Ferro-axial multiferroics: A novel combination of magnetic & polar order

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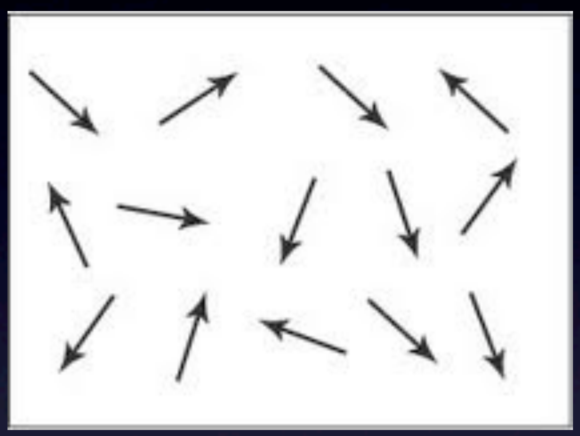
Outline

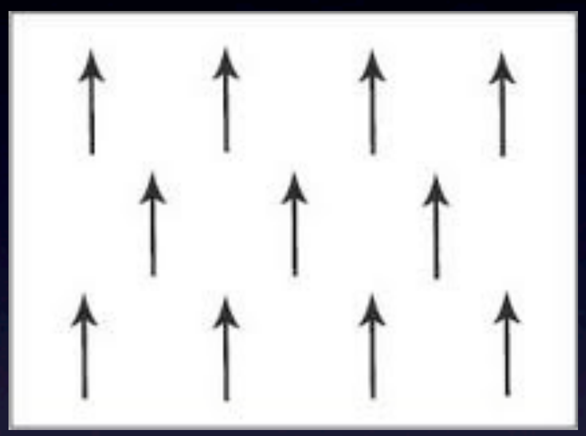
- Introduction
  - Importance, & why they are scarce
- Typical suspects
  - Mixed perovskites
  - Hexagonal manganites
  - Charge Order
  - Spiral spin systems
- Ferro-axial multiferroics: the case of $Cu_3Nb_2O_8$

Ferroics

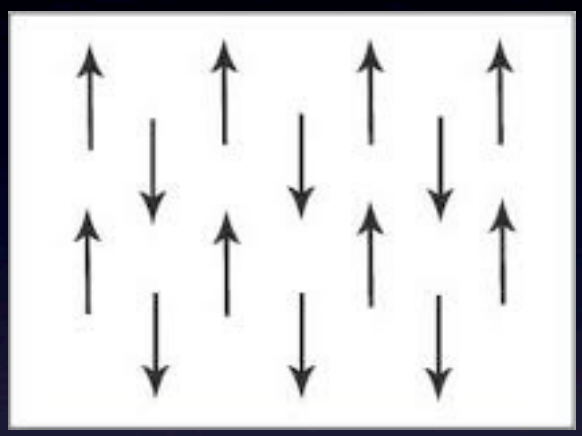
Ferro-'magnets' : long range ordering of magnetic moments



