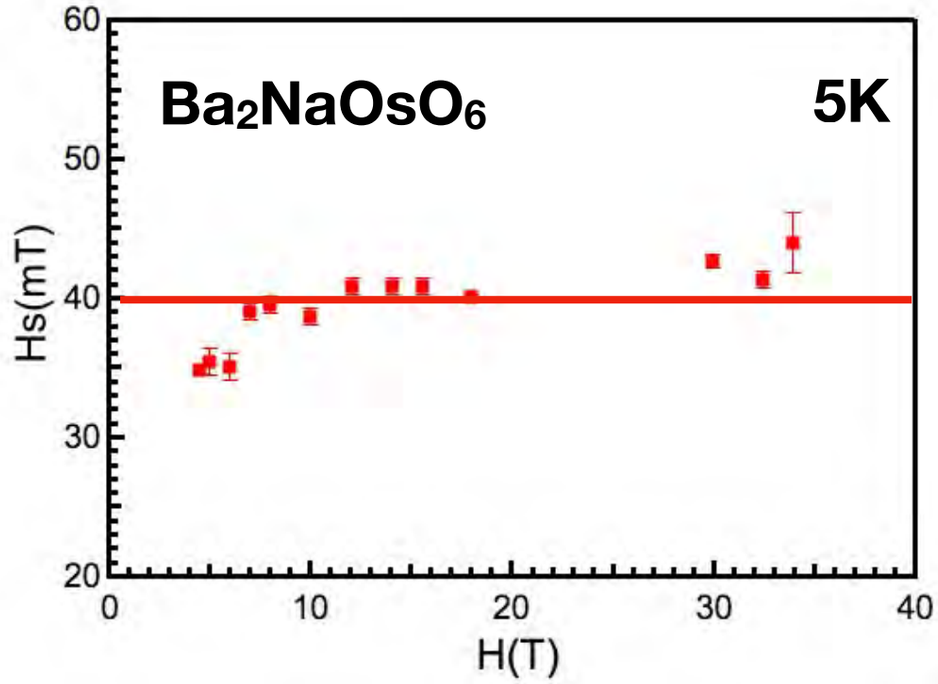
Willa. et al., PRB **100,** (2019): 041108 (R)

