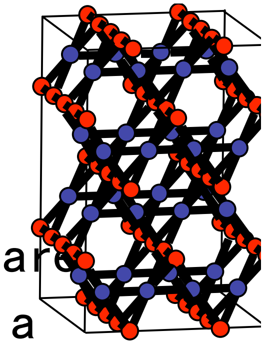
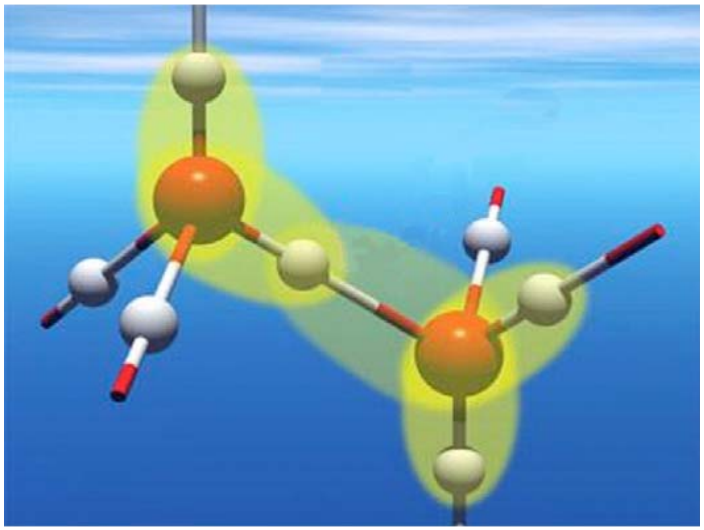
Frustration and Functionality in Complex Oxides

P.G. Radaelli
ISIS Facility - RAL
Dept. of Physics and Astronomy, UCL

Science & Technology Facilities Council

The effects of frustration: extensively degenerate GS



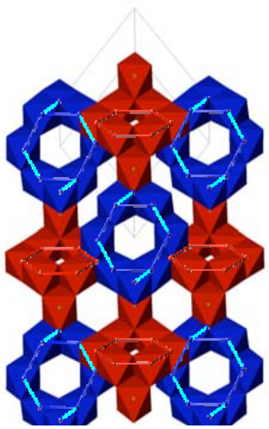


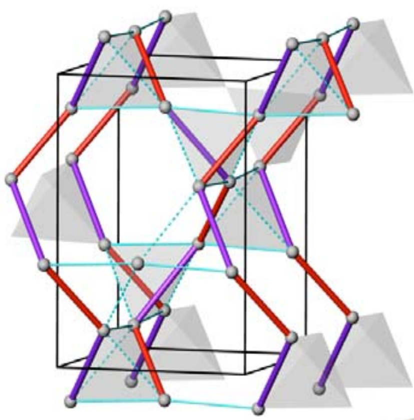
In general, ordering transitions are greatly suppressed. On cooling a frustrated system, three outcomes are possible.

1. A symmetry breaking occurs; frustration is removed and the system orders long-range.
2. The system "freezes" in a glass-like state, with finite zero-temperature entropy (ices)
3. A liquid-like ground state is promoted by quantum fluctuations

Coupled degrees of freedom → Functionality

What happens near the Mott transition?





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Outline

1. Unusual ways to relieve orbital and magnetic degeneracy
   - $AgNiO_2$
   - $NaMnO_2$
2. Magneto-elastic effects: competition vs frustration.
   - J_1-J_2: Li_2VoSIO_4 and $VOMoO_4$
   - $BiMnO_3$
3. Mechanisms of multiferroicity & functionality
   - $\mathit{RE}Mn_2O_5$

Collaborations & References

$AgNiO_2$
E. Wawrzynska, R. Coldea (Univ. of Bristol)
cond-mat/0705.0668 Phys. Rev. Lett. in press (2007).

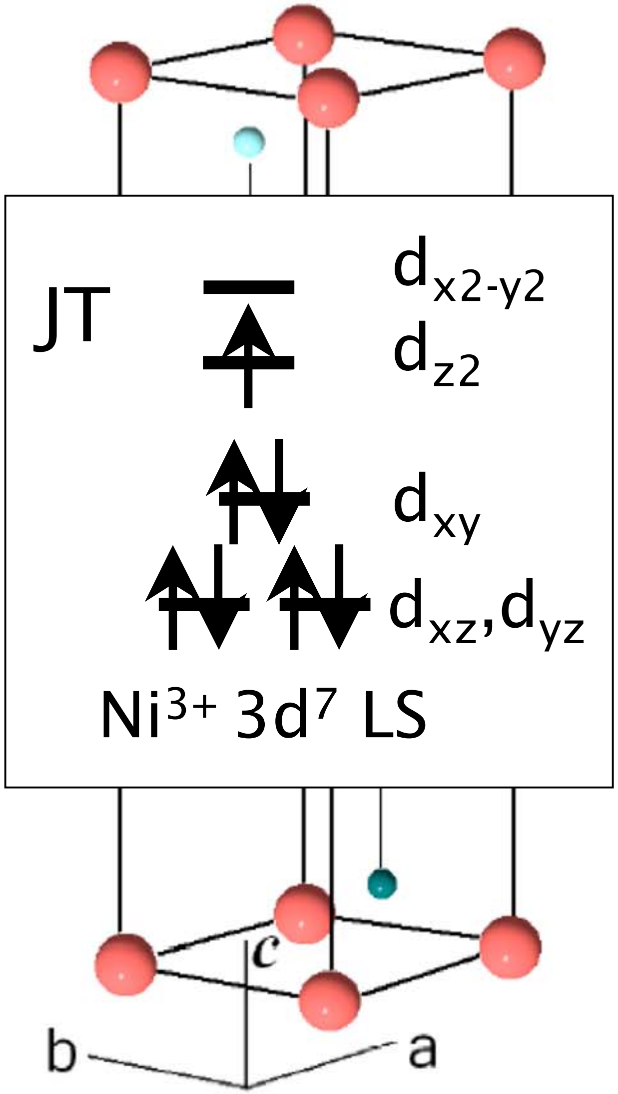
α-$NaMnO_2$
M. Giot (ISIS & IESL-FORTH, Greece), L. Chapon (ISIS) and Alex Lappas (IESL-FORTH)
Submitted to PRL.

$BiMnO_3$
E. Montanari, G. Calestani, (Univ. of Parma)
Phys. Rev. B Rapid Comm. 75, 220101 (2007).

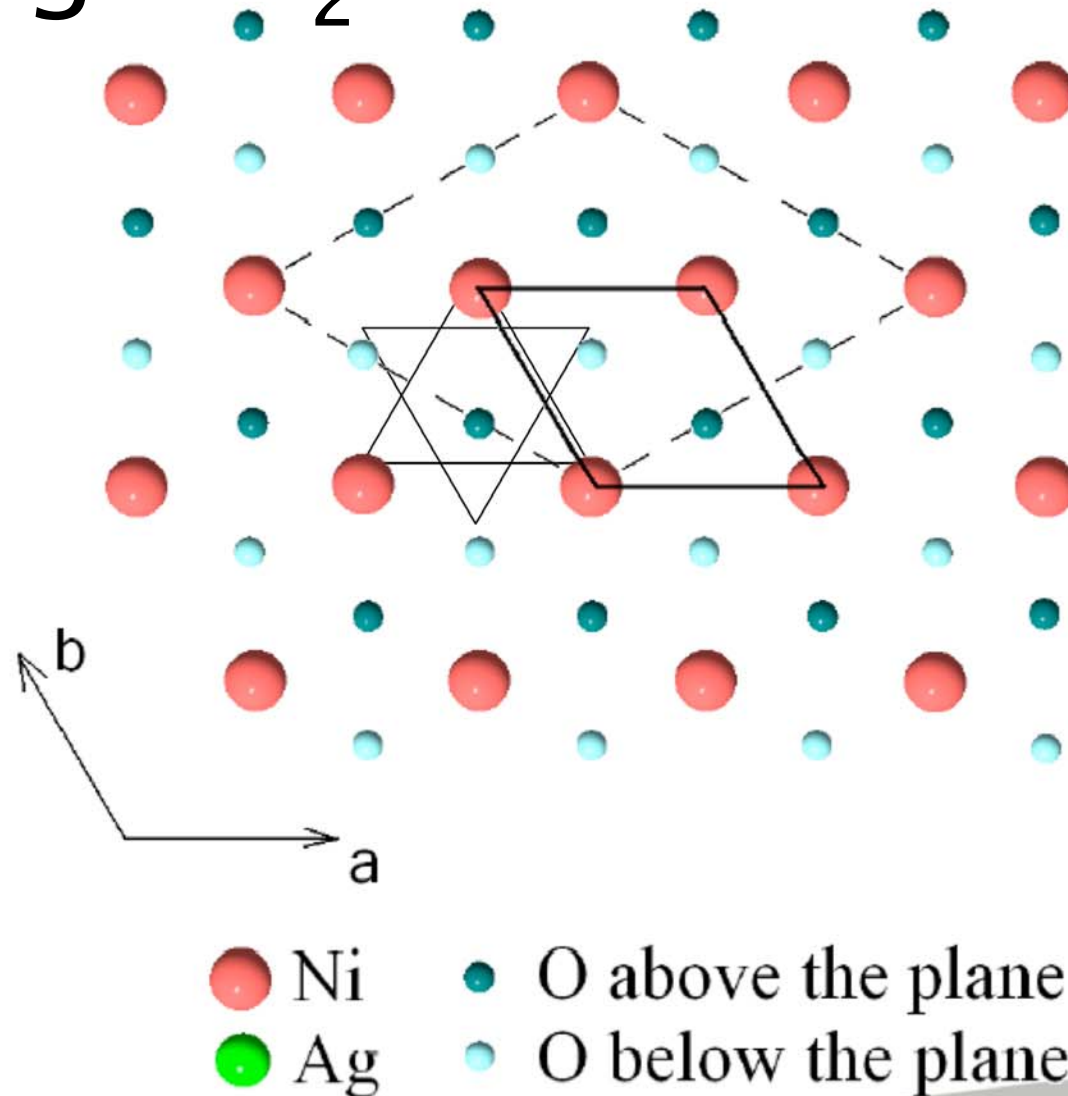
$VOMoO_4$
A. Bombardi (Diamond LS) and L.C. Chapon (ISIS)
Physical Review B **71** (2005) Art No 220406.

$\mathit{RE}Mn_2O_5$
S.-W. Cheong (Rutgers) and L.C. Chapon (ISIS)
e.g. Physical Review Letters **96**, art. no. 097601