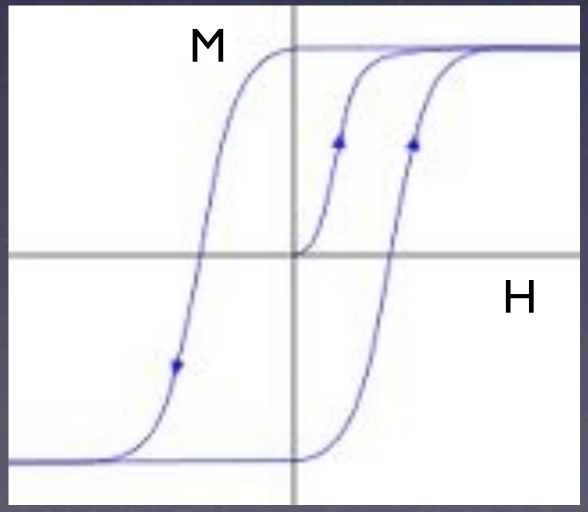
Para magnet



Ferro magnet



antiferro magnet

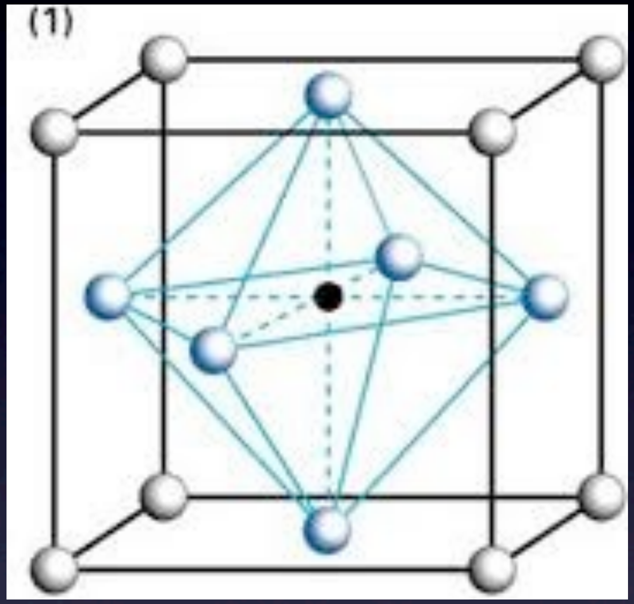


Ferromagnetic hysteresis

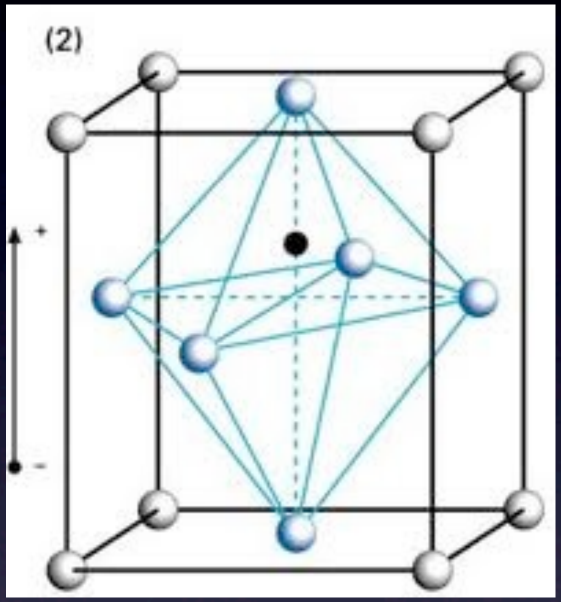
Ferroics

Ferro-‘electrics’: long range ordering of electric dipoles

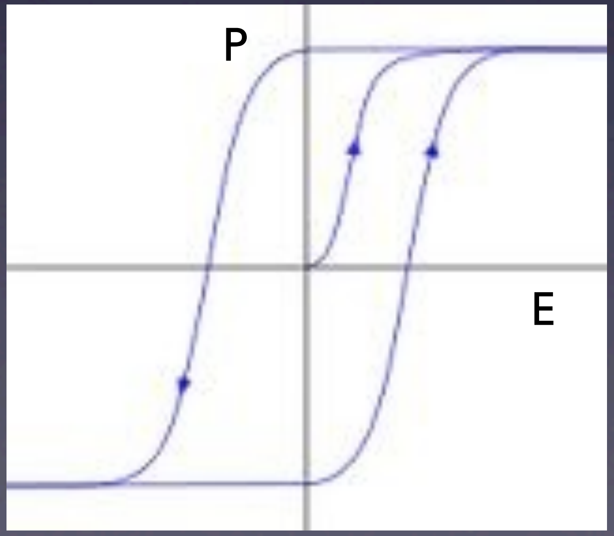
Perovskites of the form ABO_3



centro-symmetry



no centro-symmetry



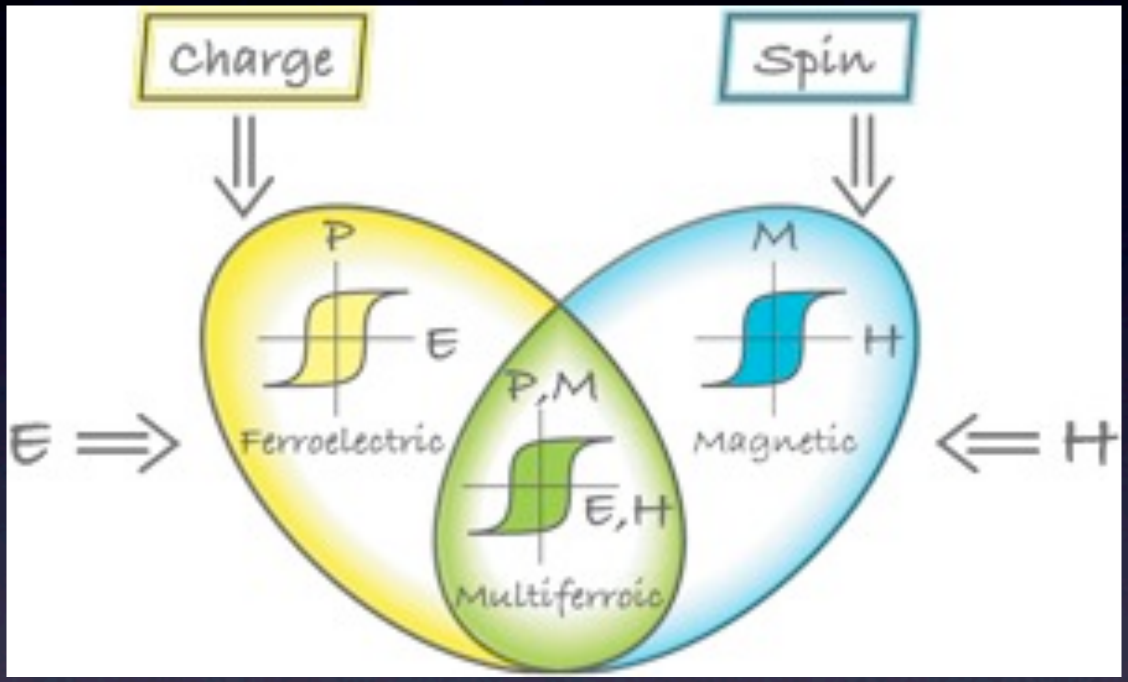
Ferroelectric hysteresis

The quest for multiferroic oxides

Multiple ferroic orders in the same materials

Spin, Charge and lattice co-related

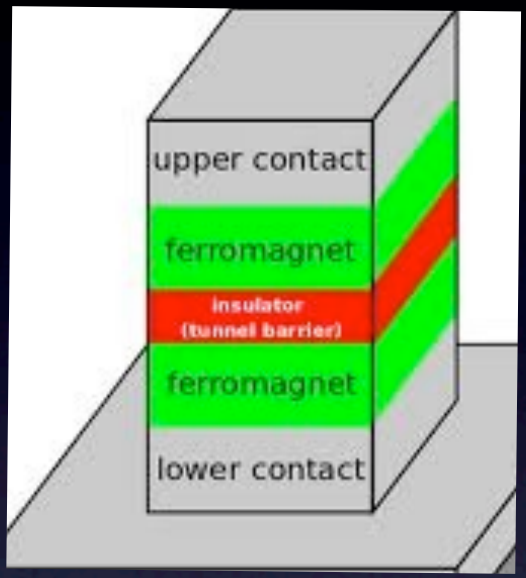
Large potential applications

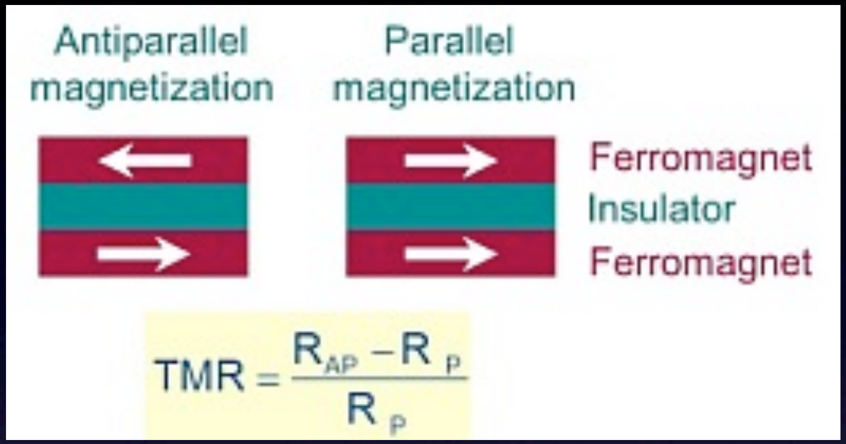


New Materials : Novel physics

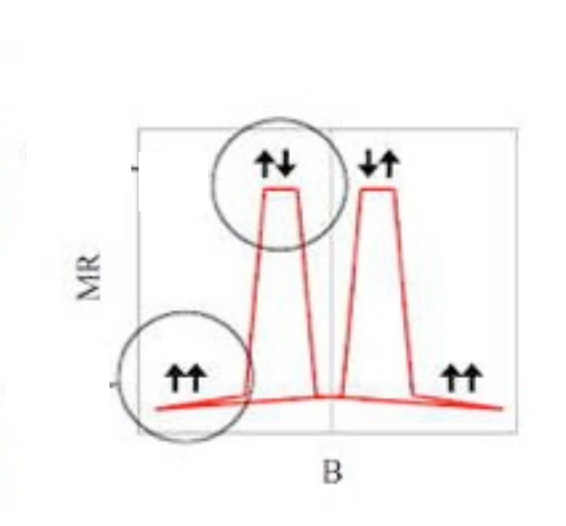
: Large coupling at room temperatures and beyond

Tunnel Magneto Resistance Devices



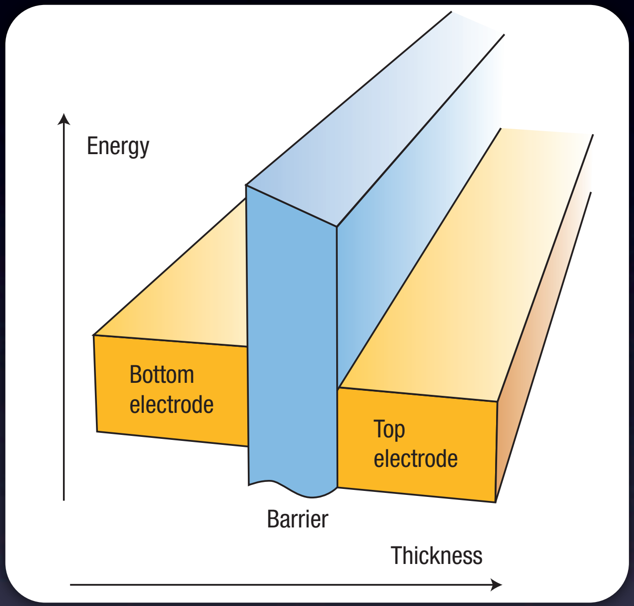


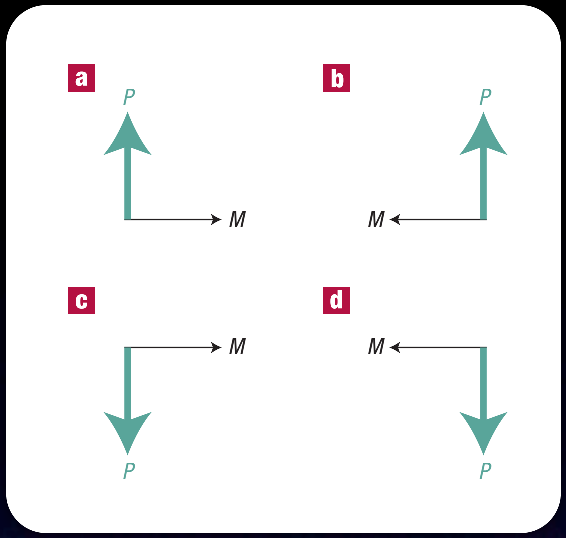
Tunnelling from a magnetic metal to another magnetic metal, through an intervening insulator

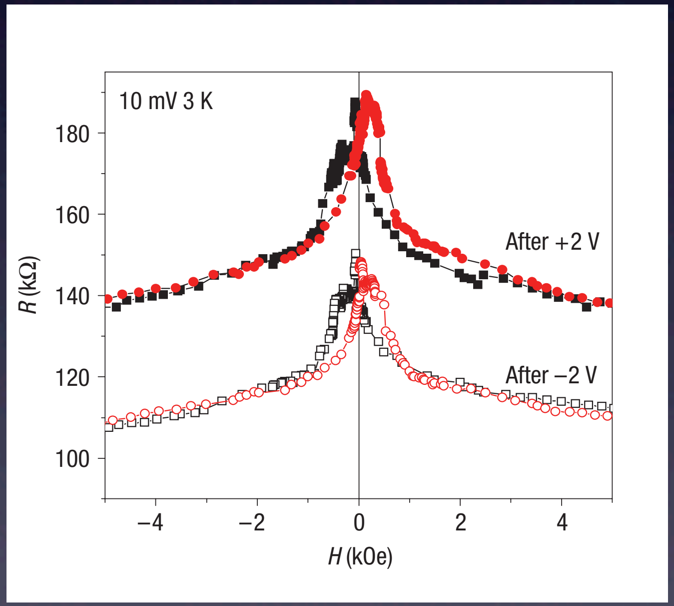


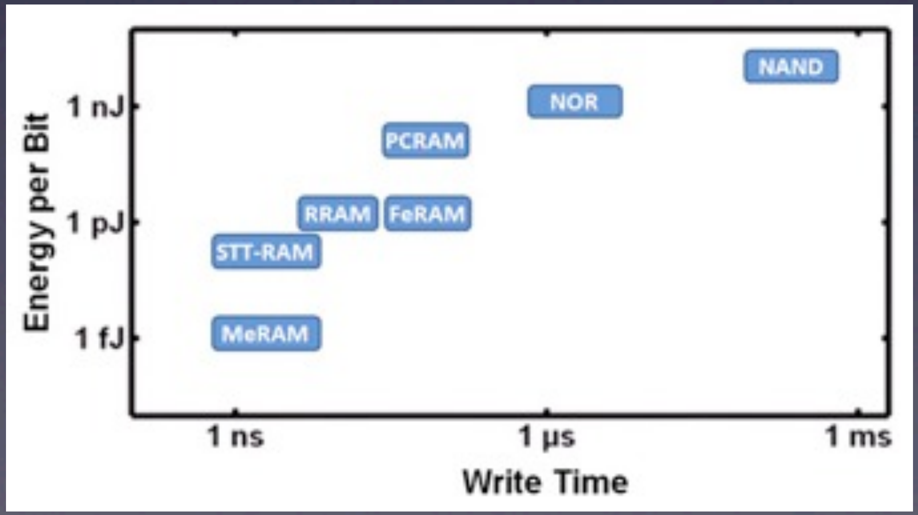
Improved memory devices ?

Combining benefits of FeRAMs and MRAMS









Electronic Engineering Times (2013)

Possible 4 state memory devices

Gajek et al., Nature Materials (2007)

Timeline

- 1888 : Roentgen
  A moving dielectric in an electric field becomes magnetised
- 1894 : P. Curie
  Crystal symmetry considerations
- 1926: P. Debye
  Coined the term 'magnetoelectric'
- 1959: I. Dzyaloshinskii
  Predicted that Cr_2O_3 is magnetoelectric
- 1960: Astrov
  measurement of *M* induced by *E*
- 1961: Rado, Folen and Stalker
  measurement of *P* induced by *H*

$$F(E,H) = F_0 - P_iE_i - M_iH_i - \frac{1}{2}\epsilon_0\epsilon_{ij}E_iE_j - \frac{1}{2}\mu_0\mu_{ij}H_iH_j - \alpha_ijE_iH_j - \frac{1}{2}\beta_{ijk}E_iH_jH_k - \frac{1}{2}\gamma_{ijk}H_iE_jE_k$$

Why are multiferroics scarce ?