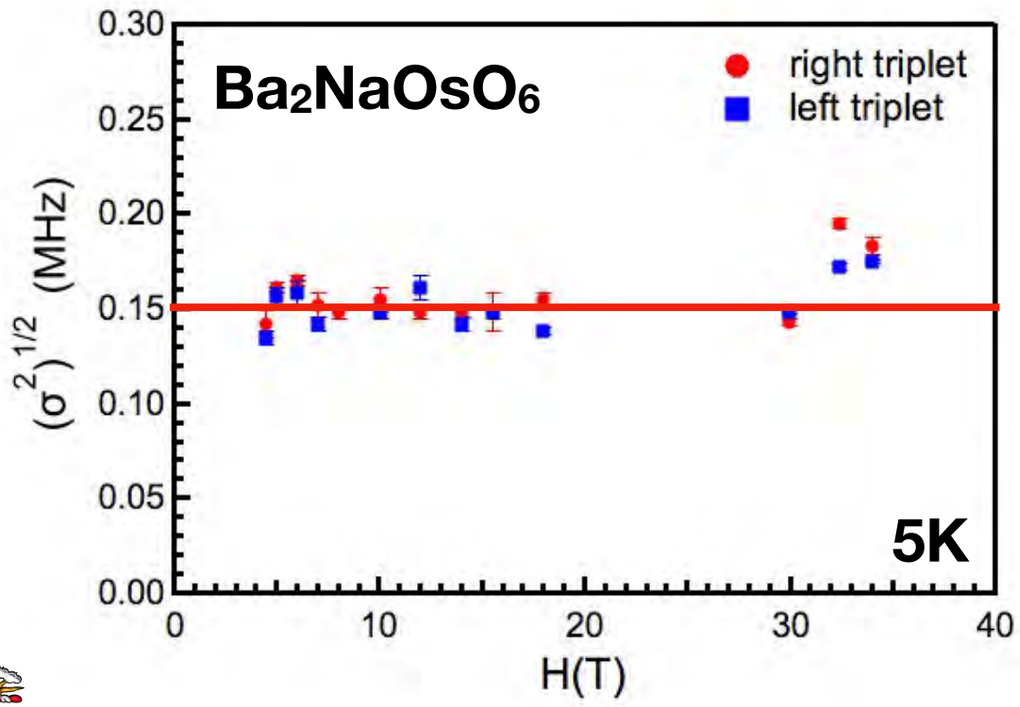
Response to external magnetic field

$$H_u = \frac{1}{2}[\langle H_I \rangle + \langle H_{II} \rangle]$$

$$H_s = \frac{1}{2}[\langle H_I \rangle - \langle H_{II} \rangle]$$



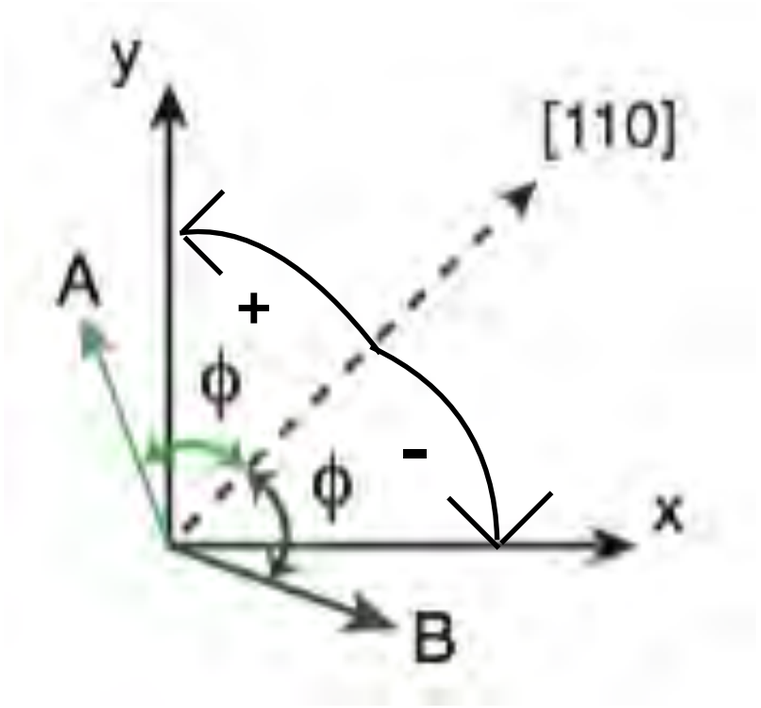




- Staggered local magnetic field and the second moments of the two triplet are constant in different magnetic fields, suggesting their non-magnetic origin.