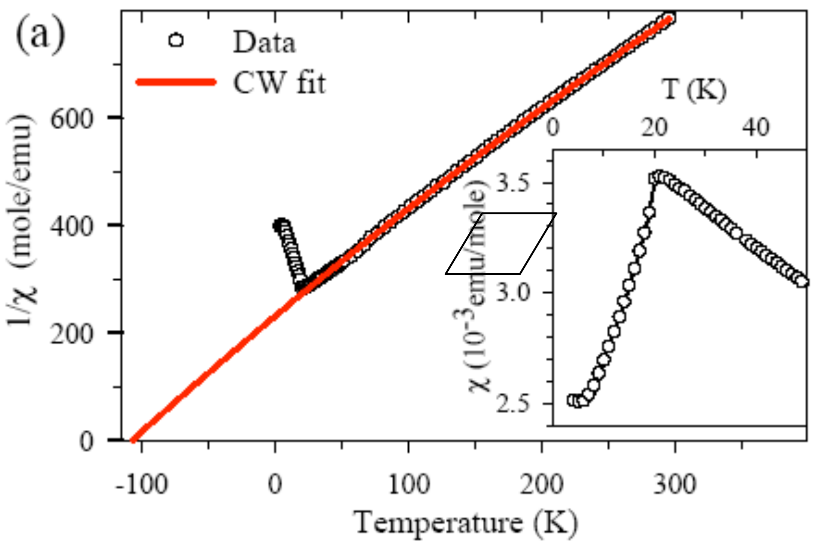
$AgNiO_2$

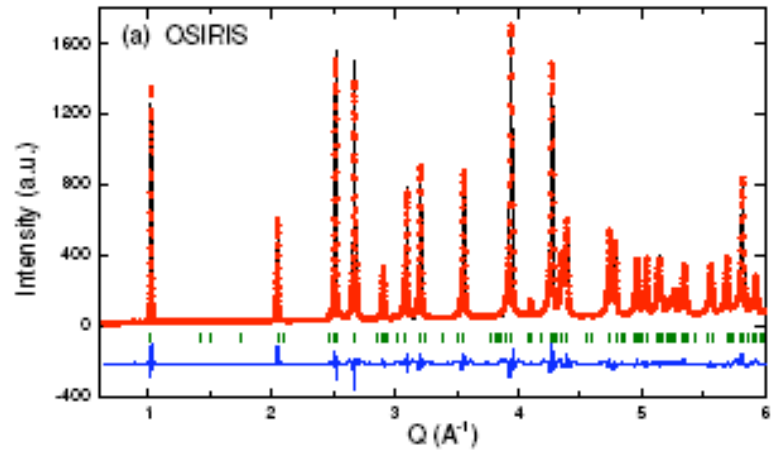


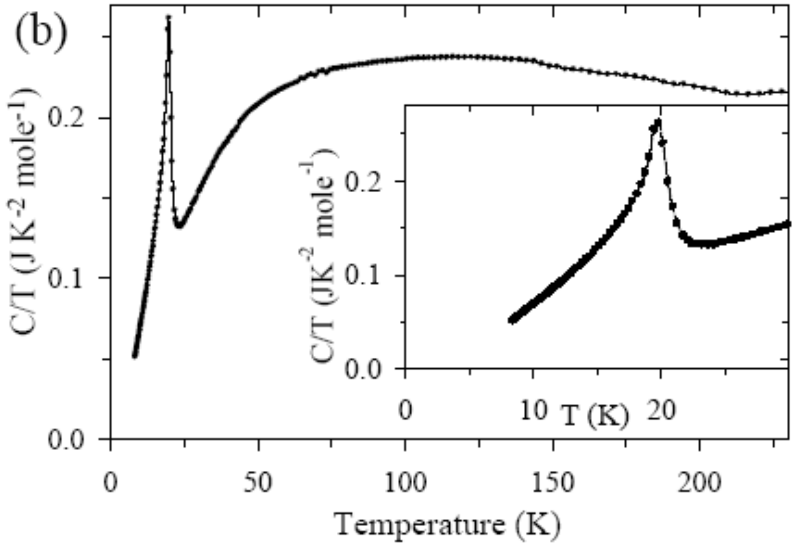
$P6_3/mmc$

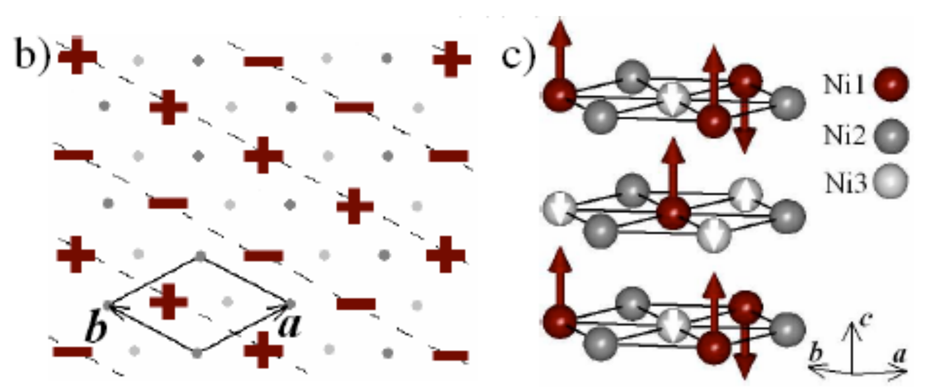


$AgNiO_2$

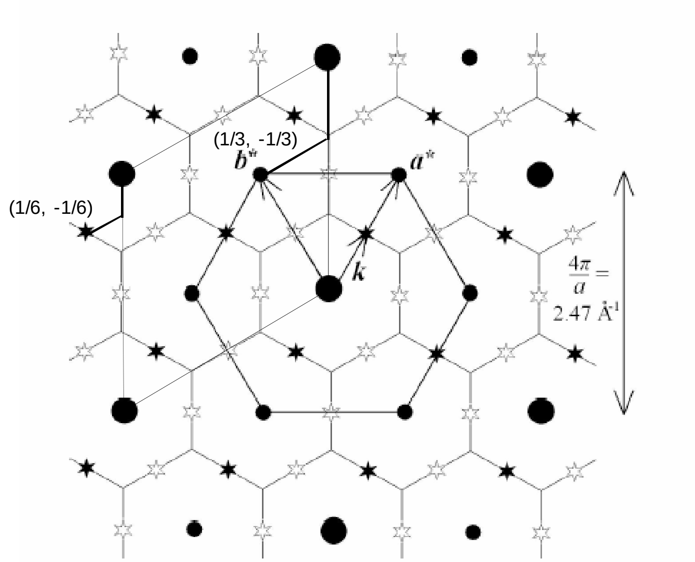

(a)
Data
CW fit
1/χ (mole/emu)
Temperature (K)
T (K)
χ (10^-3 emu/mole)

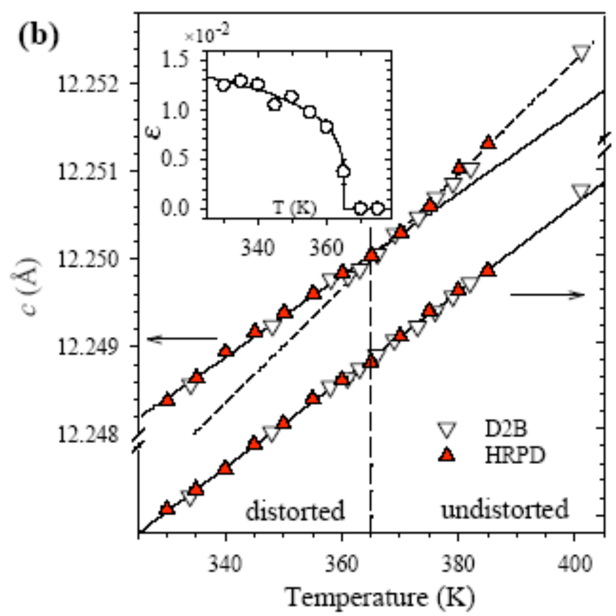

(a) OSIRIS
Intensity (a.u.)
Q (A^-1)


(b)
C/T (J K^-2 mole^-1)
Temperature (K)
C/T (JK^-2 mole^-1)
T (K)

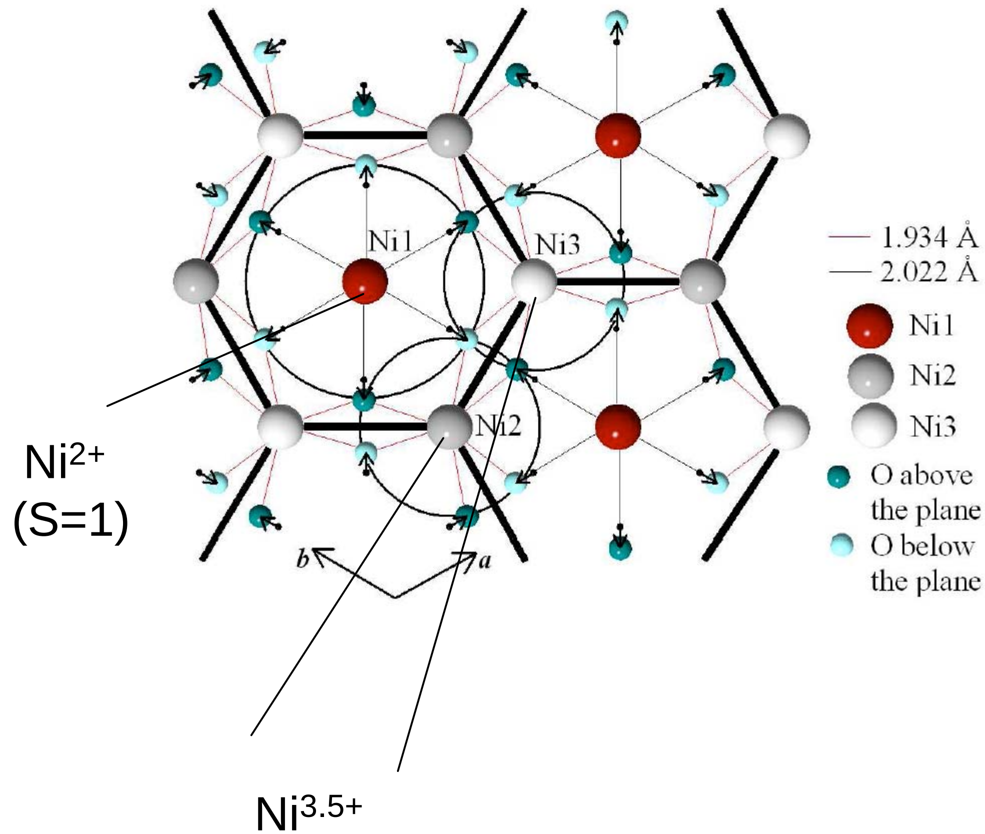

b)
c)
b
a
Ni1
Ni2
Ni3
c

$AgNiO_2$



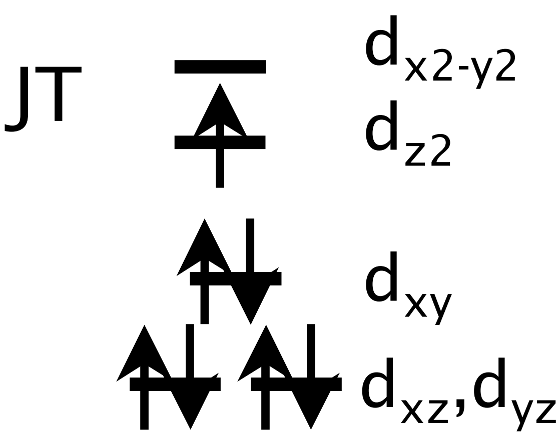


$P6_322$

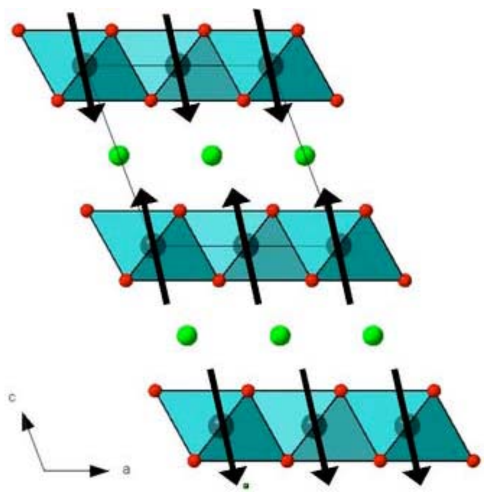


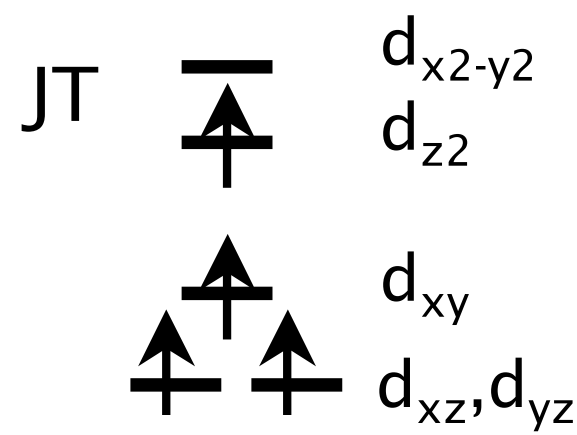
“Normal” situation: JT distortion

$NaNiO_2$



Ni^{3+} $3d^7$ LS

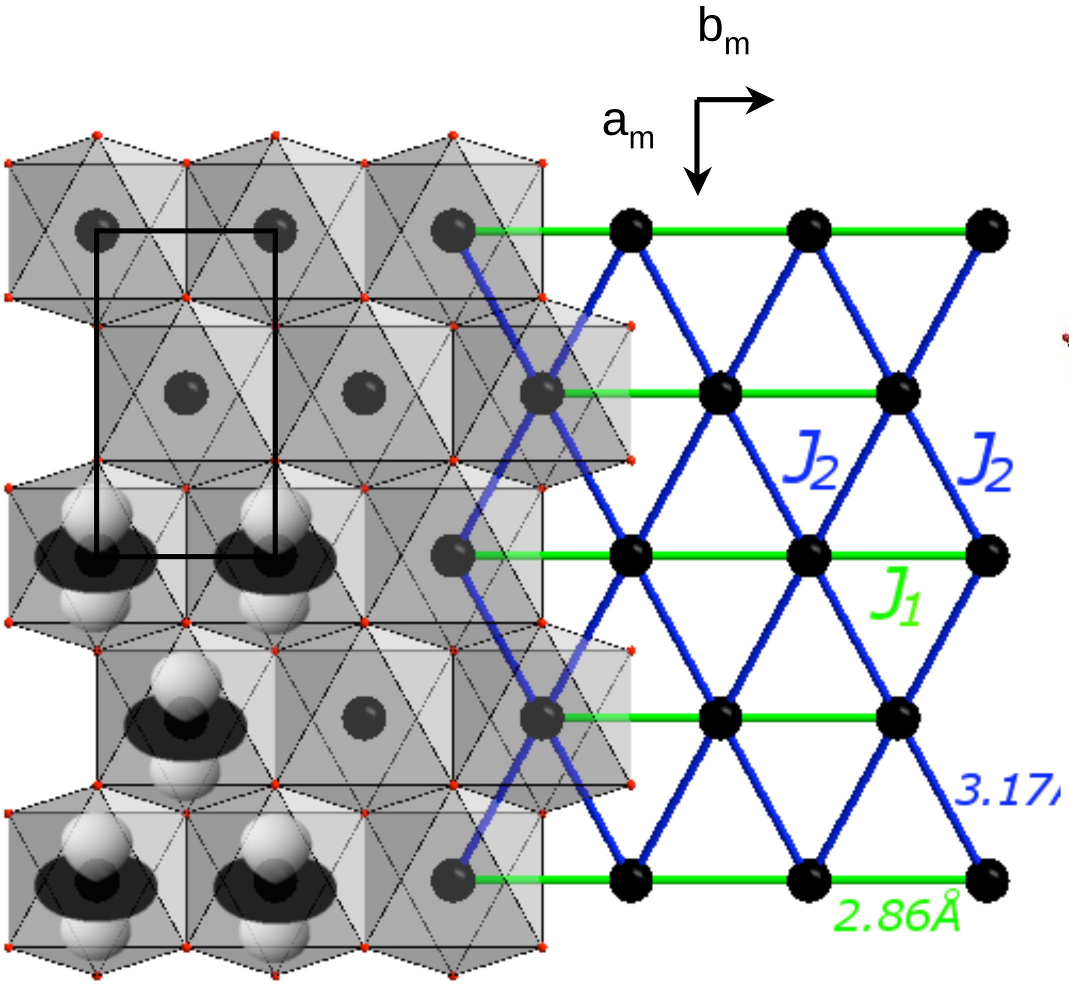




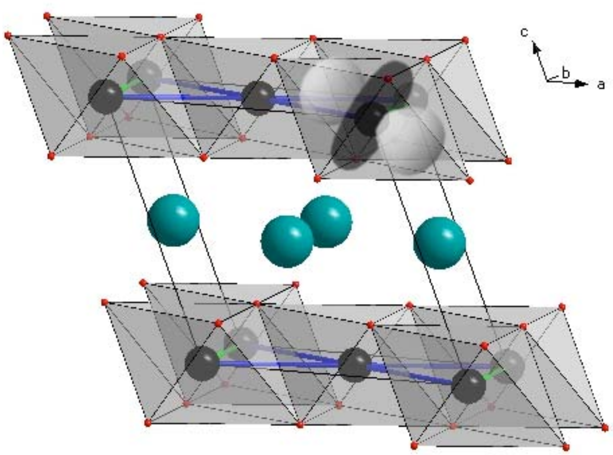
Mn^{3+} $3d^4$ HS (S=2)

JT = Jahn Teller distortion

$NaMnO_2$, $NaNiO_2$, ($LiNiO_2$?[1])