- Symmetry Considerations ?
  unlikely to be the reason

- Electrical Conductivity
  look for antiferro (ferri) magnetic systems

- the d^0 d^n problem
  typical ferroelectric perovskites: Ti^{4+}, Nb^{5+}, Zr^{4+}
  magnetism requires partially filled *d* shells

Terminology

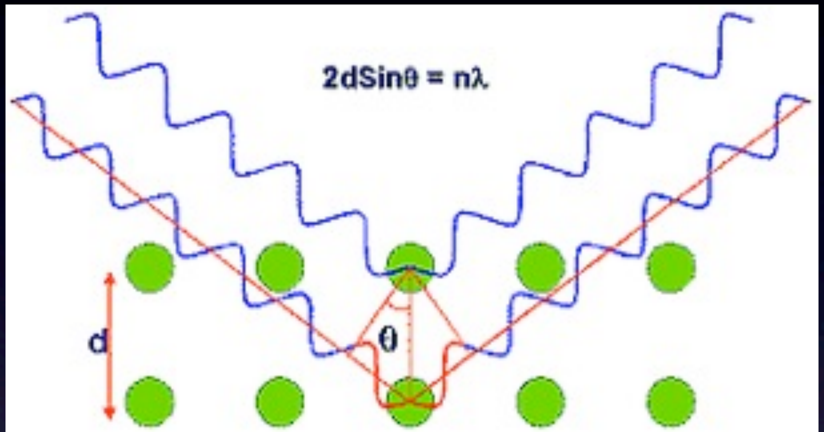
- Multiferroic
  co-existing magnetic and ferroelectric orders

- Magnetoelectric
  long range magnetic order
  H induced *P*
  not a ferroelectric (for eg. Cr_2O_3)

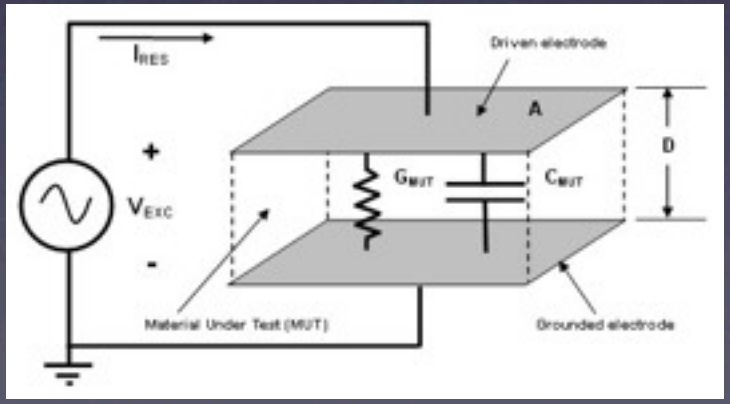
- Magneto-dielectric
  di-electric anomaly at the magnetic transition
  neither magneto-electric, nor multiferroic
  (MnO, MnF_2, $TmFeO_3$, etc)

Characterisation

Measurements of Magnetisation, Polarisation, di-electric constant, and cystallographic and magnetic structures are routine

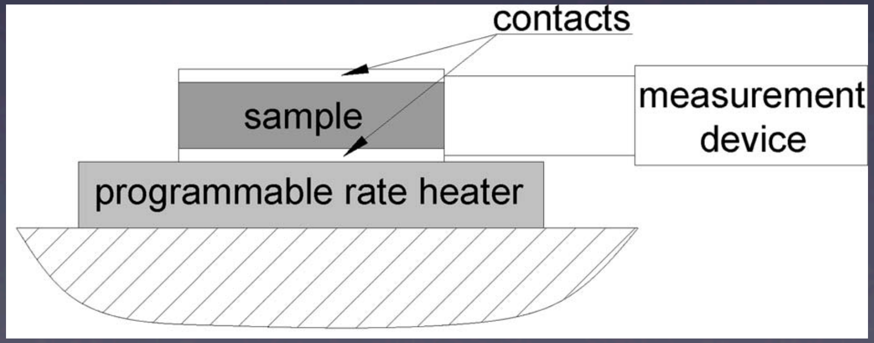


Dielectric measurements



Magneto-dielectric measurements

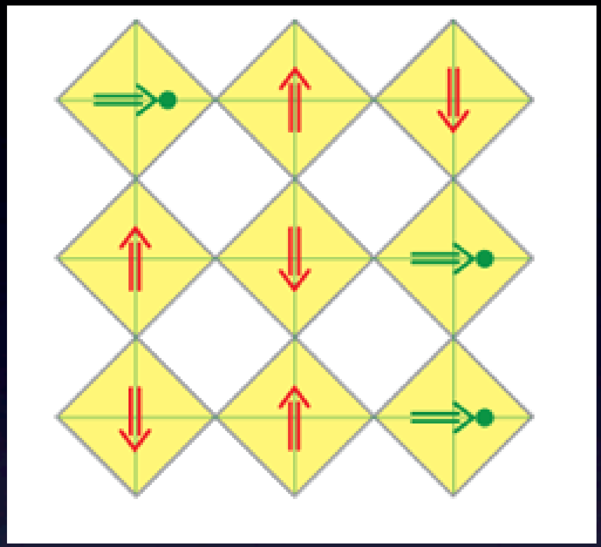
Pyroelectric measurements

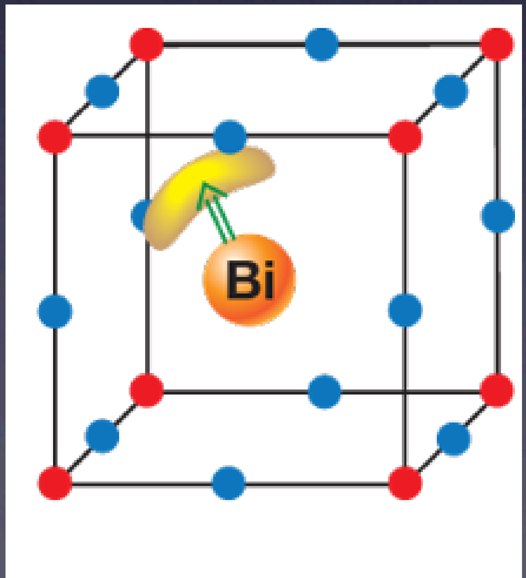


$$I = p(T)\,A\,\frac{\partial T}{\partial t} \qquad p(T) = \frac{\partial \mathbf{P}_{\mathrm{S}}}{\partial T}$$

Mixed (double) Perovskites

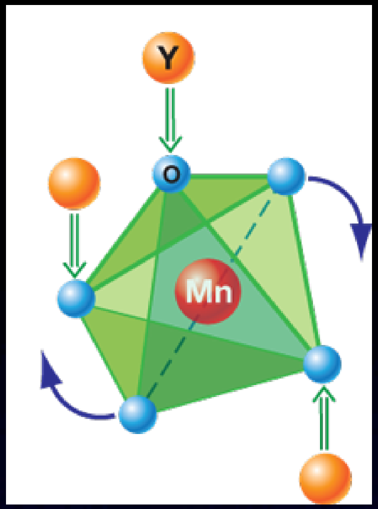
- Mix magnetic d^n ions with ferroelectric d^0 ions
- Independent origin of magnetic and ferroelectric orders
- $PbFe_{1/2}^{3+}Nb_{1/2}^{5+}O_3$
  $PbFe_{1/2}^{3+}Ta_{1/2}^{5+}O_3$
  $PbFe_{1/2}^{3+}W_{1/2}^{5+}O_3$
- Weak coupling between magnetic and ferroelectric orders
- Prototypical 'Type I' multiferroics
- Lone pair systems (Pb, or Bi based systems)