Orbital and spin magnetic moment

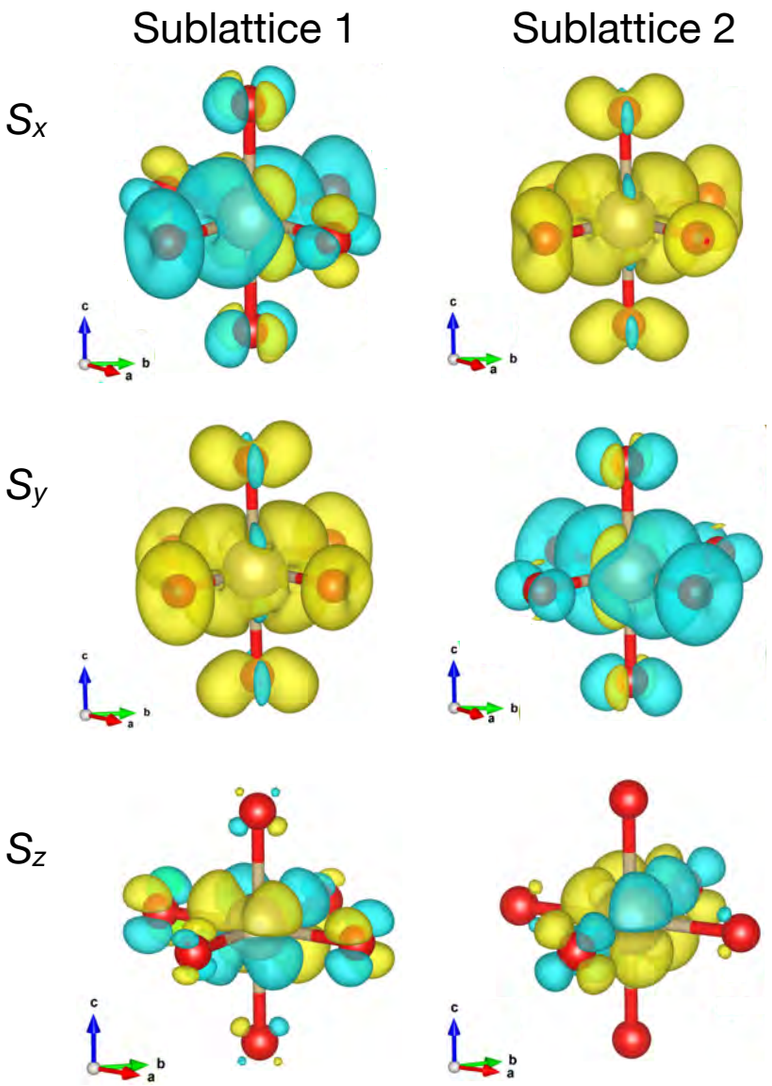
cFM	$\lvert\vec{S}\rvert$	$\phi(\vec{S})$	$\lvert\vec{L}\rvert$	$\phi(\vec{L})$	$\lvert\vec{M}\rvert$	$\phi(\vec{M})$
A Os1	0.55	-86	0.44	91	0.12	-79
A Os2	0.55	74	0.43	-76	0.11	65
B Os1	0.61	-99	0.46	79	0.15	-86
B Os2	0.60	98	0.47	-80	0.13	95
F2 Os1	0.46	-75	0.34	100	0.12	-61
F2 Os2	0.47	64	0.35	-109	0.13	46
Cubic Os1	0.60	-83	0.47	95	0.13	-76
Cubic Os2	0.60	83	0.47	-95	0.13	76
FM [110]						
A Os	0.83	[110]	0.52	-[110]	0.31	[110]
B Os1	0.82	[110]	0.52	-[110]	0.30	[110]
B Os2	0.88	[110]	0.54	-[110	0.34	[110]
F2 Os	0.45	[110]	0.25	-[110]	0.20	[110]
Cubic Os	0.85	[110]	0.54	-[110]	0.31	[110]