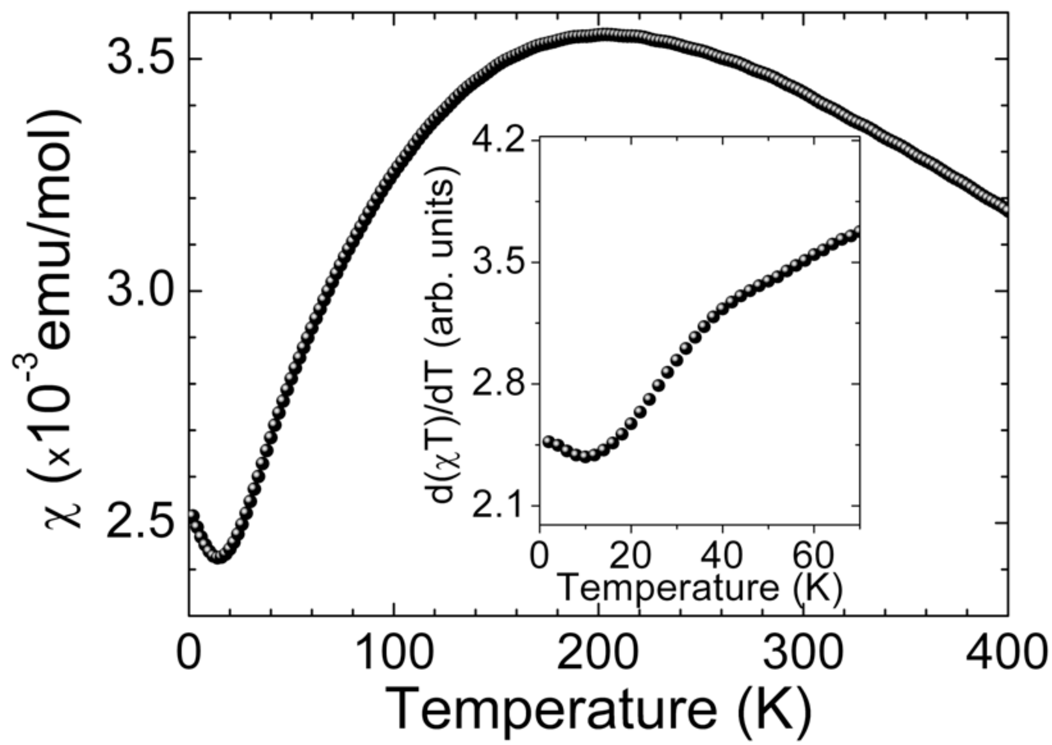


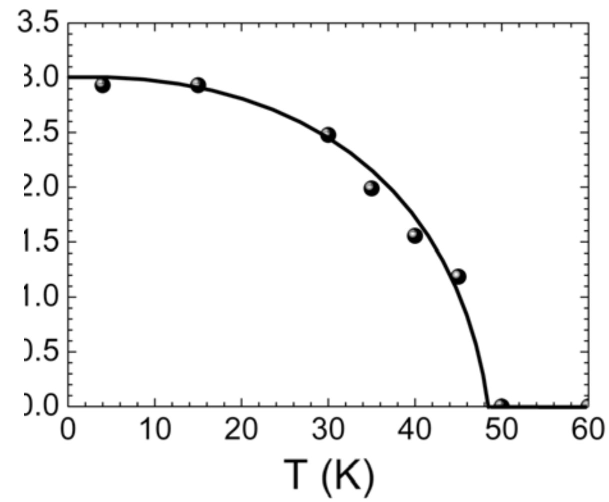
$C2/m$ ($R\bar{3}m$)



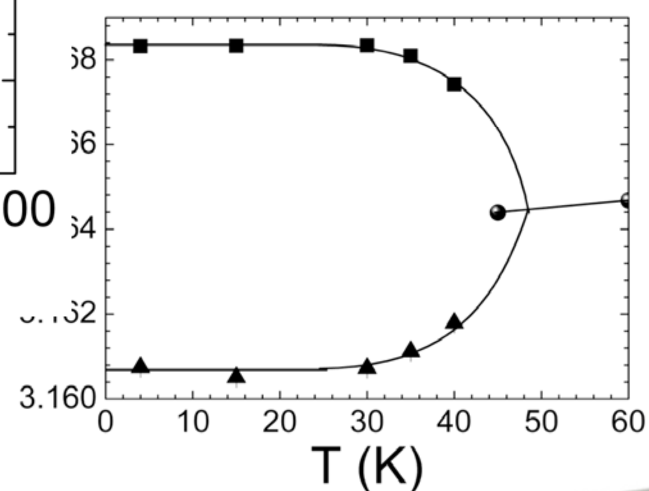
[1] Chung JH, Proffen T, Shamoto S, et al.
Local structure of **LiNiO2** studied by neutron diffraction
PHYSICAL REVIEW B 71 (6): Art. No. 064410 FEB 2005

$NaMnO_2$ – lifting of degeneracy

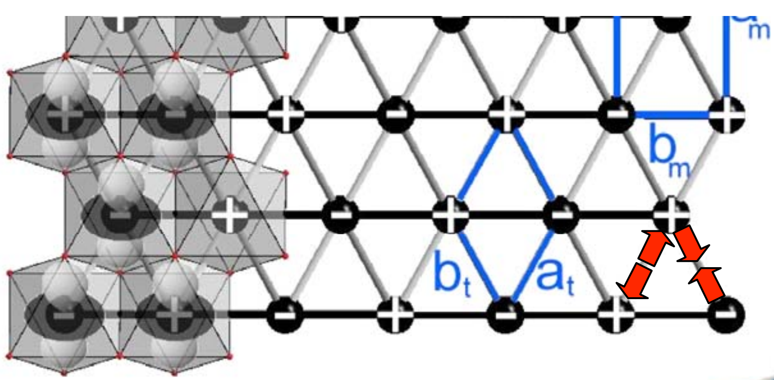




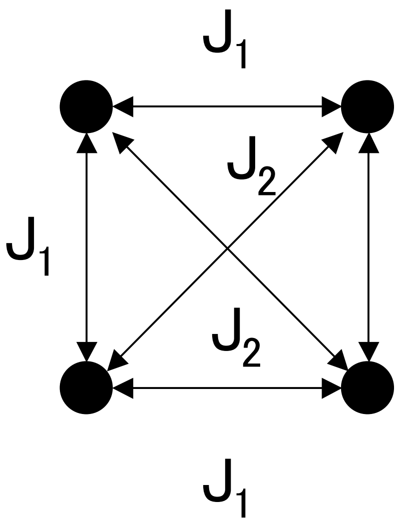
moments

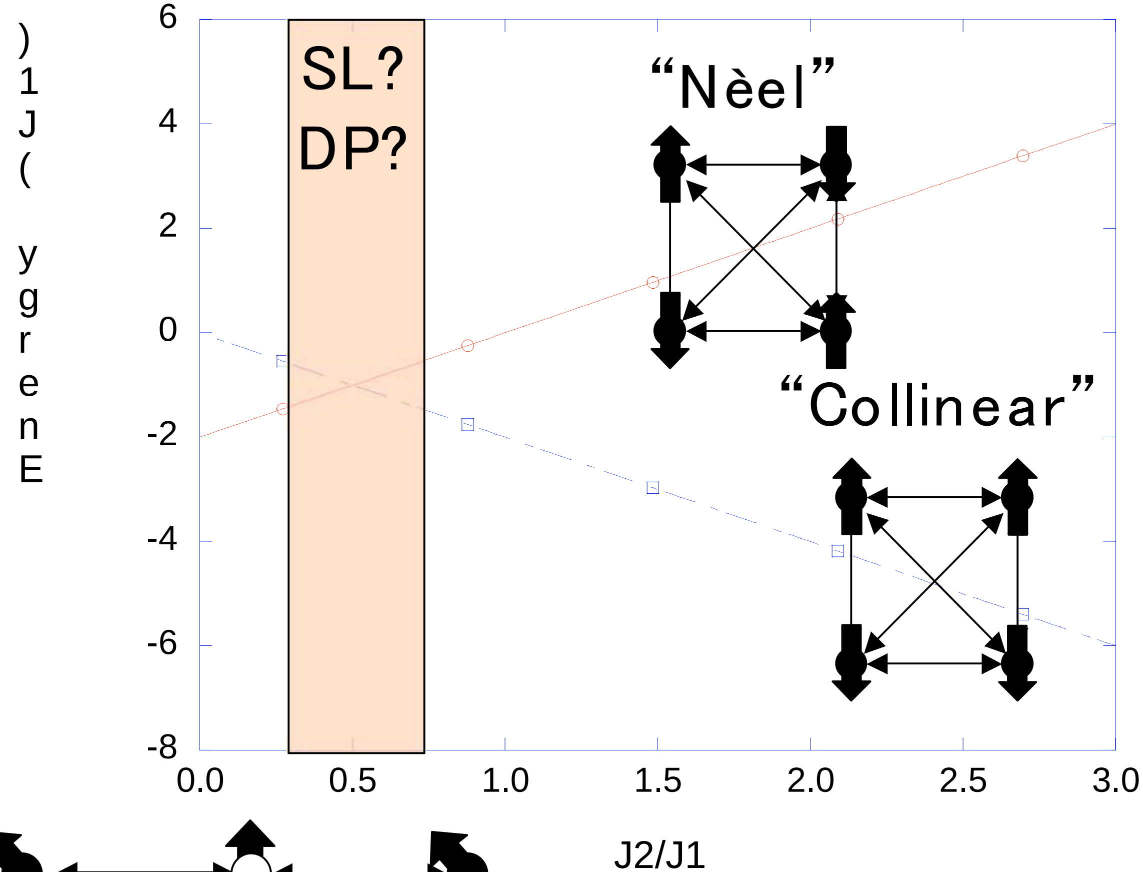


lattice



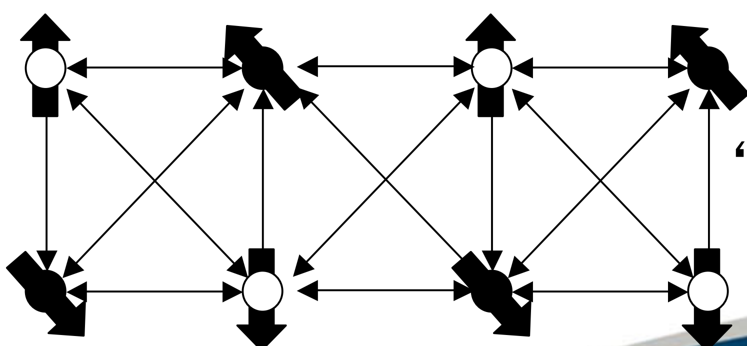
J_1-J_2 model





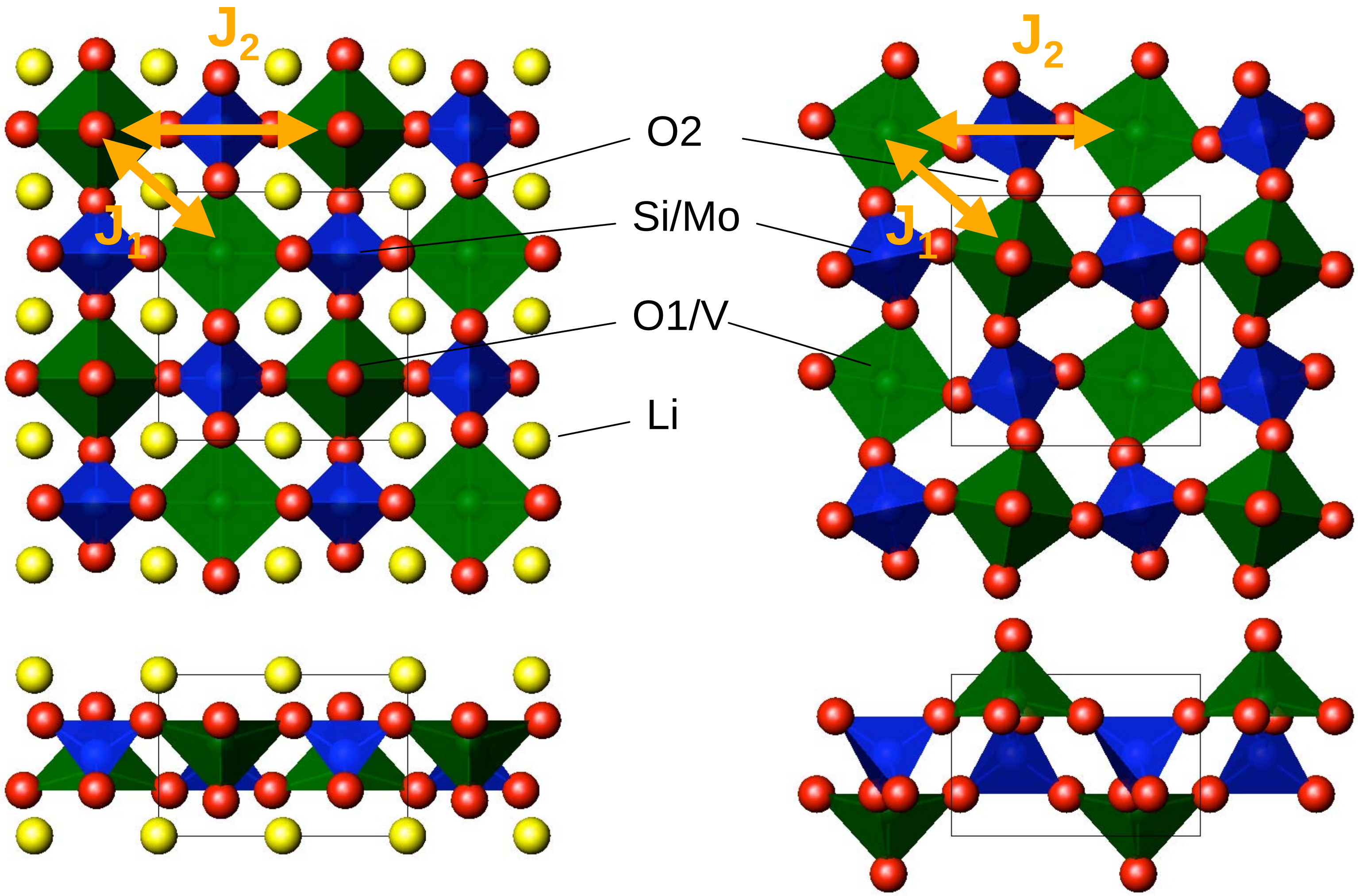
$E_{Neel} = -2\,J_1 + 2\,J_2$

$E_{Coll.} = -2\,J_2$



"Order from disorder"