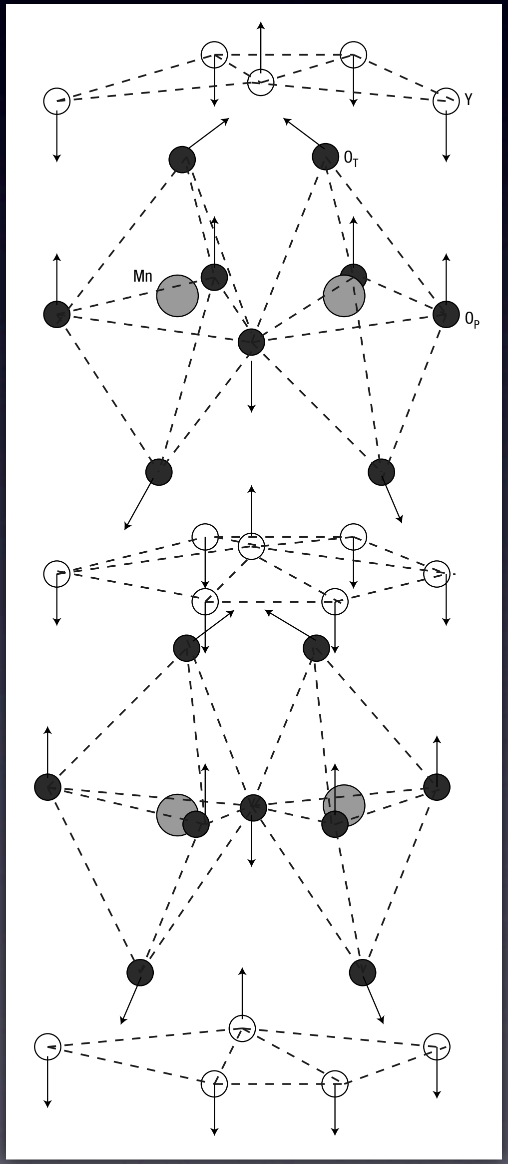


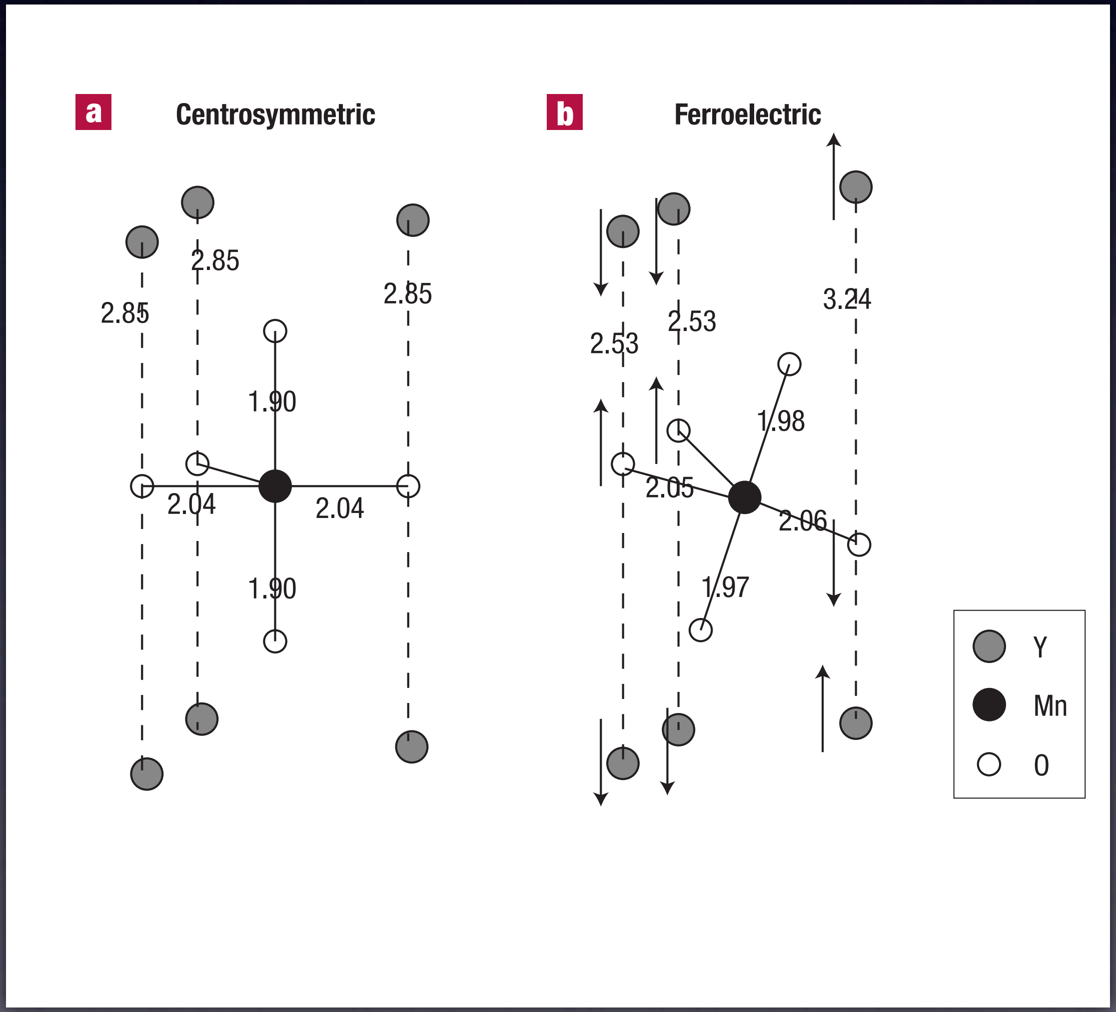


The case of $YMnO_3$

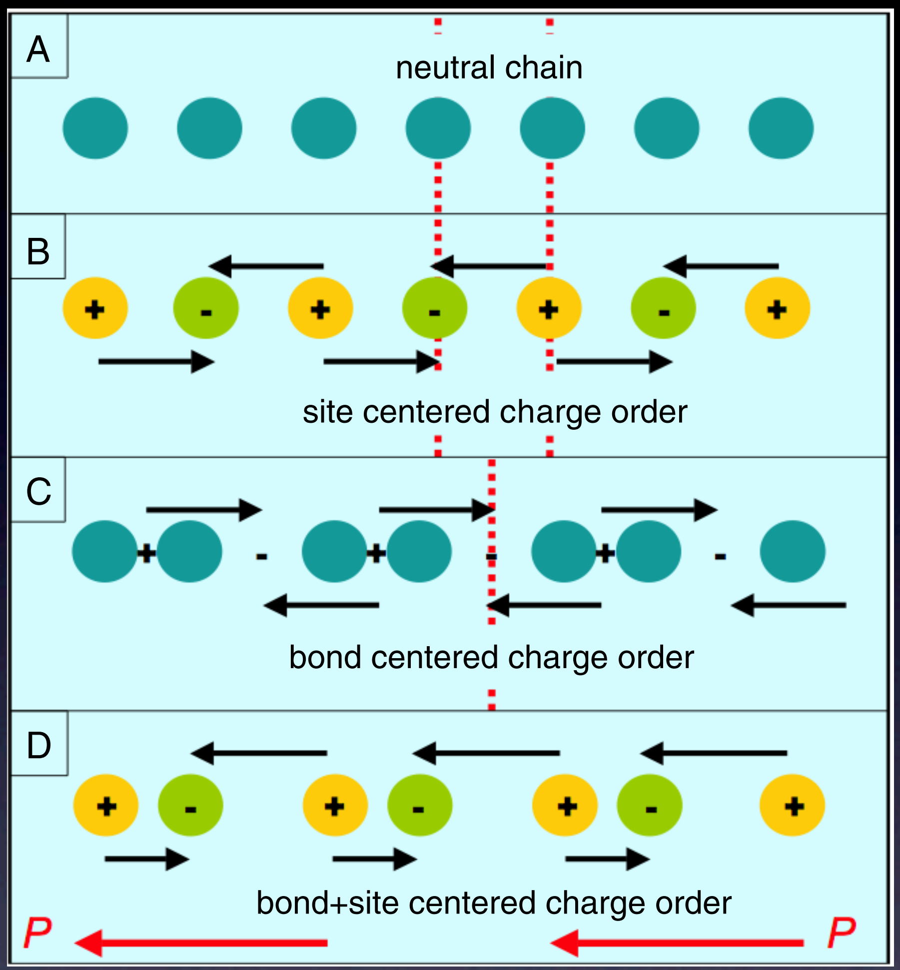
- Buckling of MnO_5 polyhedra
- Large displacements of Y atoms





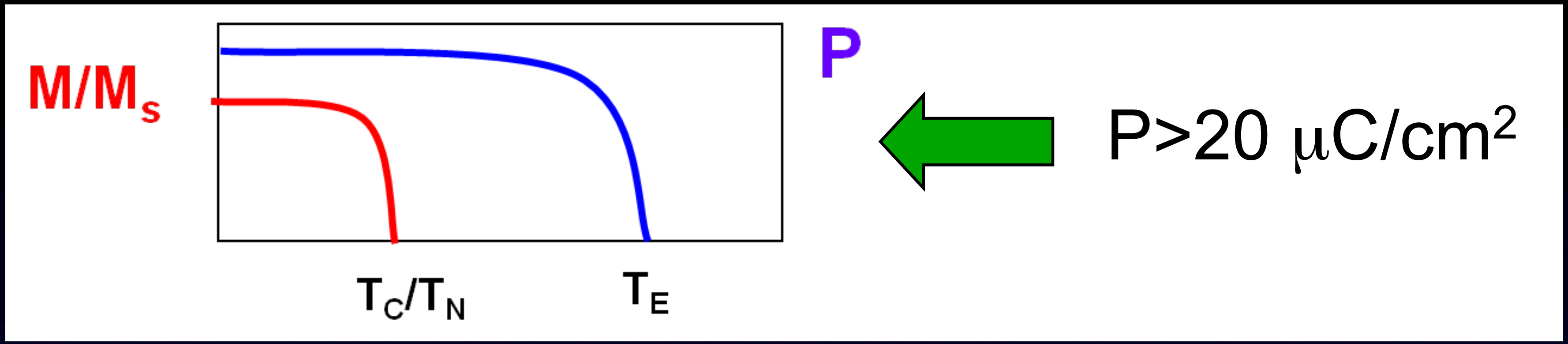


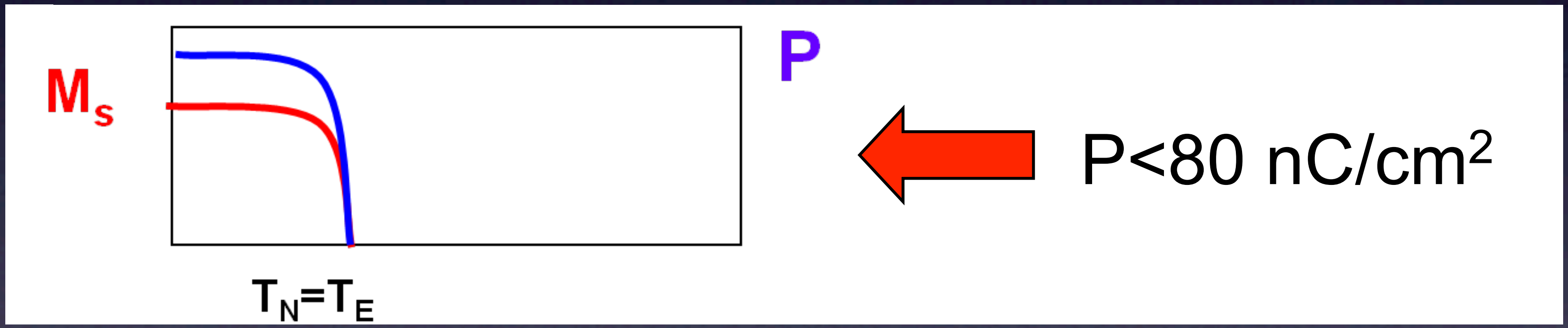
Charge Ordering



- Ferroelectricity dependent/independent of magnetisation
- potential candidates: $Pr_{1/2}Ca_{1/2}MnO_3$, Fe_3O_4, $LuFe_2O_4$, Ca_3CoMnO_6 etc