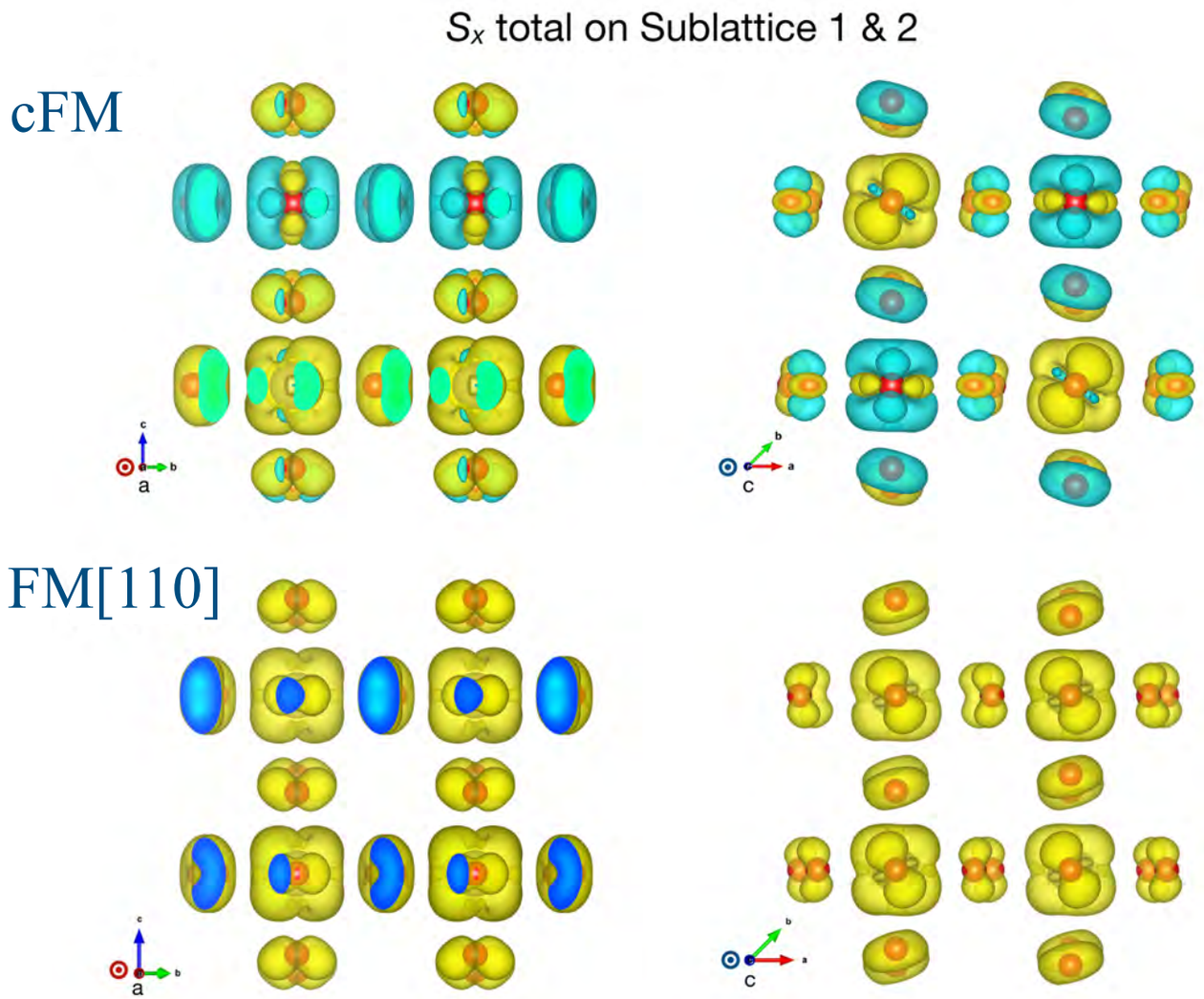


- The average canting angle of 72 degree of Model A with cFM order is closest to the 67-degree canting angle derived from NMR.