Li_2VOSiO_4 $VOMoO_4$

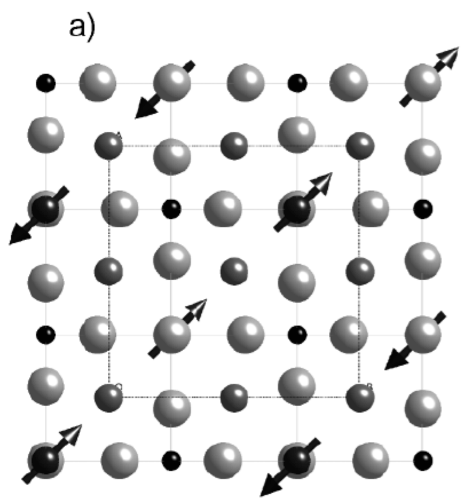


P4 / n   P4 / n m m

VOLUME 93, NUMBER 2 PHYSICAL REVIEW LETTERS week ending 9 JULY 2004

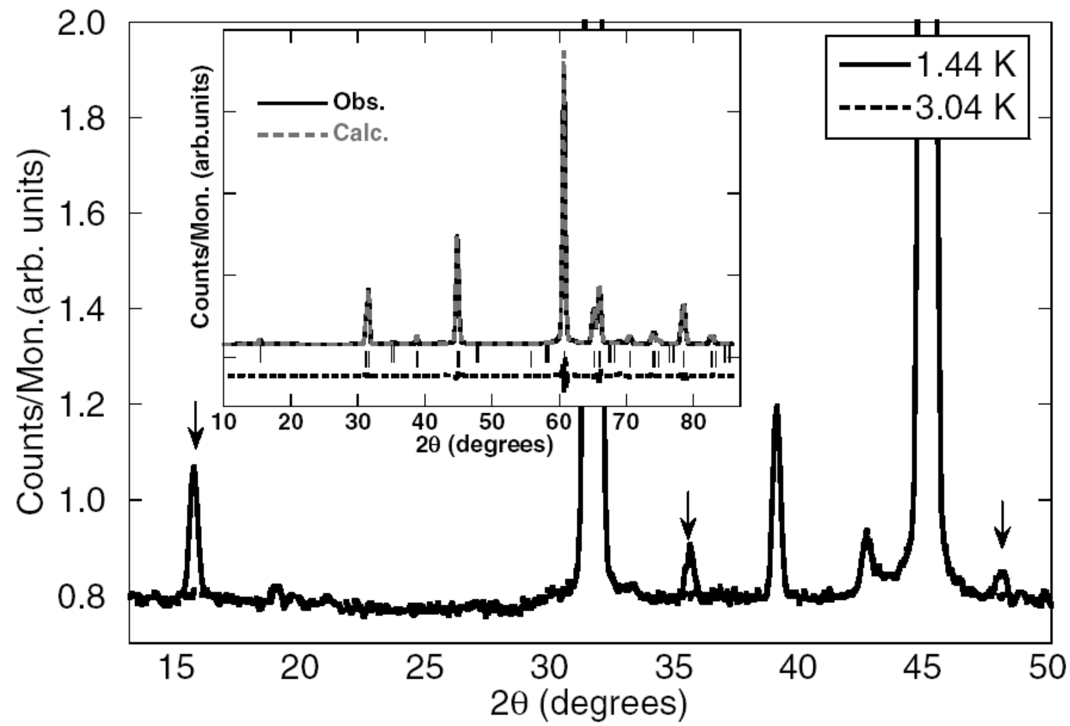
Direct Determination of the Magnetic Ground State in the Square Lattice $S = 1/2$ Antiferromagnet Li_2VOSiO_4

A. Bombardi,[1] J. Rodriguez-Carvajal,[2] S. Di Matteo,[3,4] F. de Bergevin,[1] L. Paolasini,[1] P. Carretta,[5] P. Millet,[6] and R. Caciuffo[7]



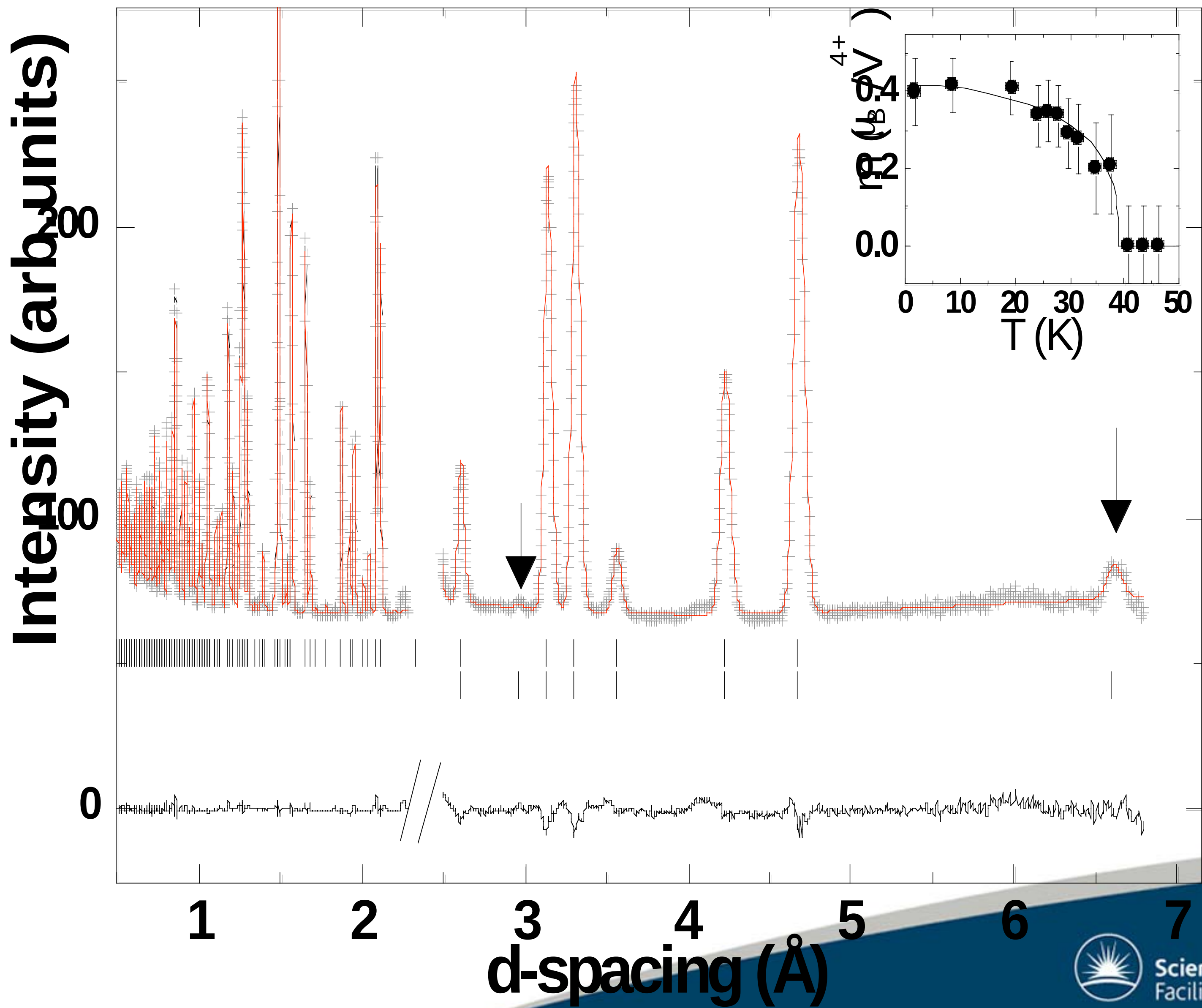
$$\mathbf{k} = \frac{1}{2}, \frac{1}{2}, 0$$