Type I vs Type II multiferroics

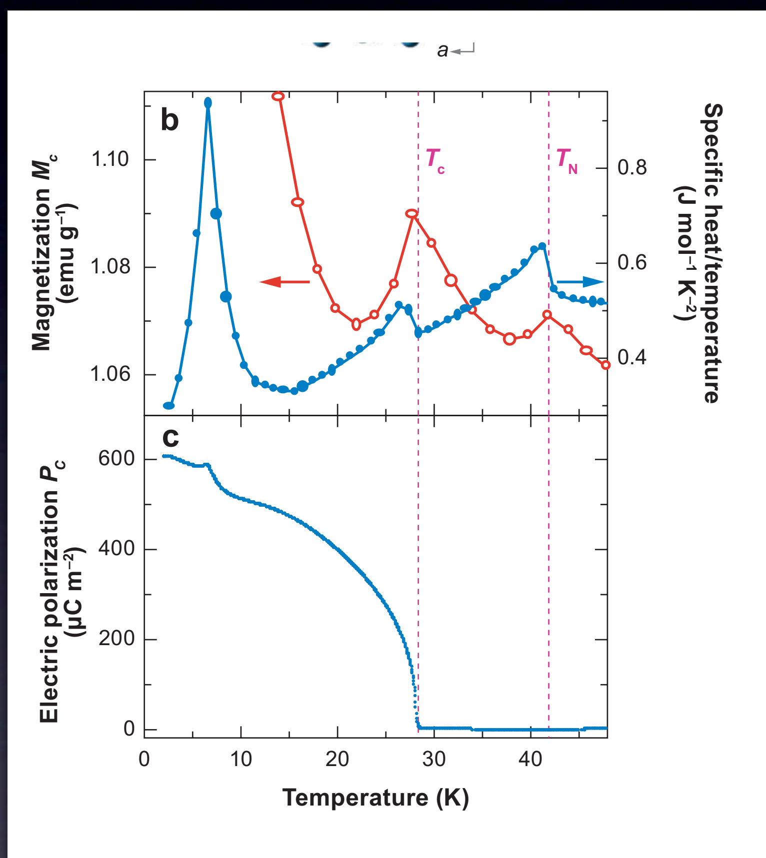


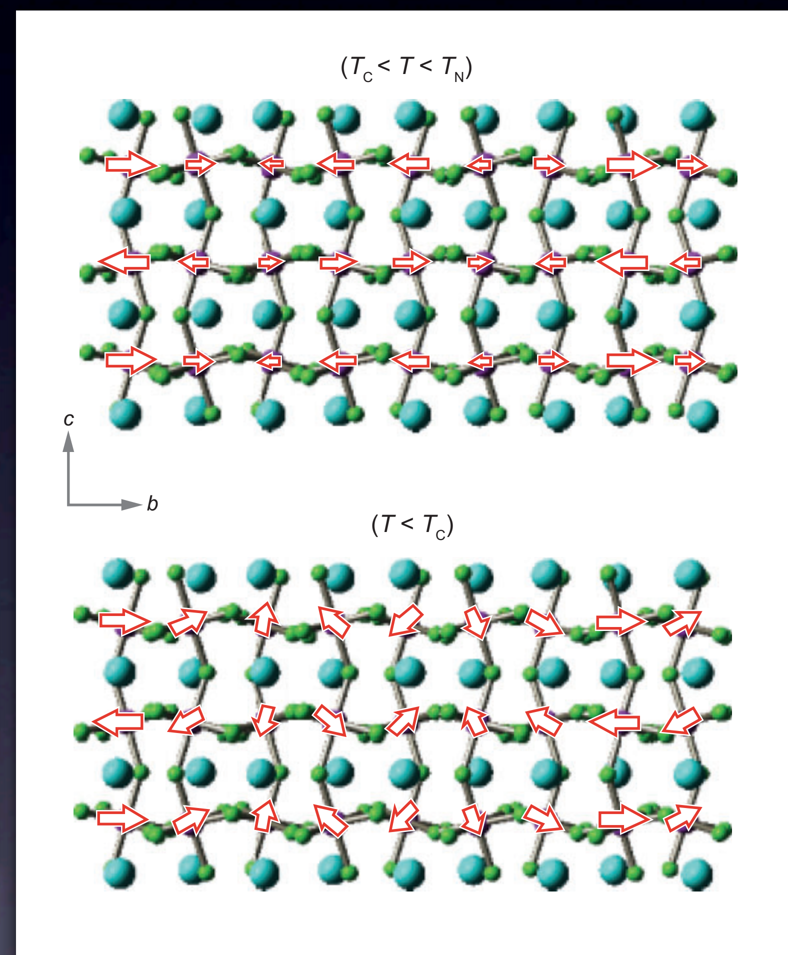


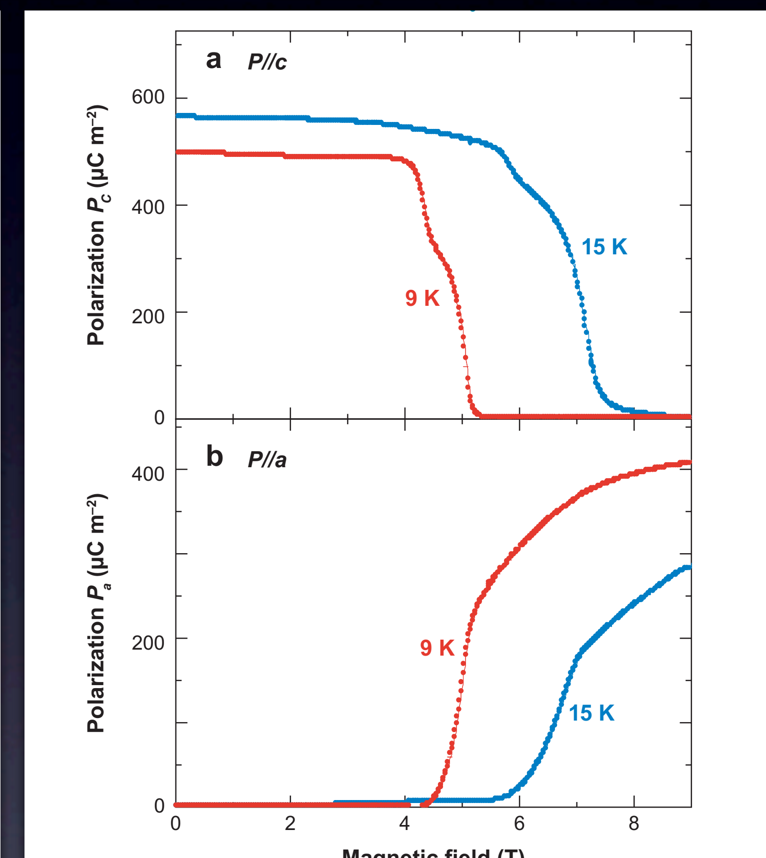
Spiral Magnets

- Type II multiferroics

- Small polarisation values, but large magnetoelectric coupling ($TbMnO_3$)