Spin density

cFM

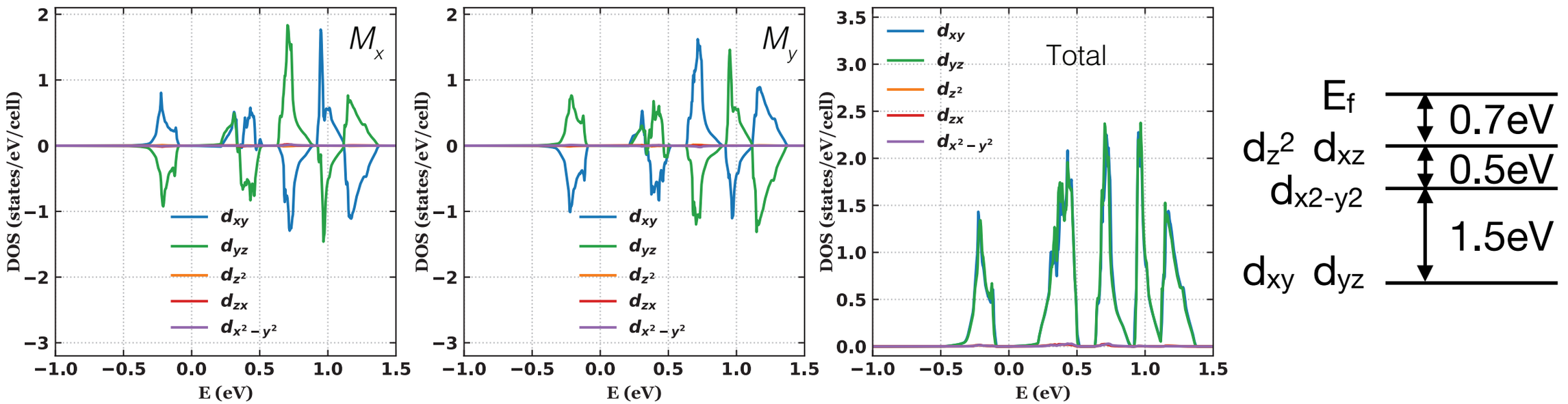




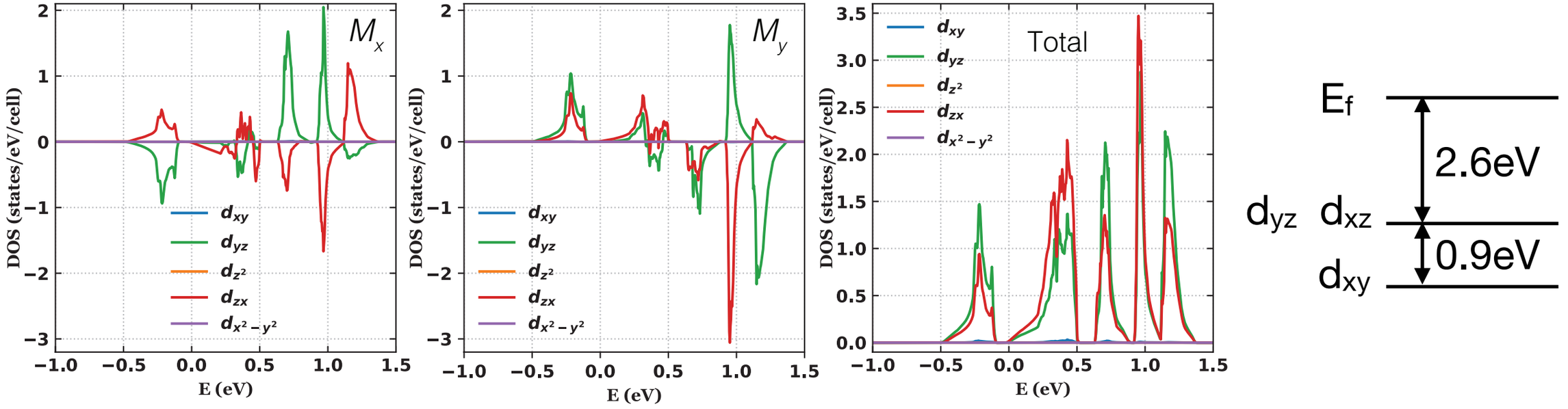
- Spin density $\langle \Delta^{\sigma}(\vec{r}) \rangle = Tr[\rho \sum_i \delta(\vec{r}_i - \vec{r}) S_i^{\sigma}] \qquad \sigma = x, y, z$
- Distinct spatial distribution of spin density on Os cites for cFM order suggests orbital ordering