$$m \quad 0.633\,\mathrm{m}_B$$

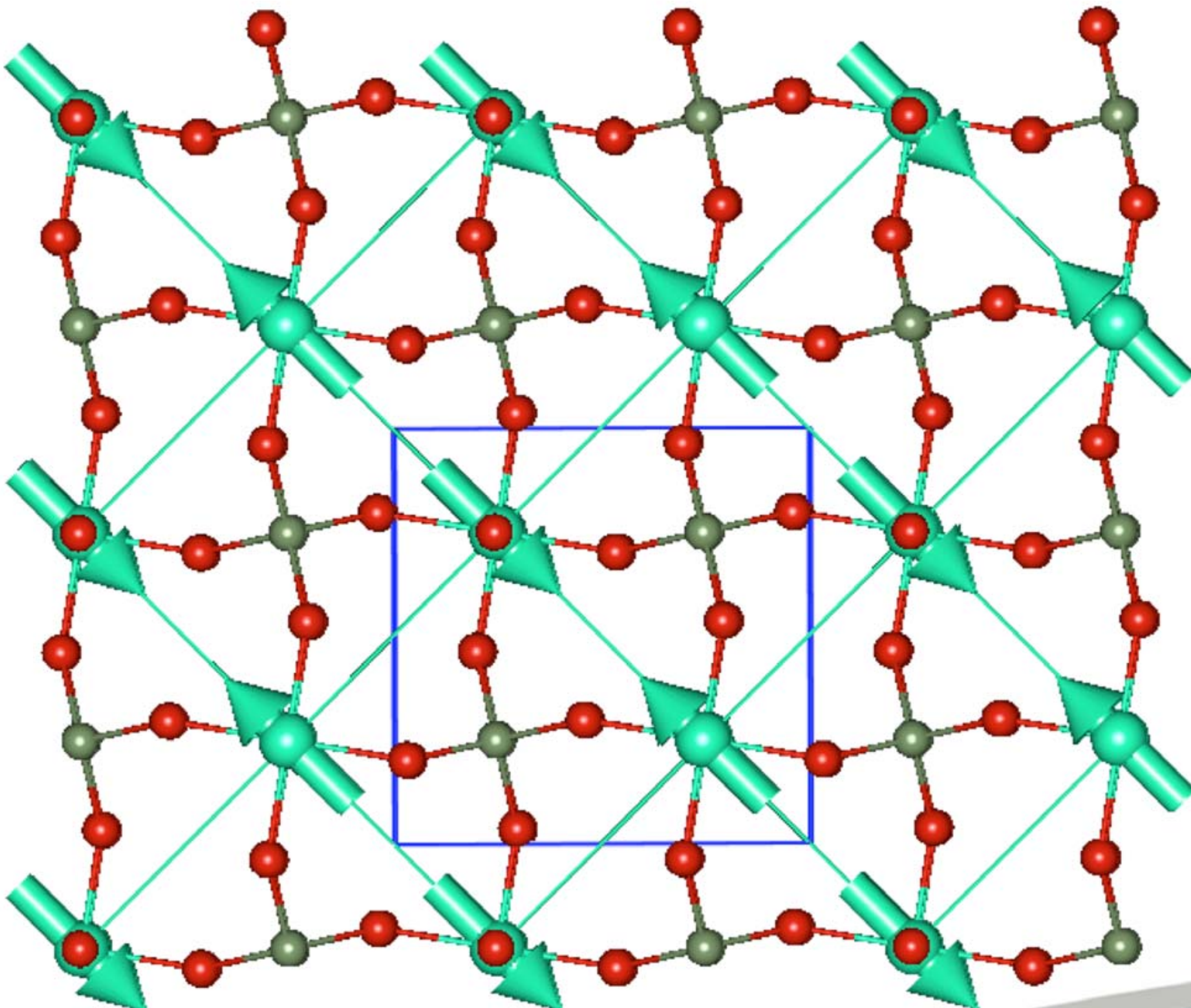


GEM

$VOMoO_4$: NPD data

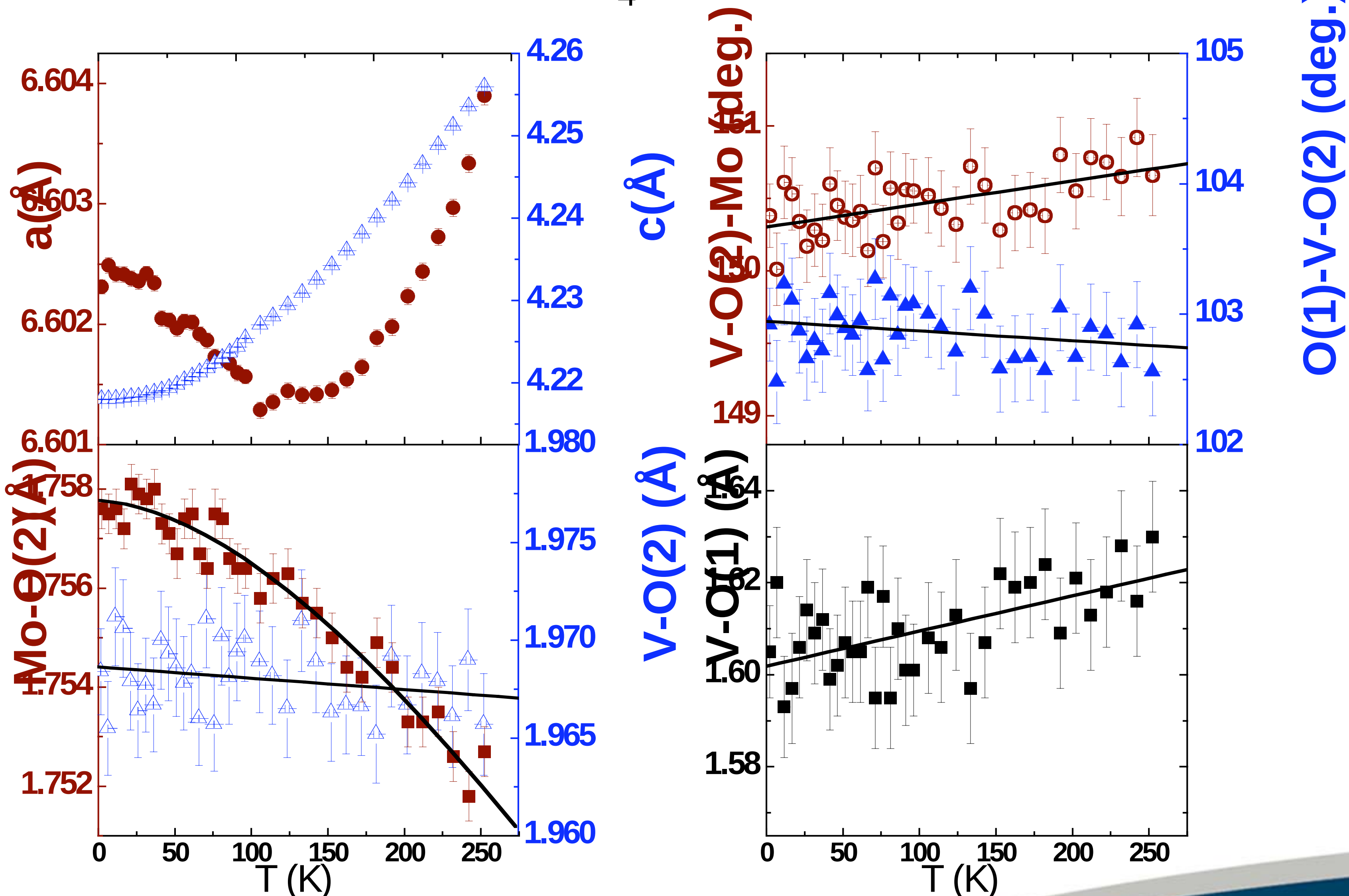


$VOMoO_4$: Magnetic Structure



$\vec{k} = 0$

VOMoO$_4$: Structural anomalies



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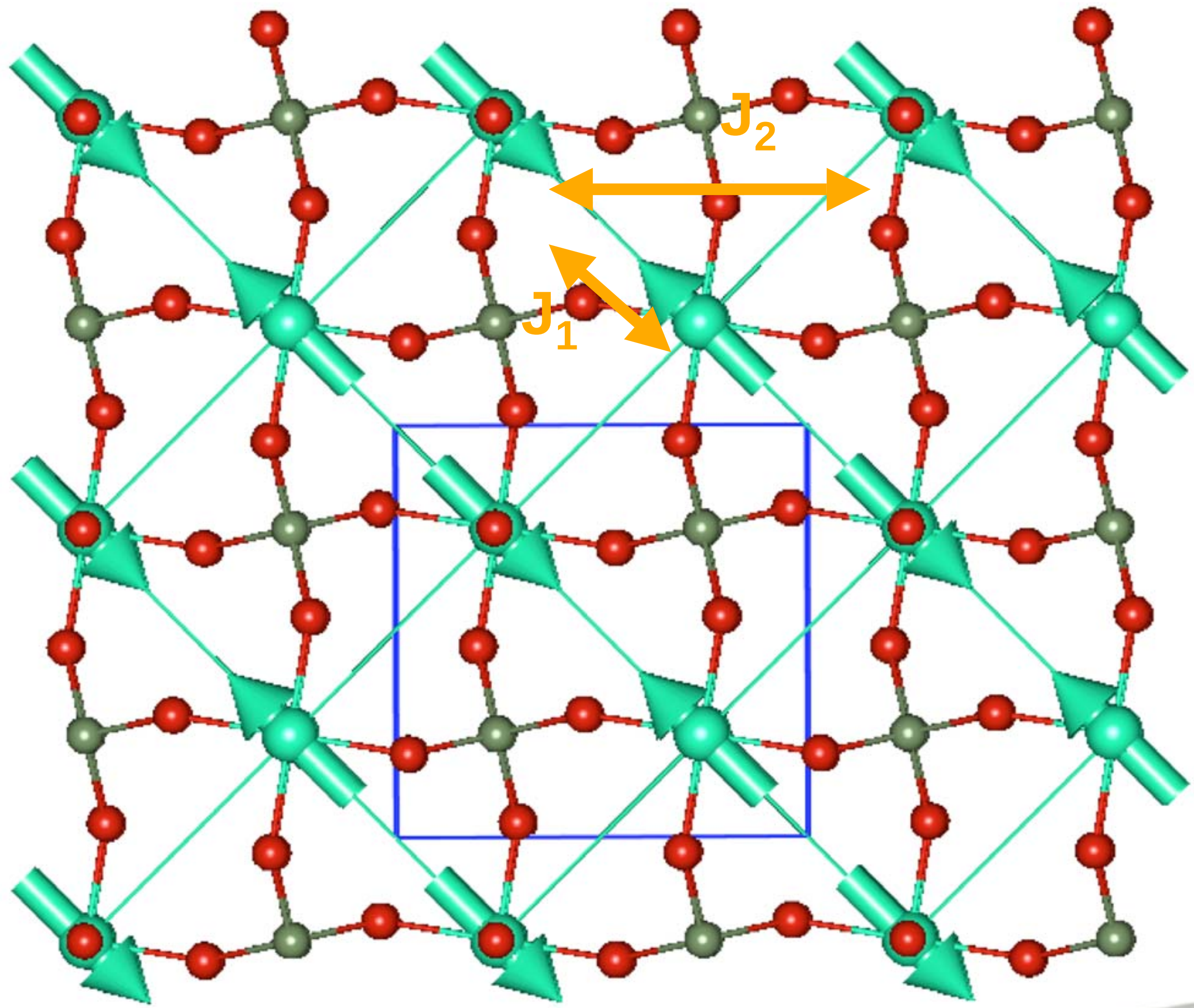
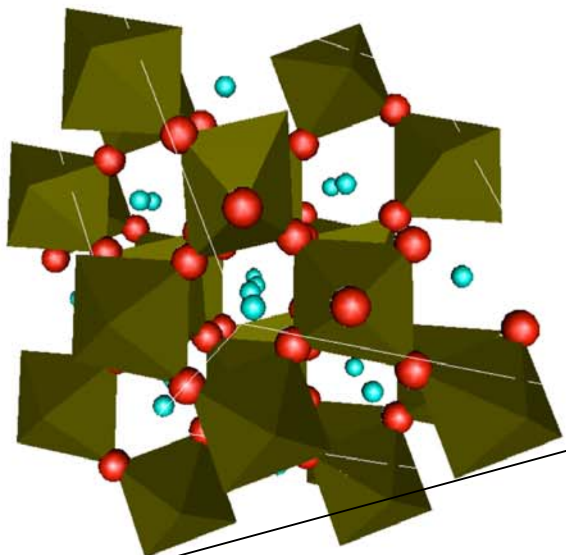
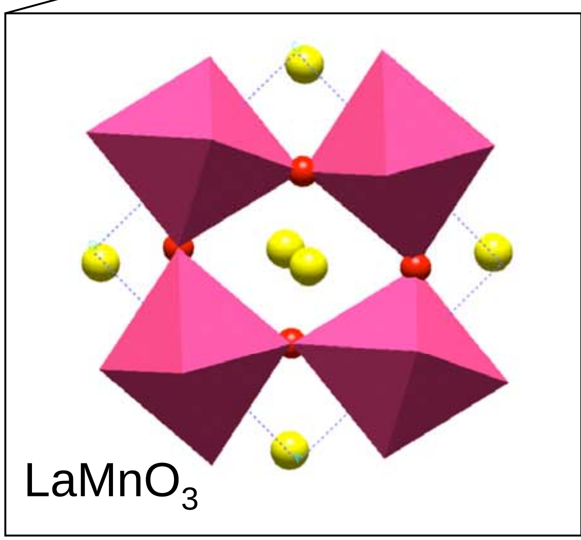
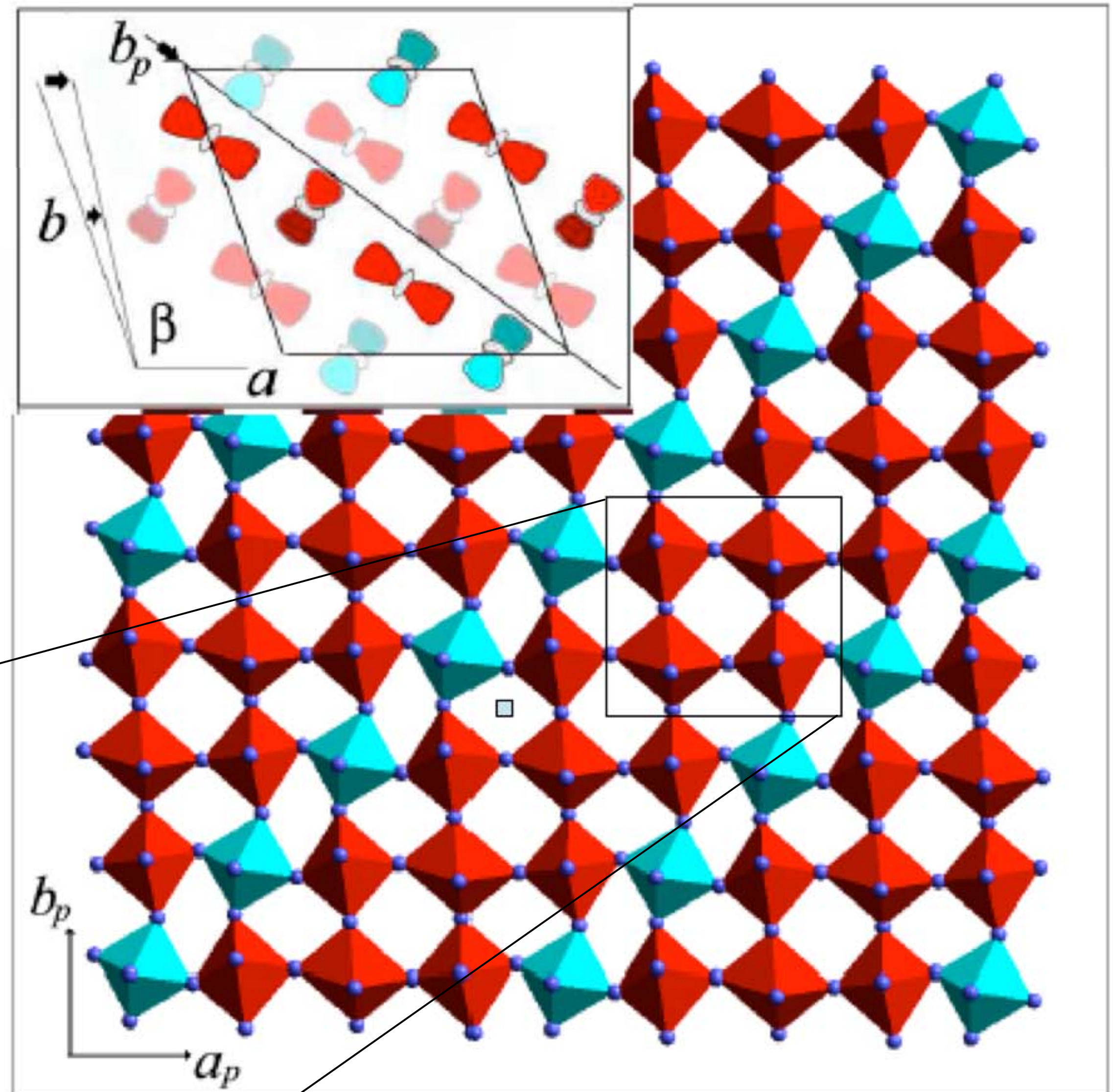
$VOMoO_4$: origin of the structural anomalies