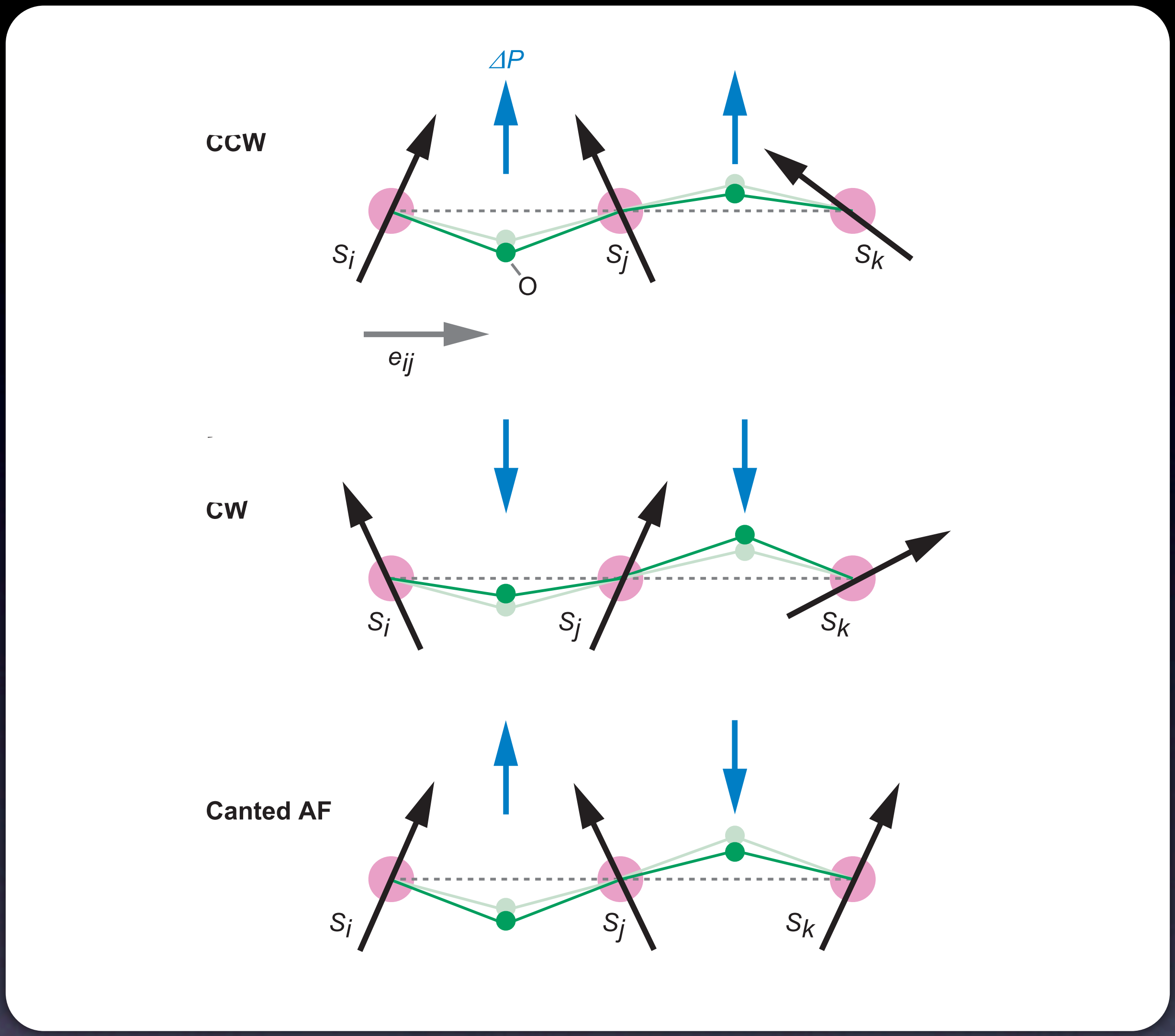


- A spiral spin structure stabilises a ferroelectric state

- Polarisation can be flipped by the application of magnetic fields

Spiral Magnets

- Displacement of Oxygen between two moments



T. Kimura, Annu. Rev. Mater. Res (2007)

- A canted AFM has no net (macroscopic) polarisation

$$\vec{P} \propto \gamma \vec{e}_{ij} \times (\vec{S}_i \times \vec{S}_j)$$

Typically, the polarisation lies in the plane along which the spins rotate

Exploring new multiferroics

- New materials with magnetic cations on geometrically frustrated lattices, leading to spiral / canted magnetic structures

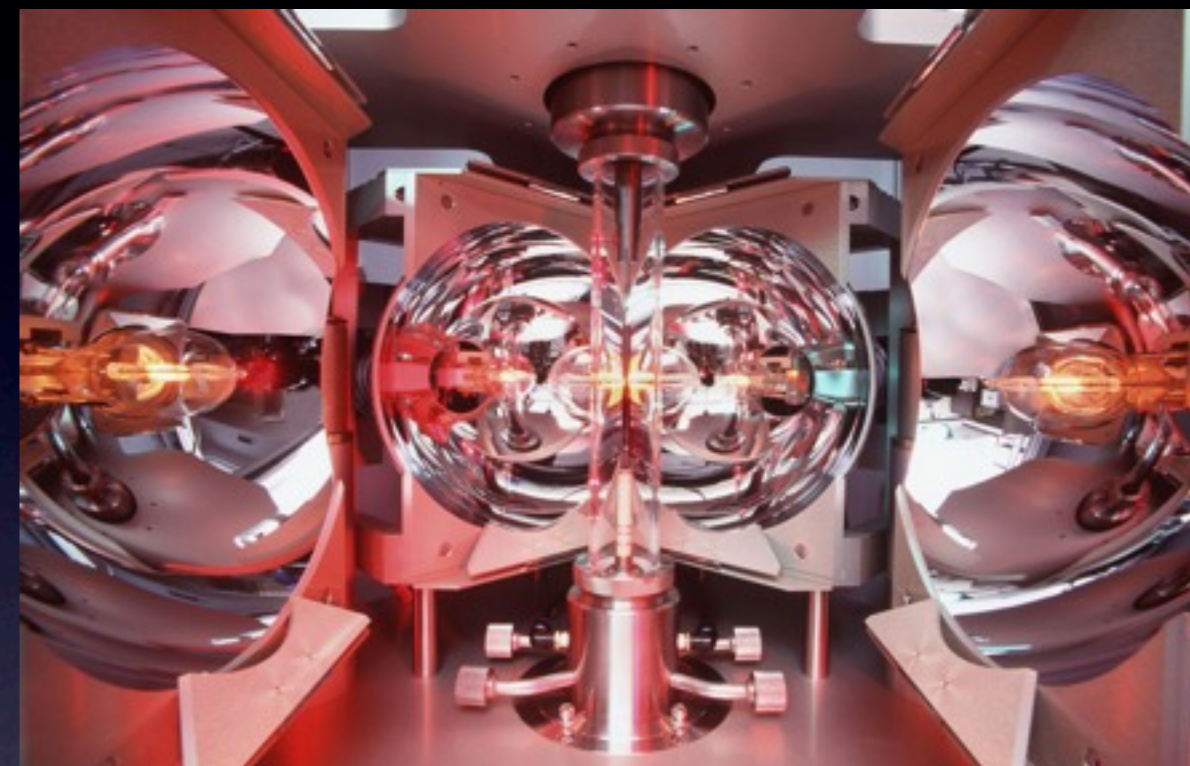
- Compounds where previous studies have indicated spin canted /spiral structures, but have not been investigated for multiferroicity

- Compounds where weak ferromagnetism has been reported/inferred

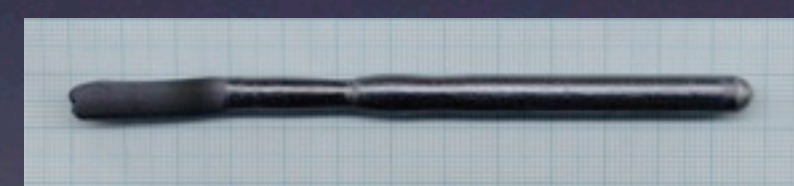
- Compounds belonging to classes where ferroelectricity has either been reported, or predicted on structural considerations