Partial density of states

Os1



Os2

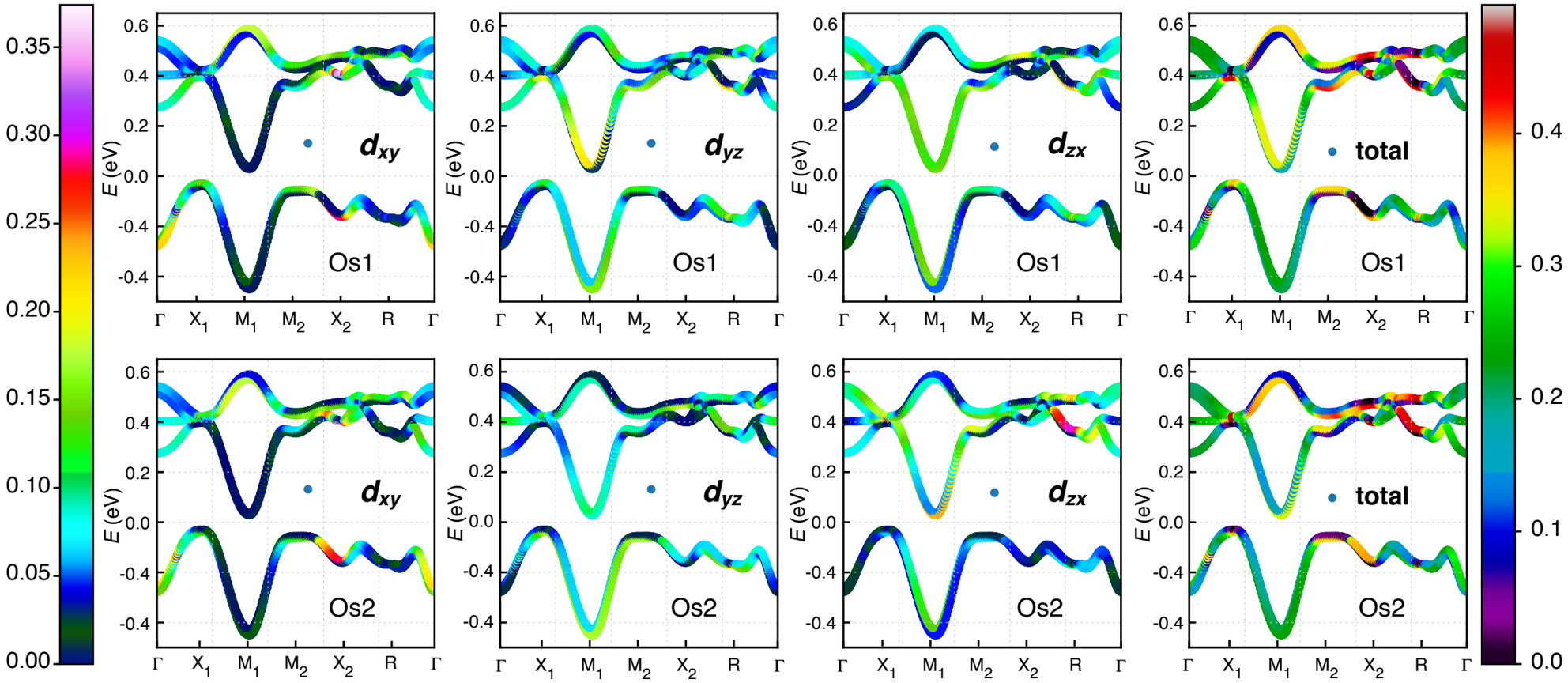


- Different selective occupation of t_{2g} orbitals for the two Os sublattices in the vicinity of Fermi energy.