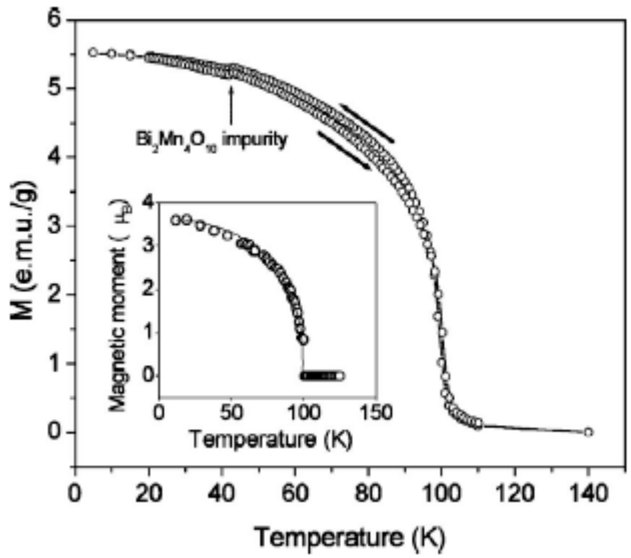
$BiMnO_3$

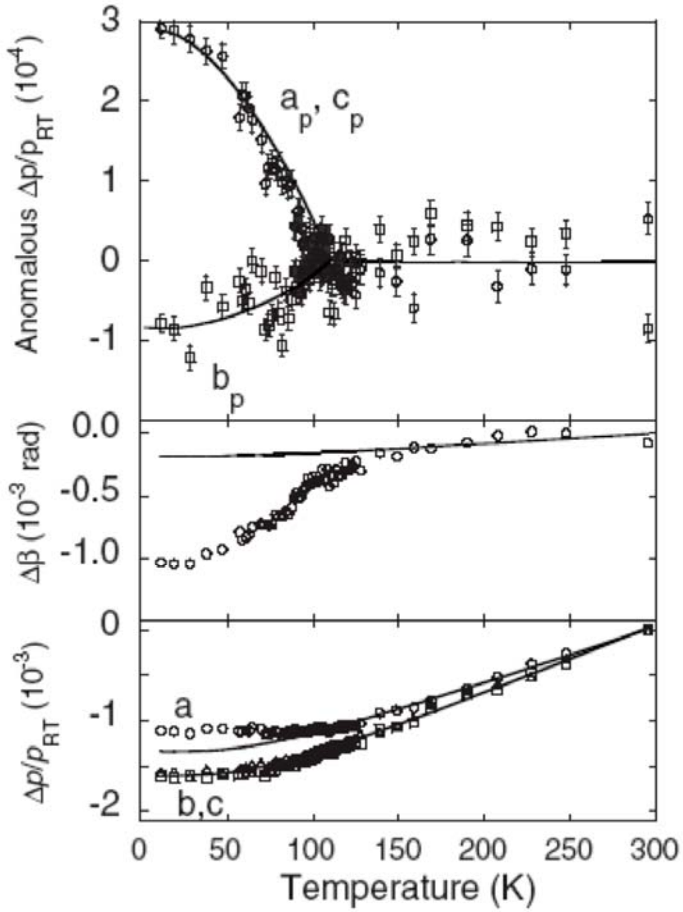


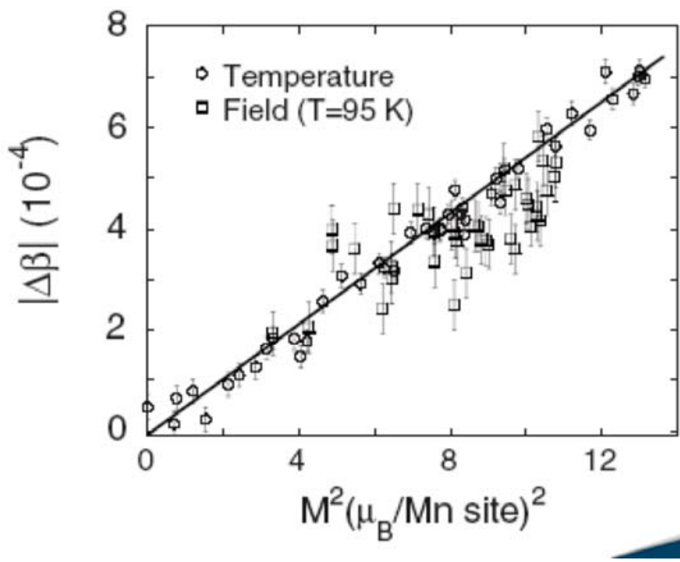




$BiMnO_3$ – magneto-elastic coupling







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letters to nature

Magnetic control of ferroelectric polarization

T. Kimura[1*], T. Goto[1], H. Shintani[1], K. Ishizaka[1], T. Arima[2] & Y. Tokura[1]

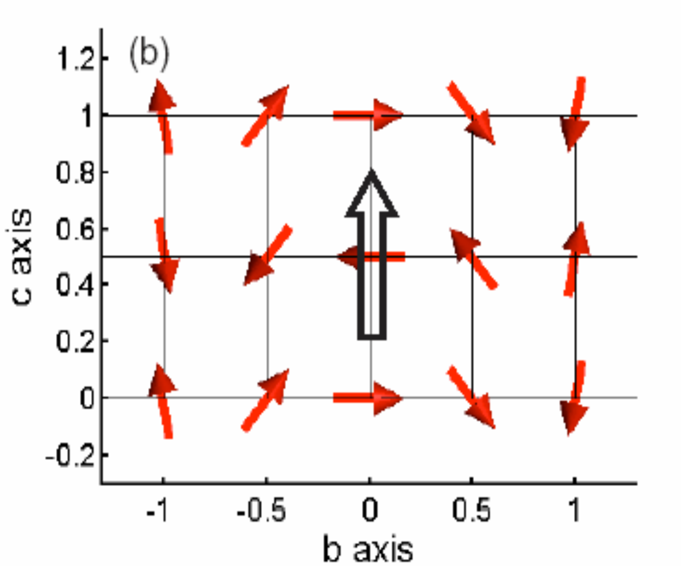
[1]*Department of Applied Physics, University of Tokyo, Tokyo 113-8656, Japan*
[2]*Institute of Materials Science, University of Tsukuba, Tsukuba 305-8573, Japan*

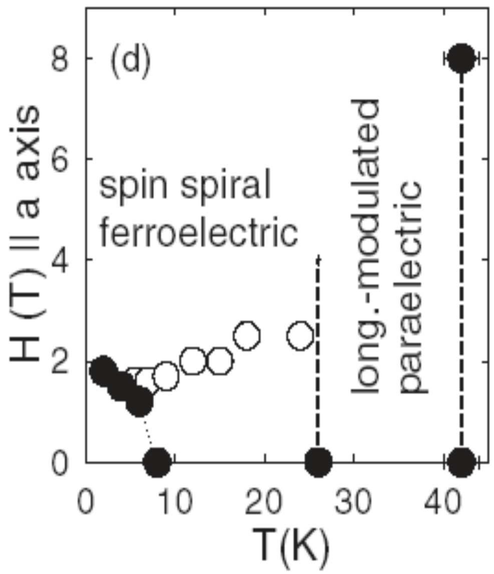
* Present address: Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

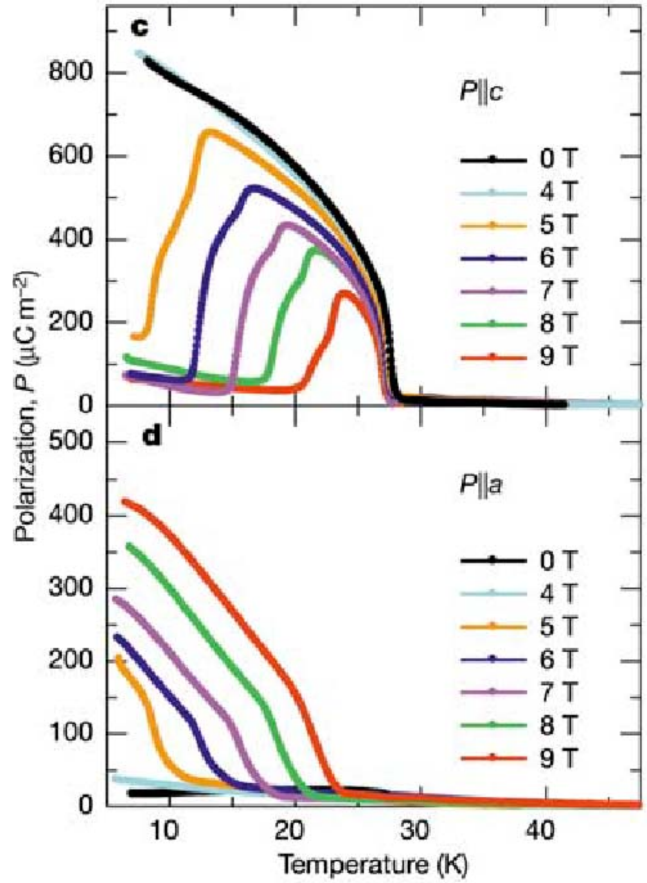
sinusoidal antiferromagnetic ordering. The modulated magnetic structure is accompanied by a magnetoelastically induced lattice modulation, and with the emergence of a spontaneous polarization. In the magnetic ferroelectric $TbMnO_3$, we found gigantic magnetoelectric and magnetocapacitance effects, which can be attributed to switching of the electric polarization induced by magnetic fields. Frustrated spin systems therefore provide a new area to search for magnetoelectric media.

The room-temperature crystal structure of $TbMnO_3$ investigated here is the orthorhombically distorted perovskite structure (space group *Pbnm*; Fig. 1a). We note that the perovskite structure of

$TbMnO_3$

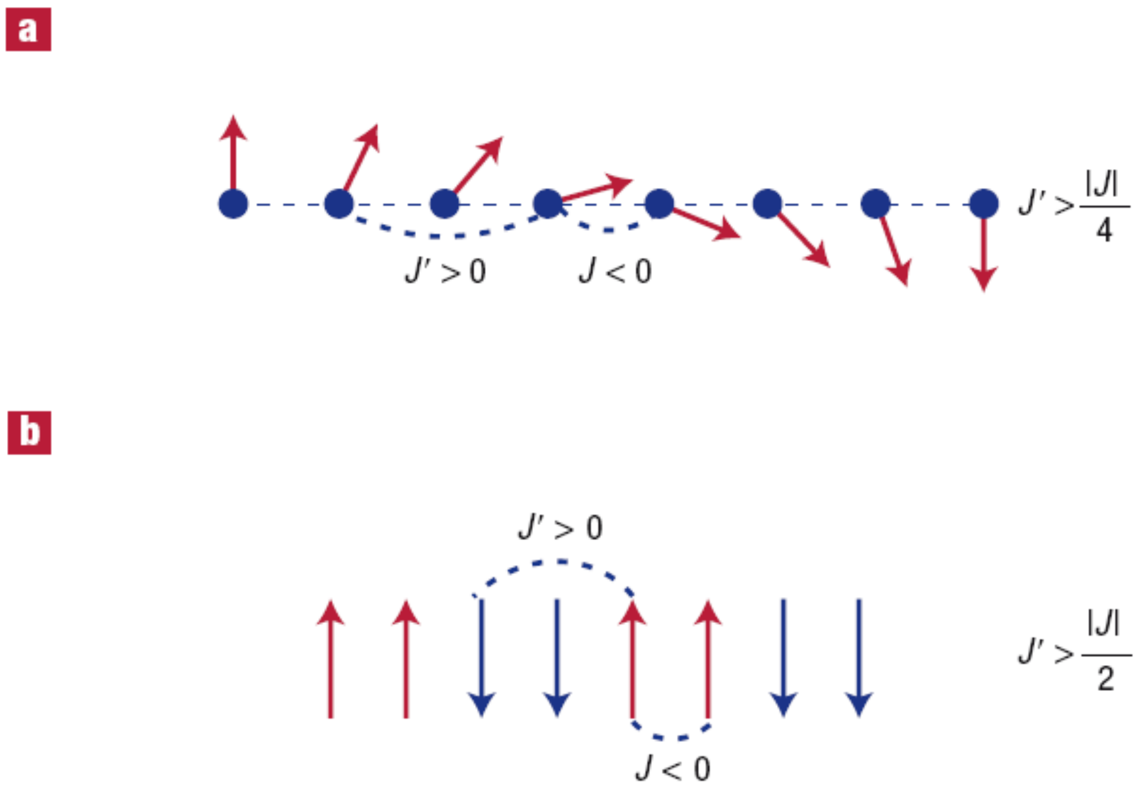




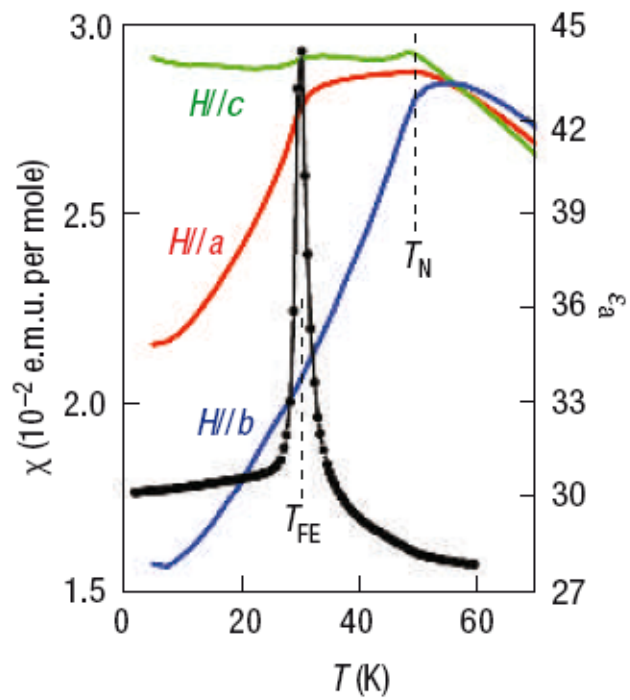


M. Kentzelmann *et* al., PRL **95,** 087206 (2005)

What stabilises spirals?



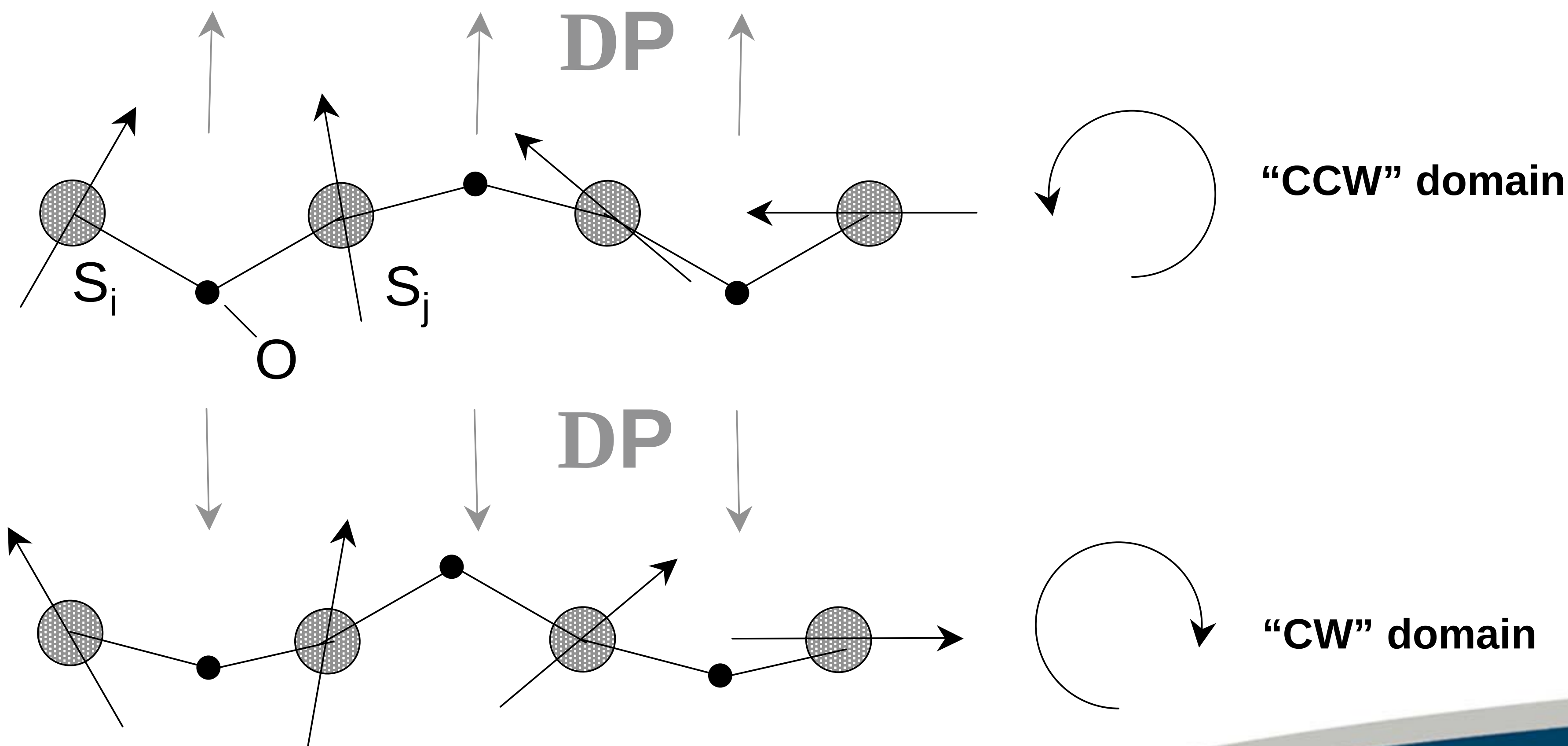
$TbMnO_3$



Other materials - $Ni_3V_2O_8$, delafossite, $CuFeO_2$,spinel $CoCr_2O_4$, $MnWO_4$…