- Possible candidates from first principle calculations

Single crystal growth



Crystal growth using the floating Zone method



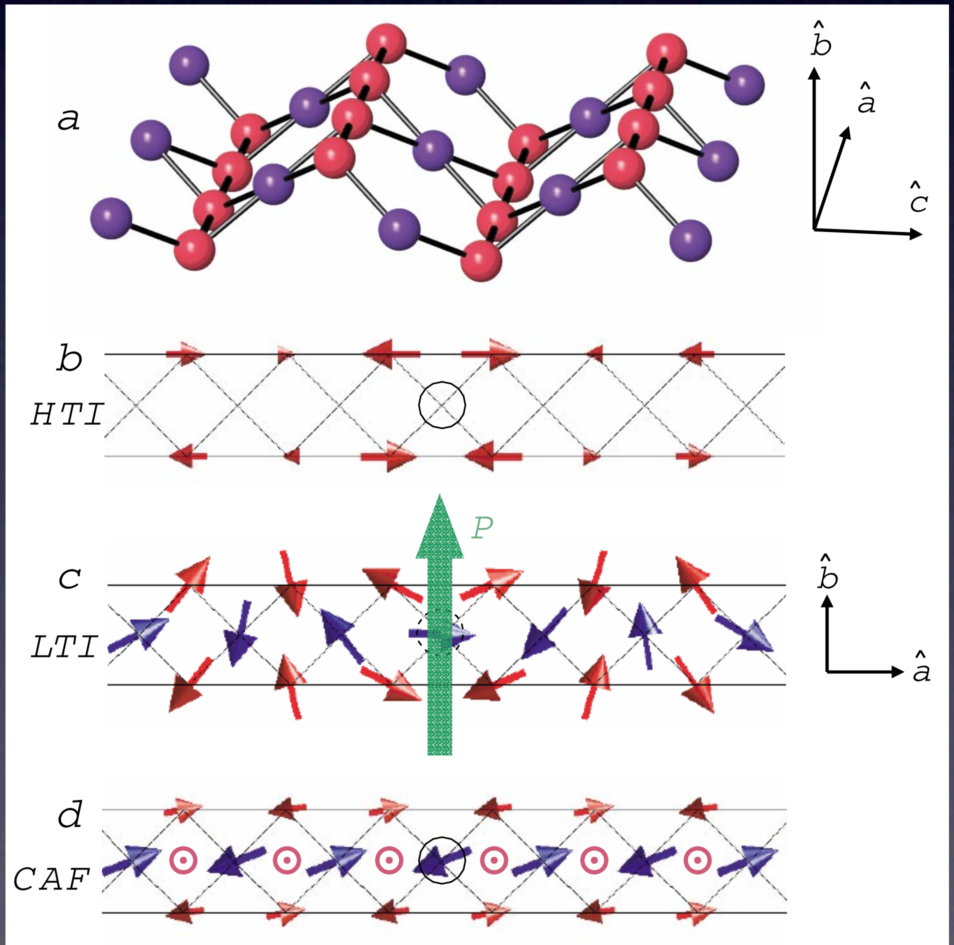
$Pr_1Sr_2Mn_2O_7$

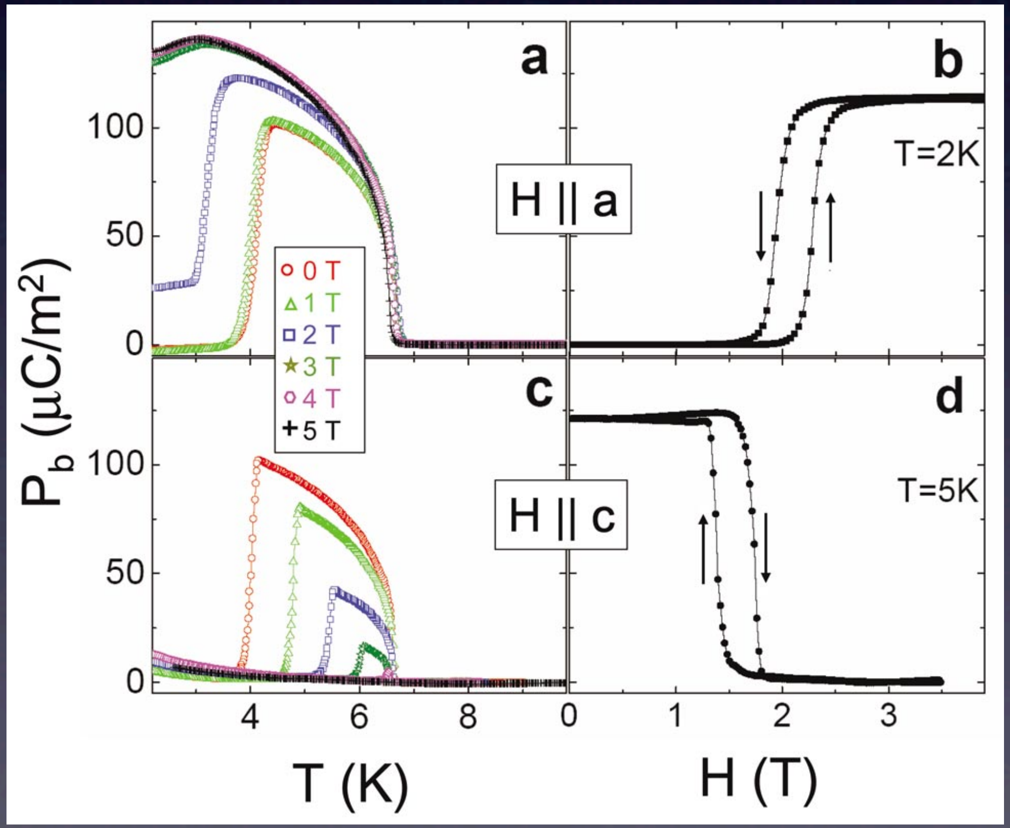
$Ca_2Fe_2O_5$

The case of $Ni_3V_2O_8$

$Cmca$

$$a = 5.9178\mathring{A}$$
$$b = 11.3652\mathring{A}$$
$$c = 8.2896\mathring{A}$$



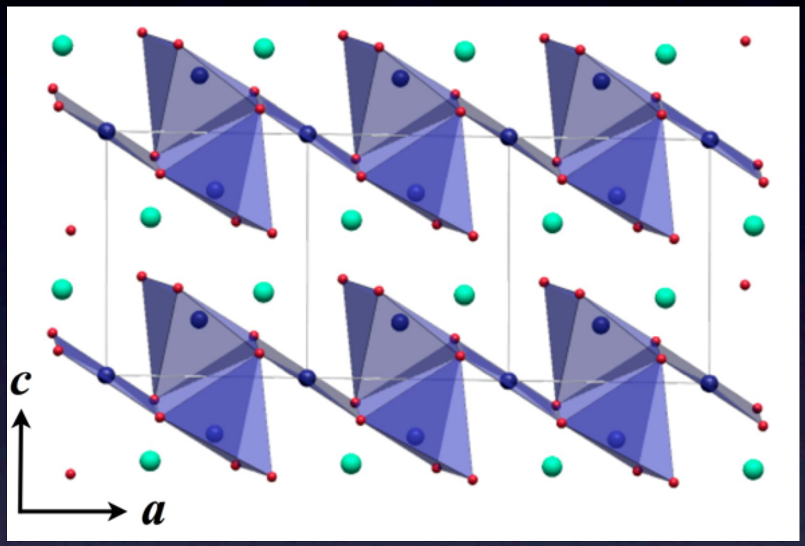


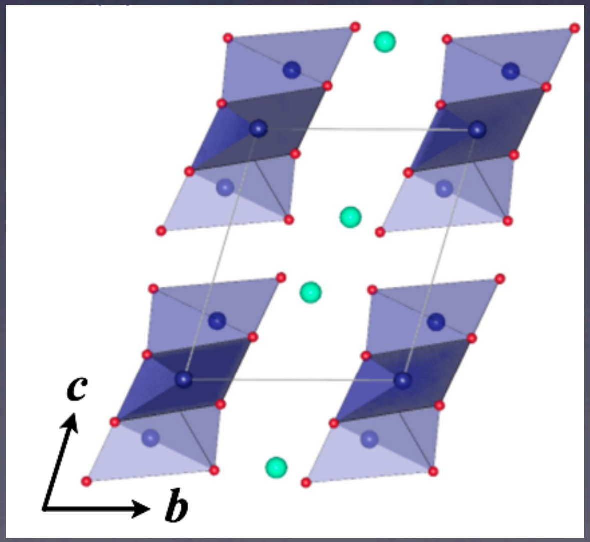
G. Lawes, et al., Phys. Rev. Lett. **95**, 872205 (2005)
I. Cabrera et al., Phys. Rev. Lett. **103**, 87201 (2009)

$Cu_3Nb_2O_8$

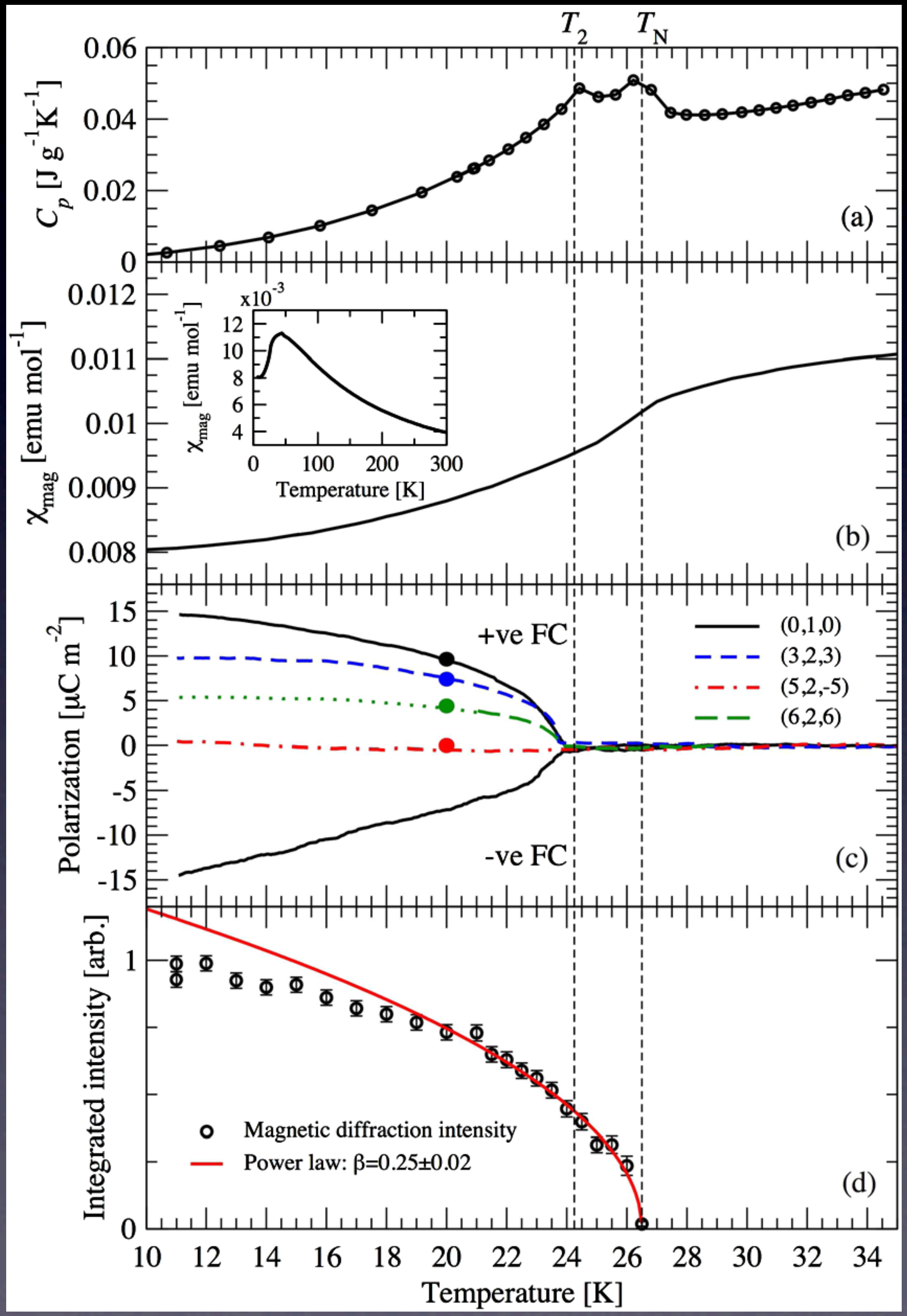
- Centrosymmetric Triclinic (P-1)

$$a = 5.1829\AA$$
$$b = 5.4857\AA$$
$$c = 6.1144\AA$$
$$\alpha = 72.58^o$$
$$\beta = 83.421^o$$
$$\gamma = 65.71^o$$





$Cu_3Nb_2O_8$



- Transitions at 26 K and 24 K
- Ferroelectric polarisation sets in at the lower transition
- A new type II multiferroic !

Rietveld refinement

Hugo Rietveld realized that if a diffraction pattern could be modeled, the fit between these data and the a computed pattern could be optimized.