Band structures

Os1

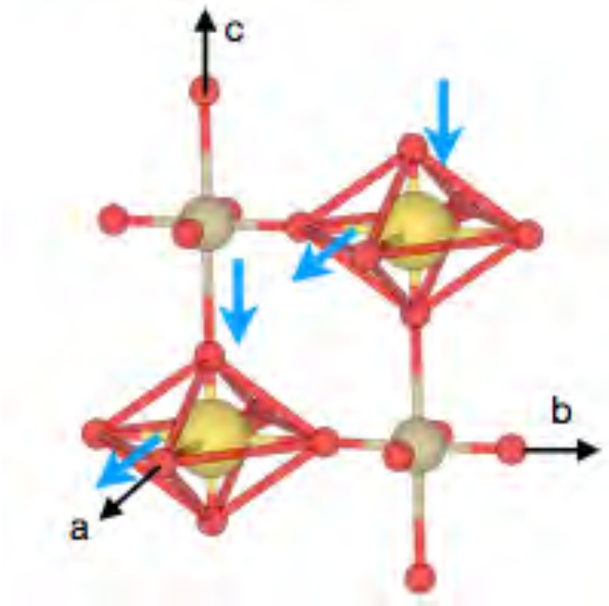
Os2



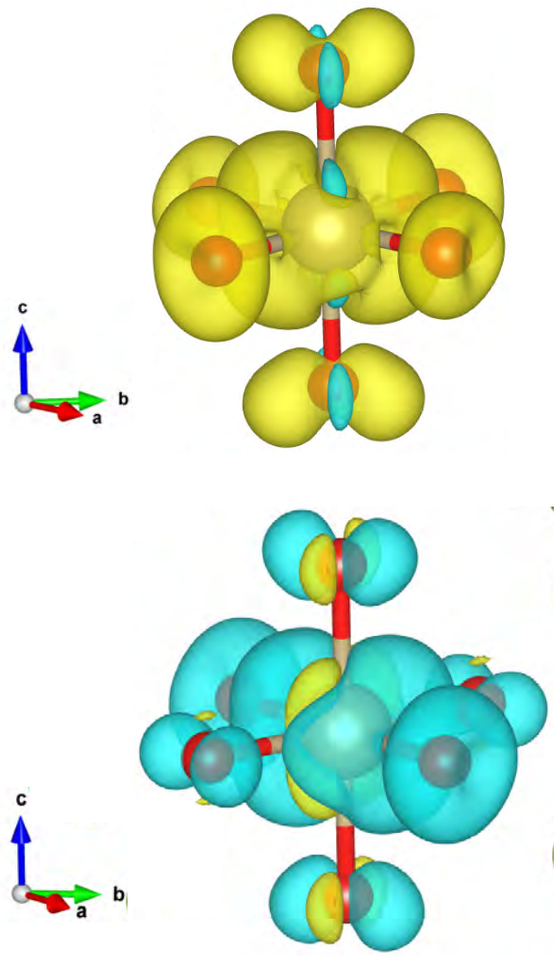
U (eV)	**J** (eV)	ν_Q (kHz)	η	**gap** (eV)
3.3	0.5	194	0.866	0.06
4.0	0.5	194	0.873	0.244
4.5	0.5	193	0.863	0.388
5.0	0.5	190	0.852	0.556
3.3	0.6	191	0.819	0.04

Summary

- We found that a local orthorhombic distortion where the Na-O bond elongate and compress along two crystalline axes respectively is the main driving force for the non-zero EFG of the breaking local point symmetry phase for Ba_2NaOsO_6.



- Assuming an experimentally determined canted ferromagnetic ordering, we predicted a possible two-sublattice orbital ordering of Os ions on alternating planes where the total magnetic moment resides. This is due to strong spin-orbit coupling.



Remaining questions

- Complexity of hyperfine coupling tensor that does not reflect atomic or magnetic symmetry.

- Reduced entropy of Rln2 across the magnetic transition, energy level splitting on the two Os sites.

Thanks!