S.-W. Cheong & M. Mostovoy, Nature Materials **6** 13 (2007)

FE domain with spirals ($TbMnO_3$)



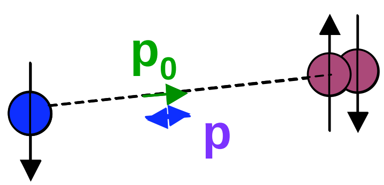
What if dipole moments already exist?

$$\mathbf{p} \propto r_{ij} \times (S_1 \times S_2)$$

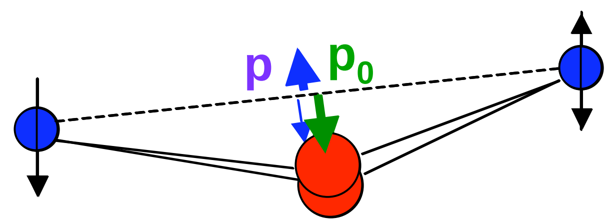
Vector Coupling – Requires non-collinearity

$$\mathbf{p} = \mathbf{p}_0 (S_1 \cdot S_2)$$

Scalar Coupling – Works with collinear spins



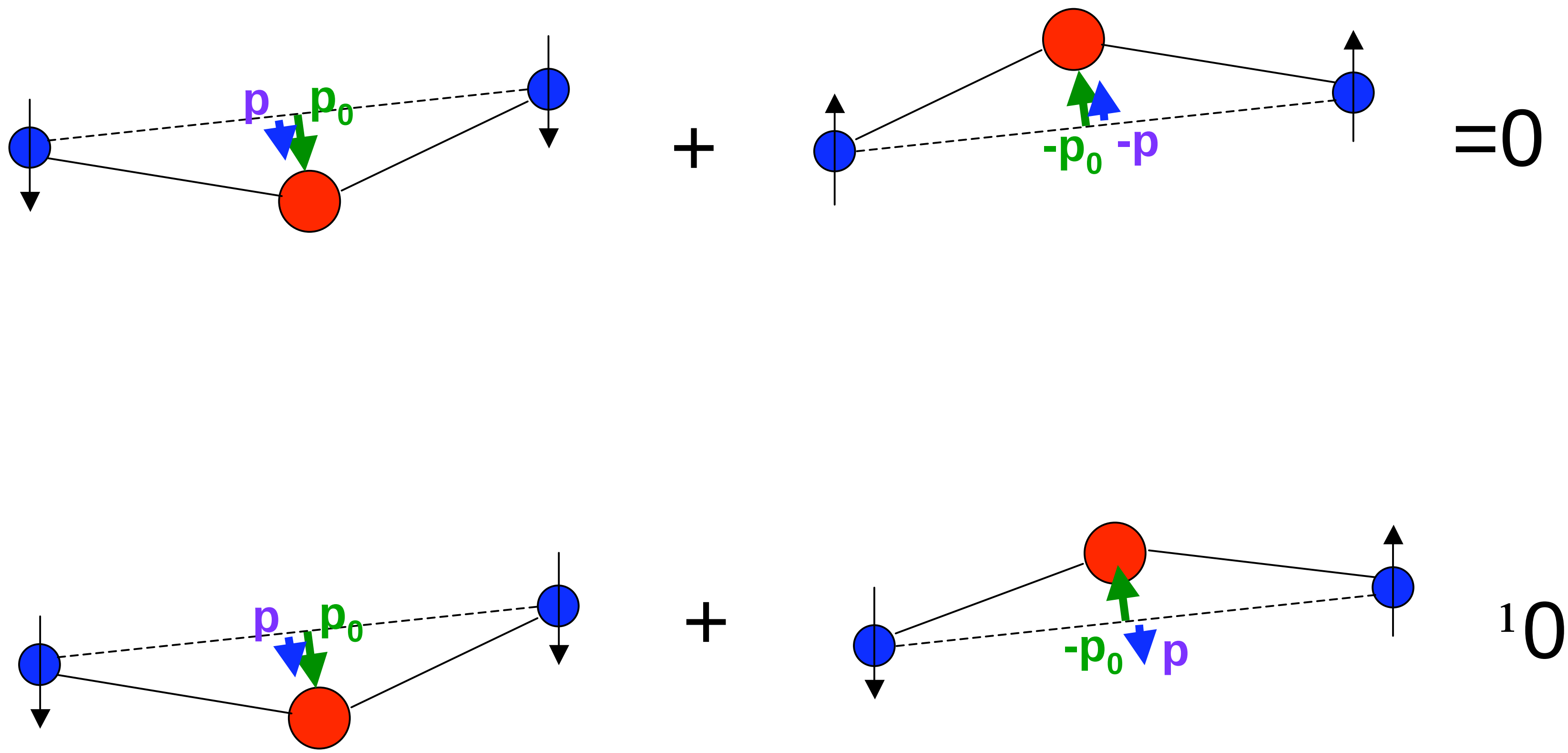
Direct exchange striction



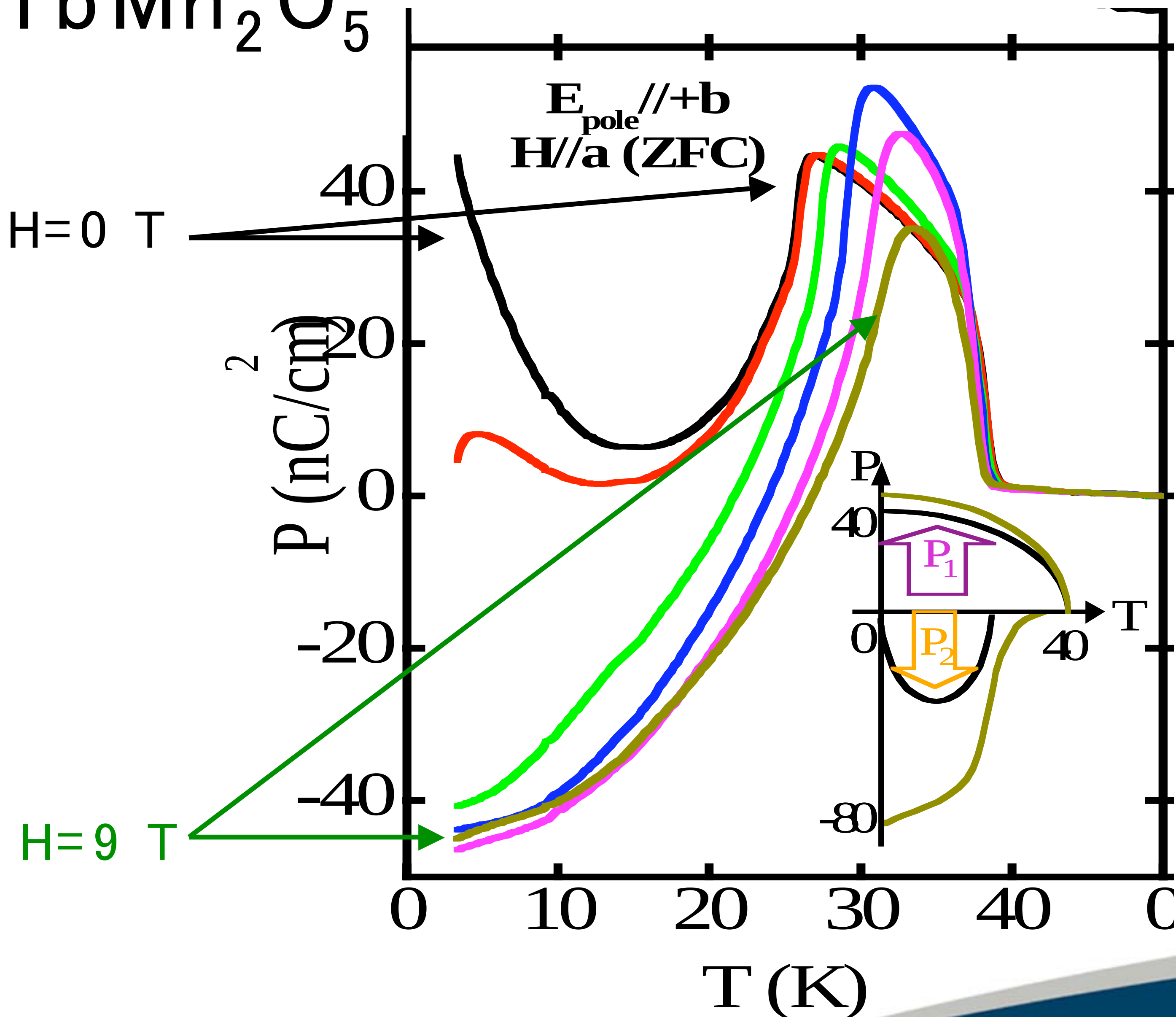
Superexchange striction

How to avoid cancellations
Role of frustration

Through centre of symmetry



$TbMn_2O_5$

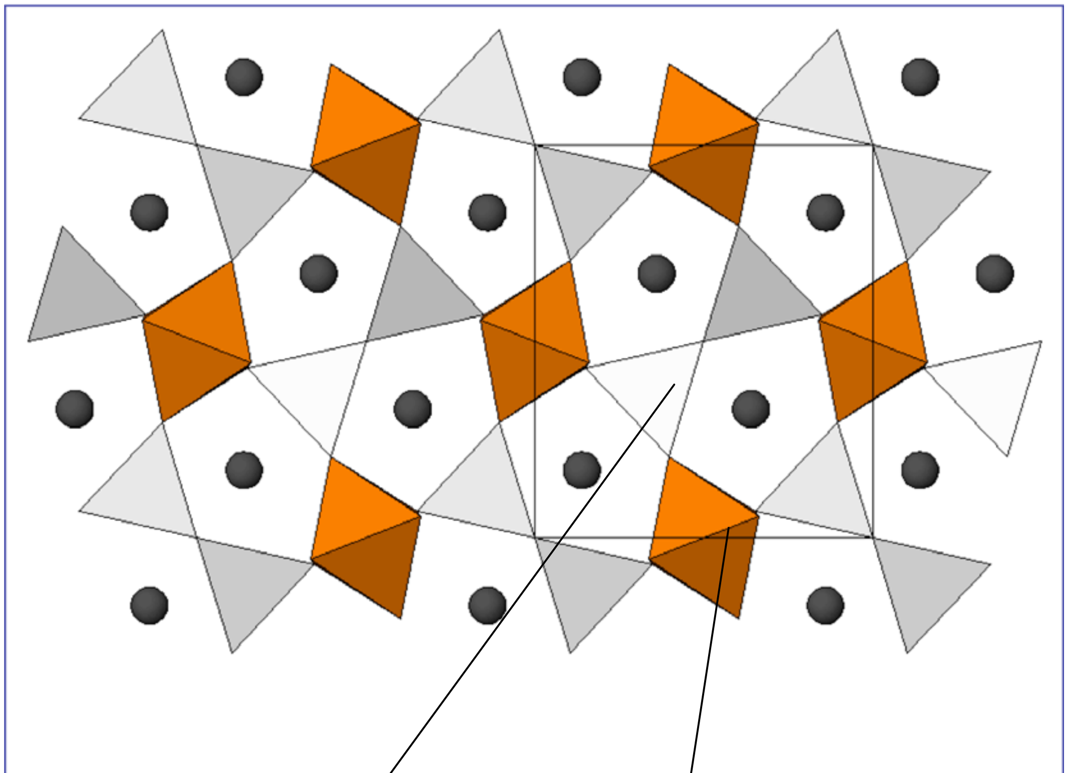


N. Hur et al. Nature, 429, 392 (2004)

Crystal structure of $REMn_2O_5$

- *Pbam symmetry*
- edge sharing octahedra along the c-axis.
- Mn^{3+}/Tb^{3+} layers alternate

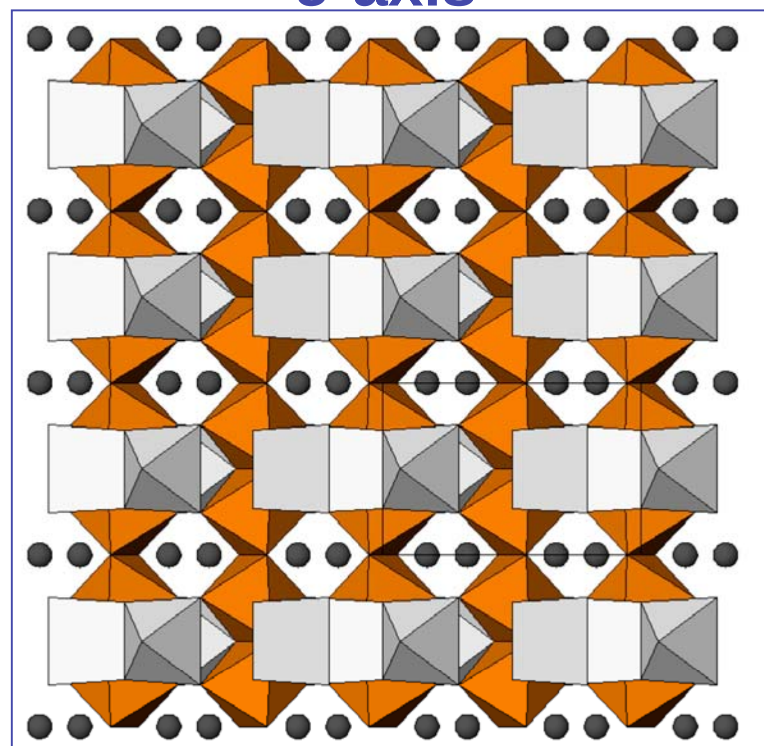
***ab*-plane**



$Mn^{3+}O_5$

$Mn^{4+}O_6$

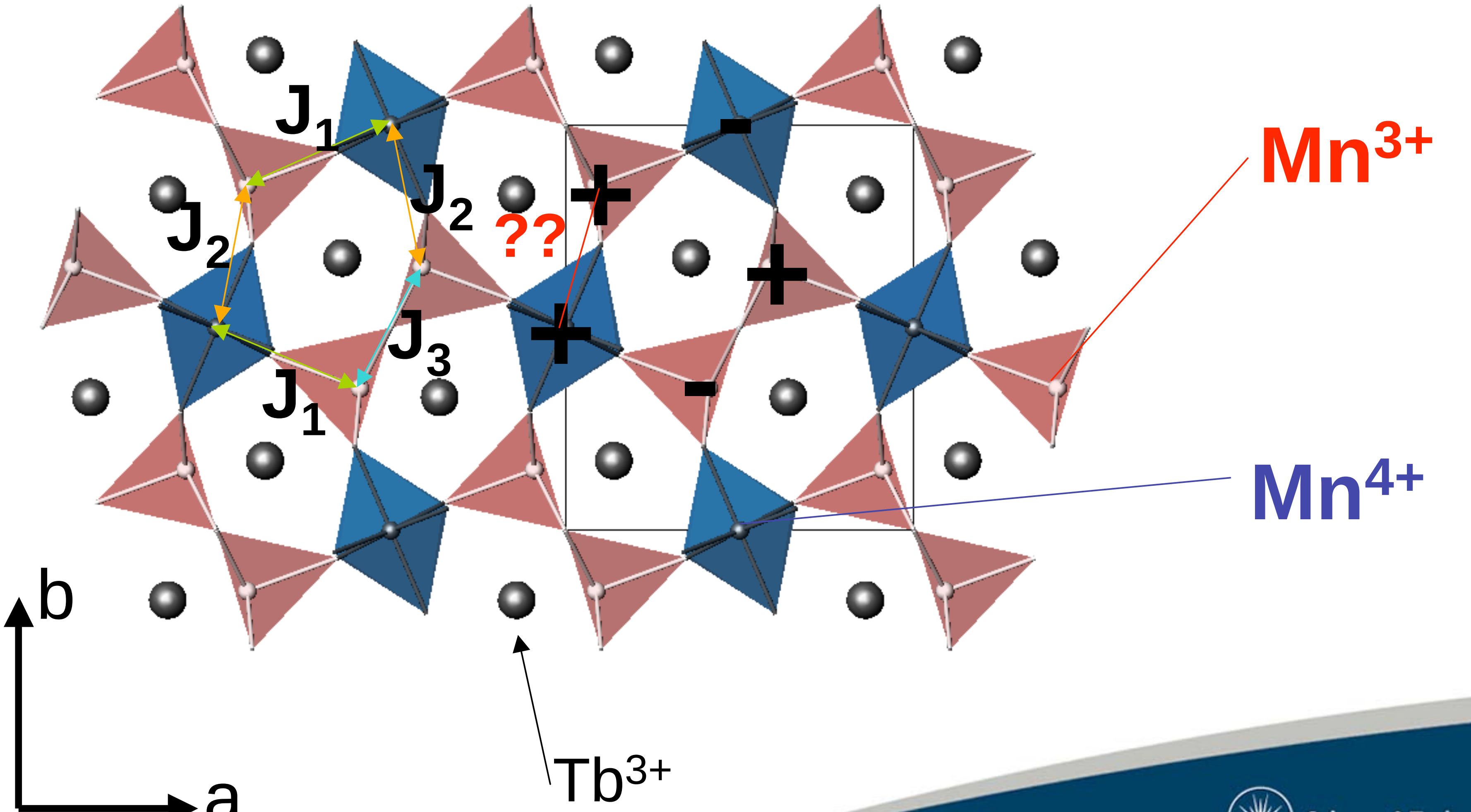
***c*-axis**



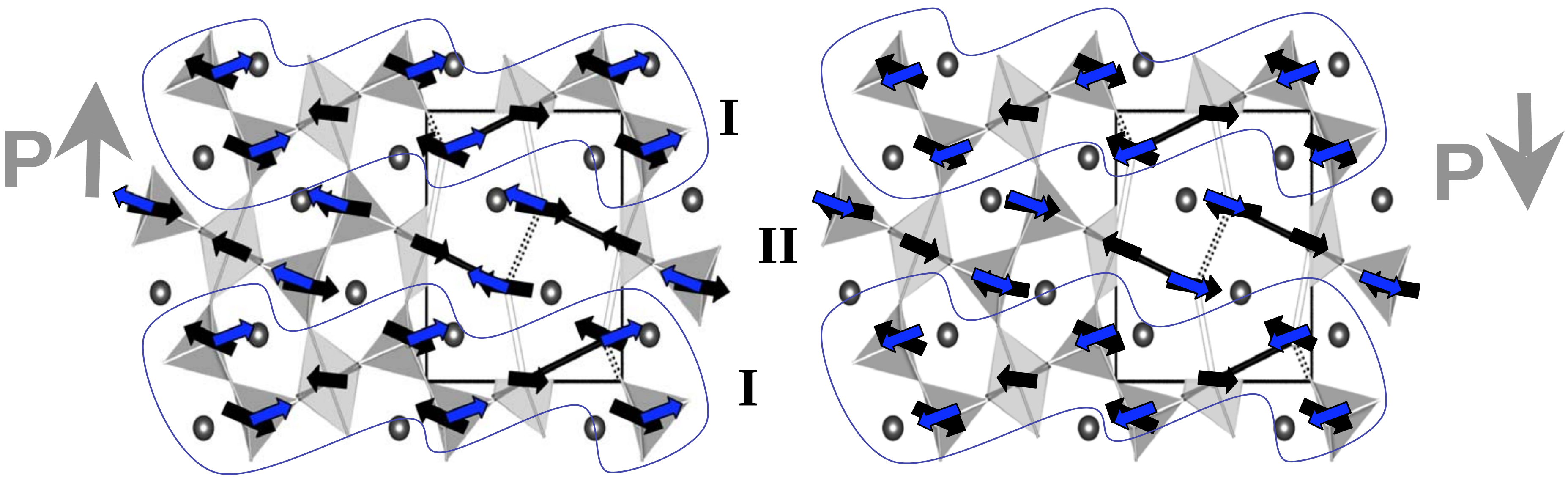
Frustration in RMn_2O_5

Space group *Pbam.*

- Competing-interactions in the ab-plane



Ferroelectric Domains



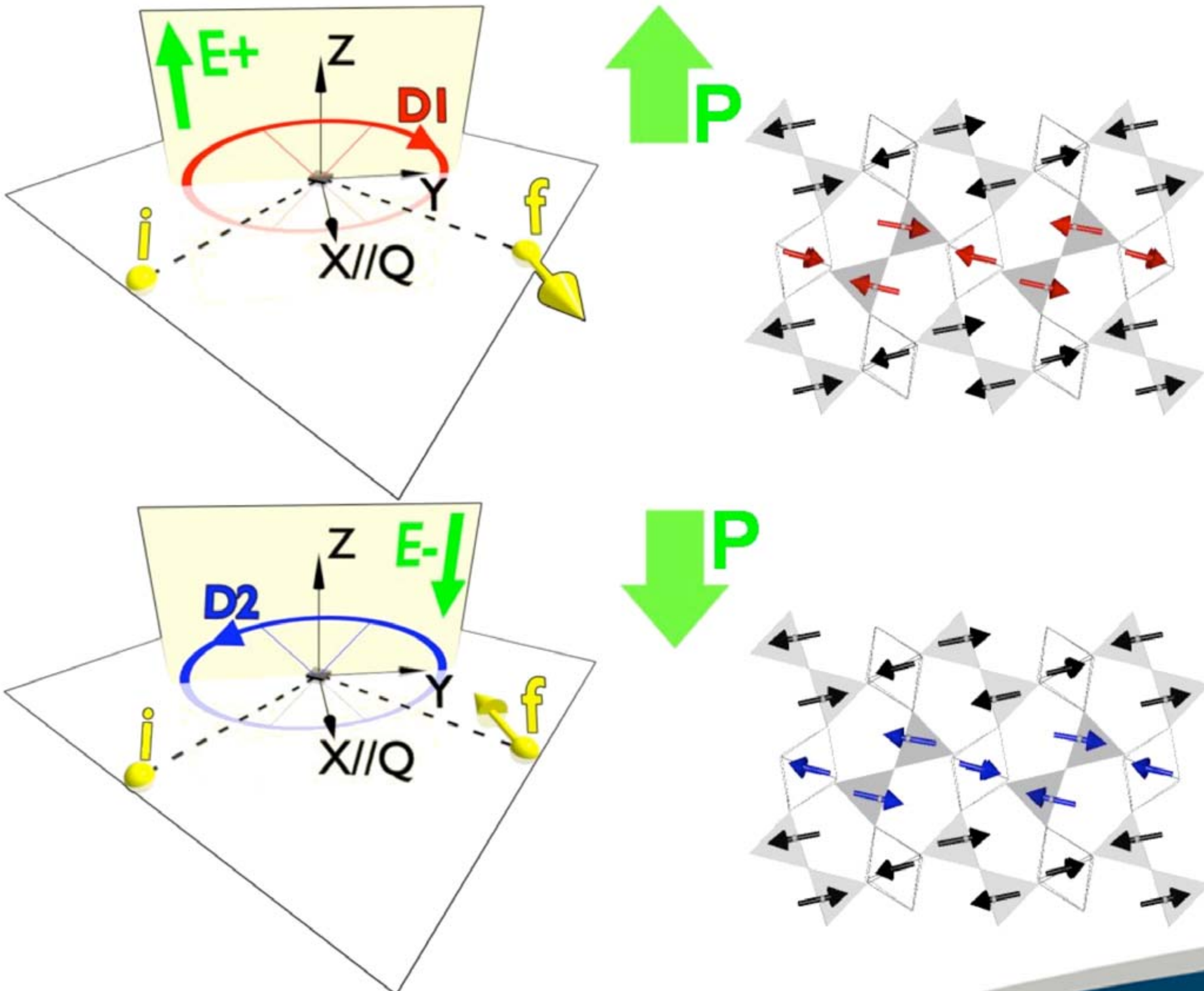
•The orientation of P in the b-direction is determined by the **phase relation between chain I and II**.

•By flipping one or both chains in the magnetic structure we can obtain 4 domains

(++)b^+ (--)b^+ (+-)b^- (-+) b^-.

•Phase coherence *between* layers is required to have P≠0

Neutron Spherical Polarimetry



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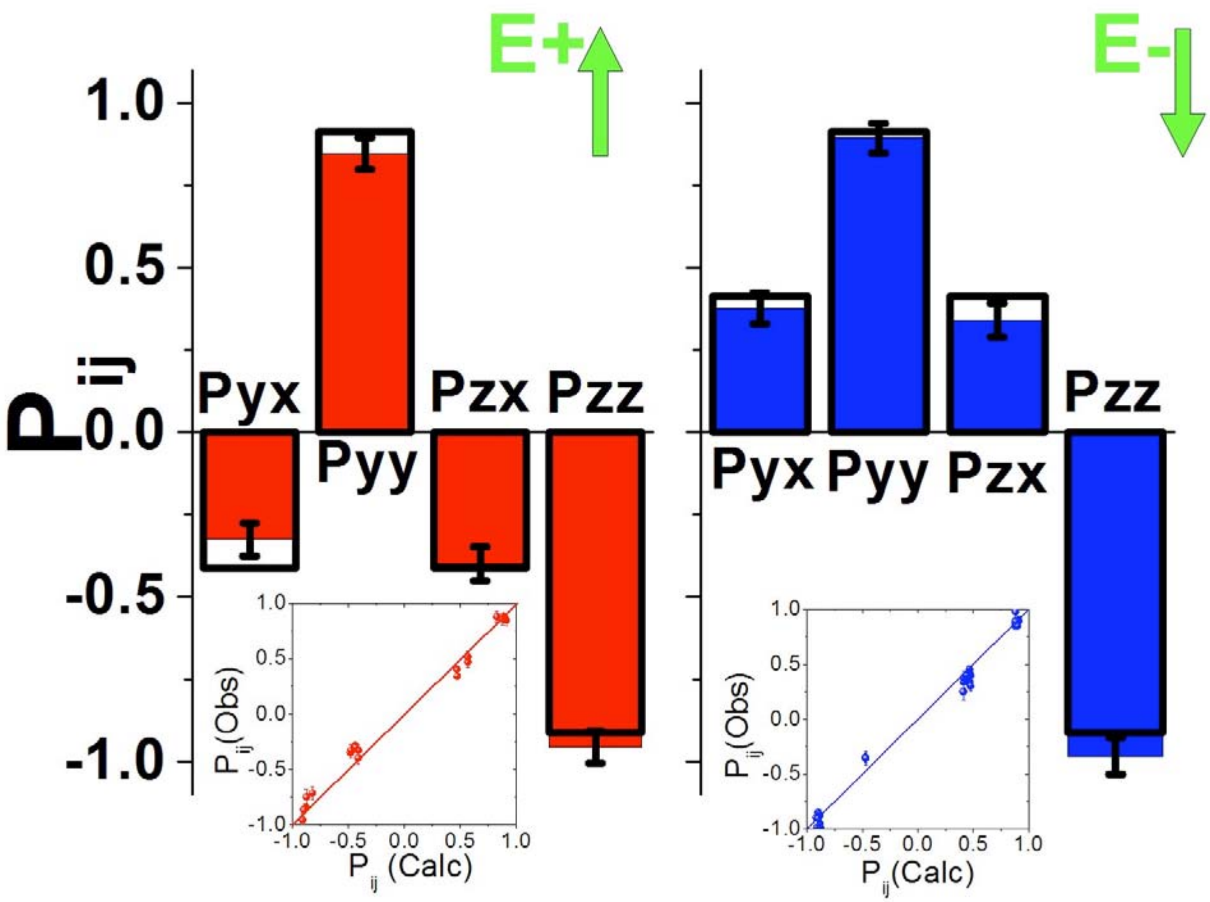
Field-cooling 25 K



Hysteresis loop – 35 K