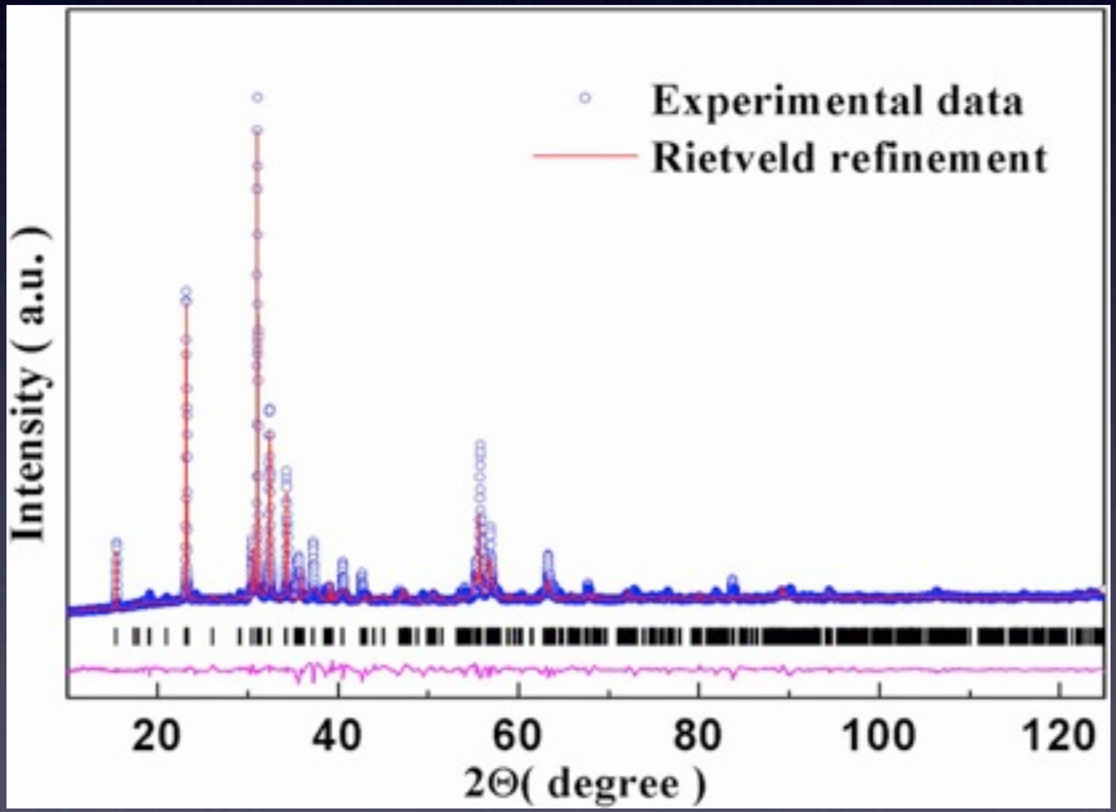
Starting with a model

Generate reflections list

Generate peak heights

Add broadening and other effects

Optimise model to improve fit

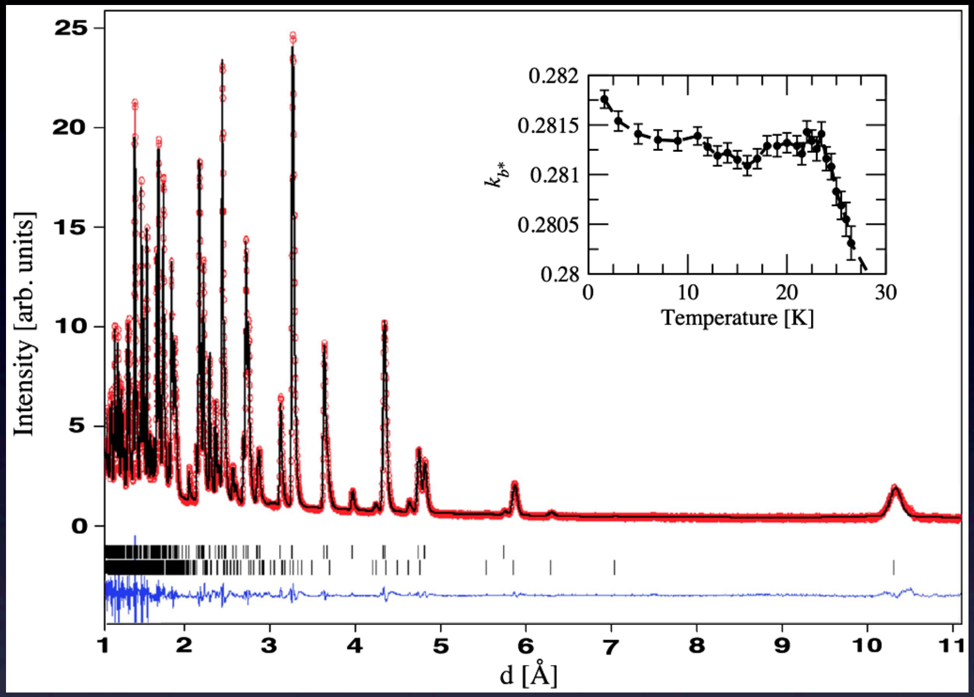


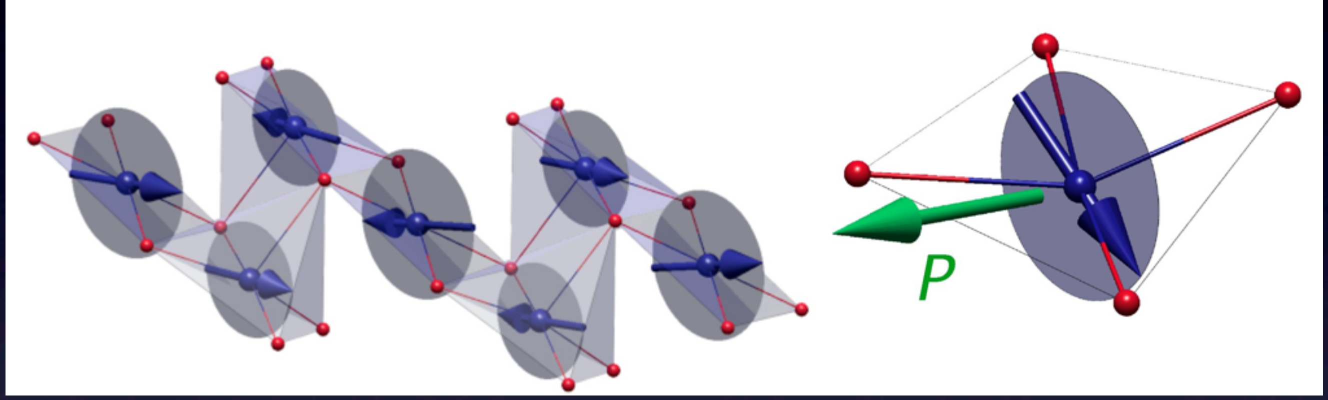
Cons: needs a sensible starting model
large number of variables

A Rietveld refinement is never perfected, merely abandoned !

$Cu_3Nb_2O_8$

- Powder neutron diffraction at WISH (ISIS), and xray diffraction at I16 (Diamond)





- Polarisation nearly perpendicular to plane of rotation of spins

$$D_{ij} = P_{ij} \times r_{ij} + \sigma_{ij} r_{ij}$$

$$Polarisation, P = \sum_{ij} P_{ij}$$

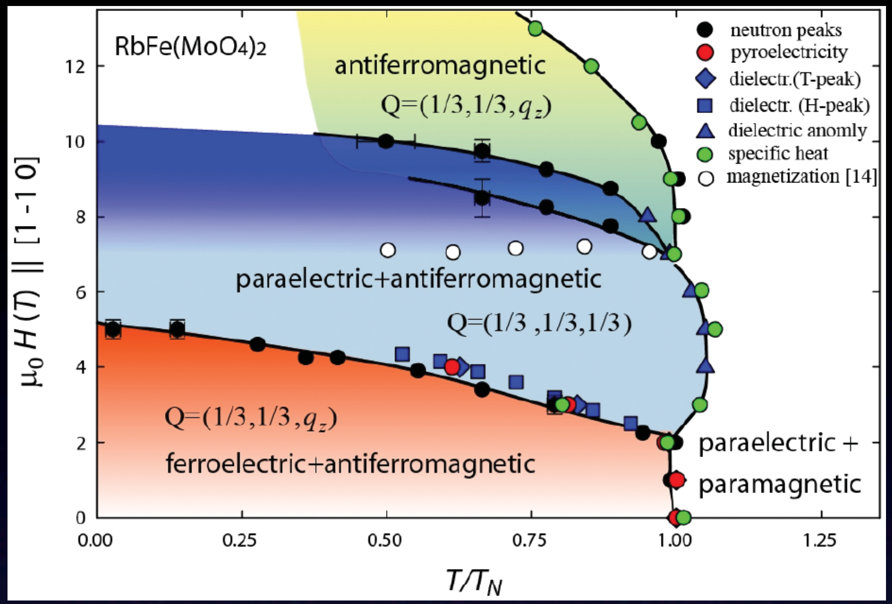
$$Chirality, \sigma = \sum_{ij} \sigma_{ij}$$

Structure supports an axial vector

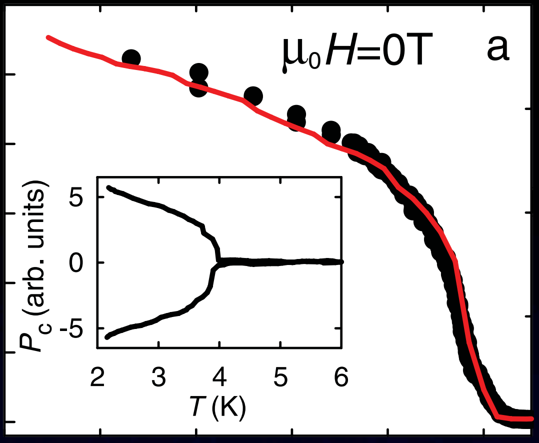
$$P = \gamma \sigma A$$

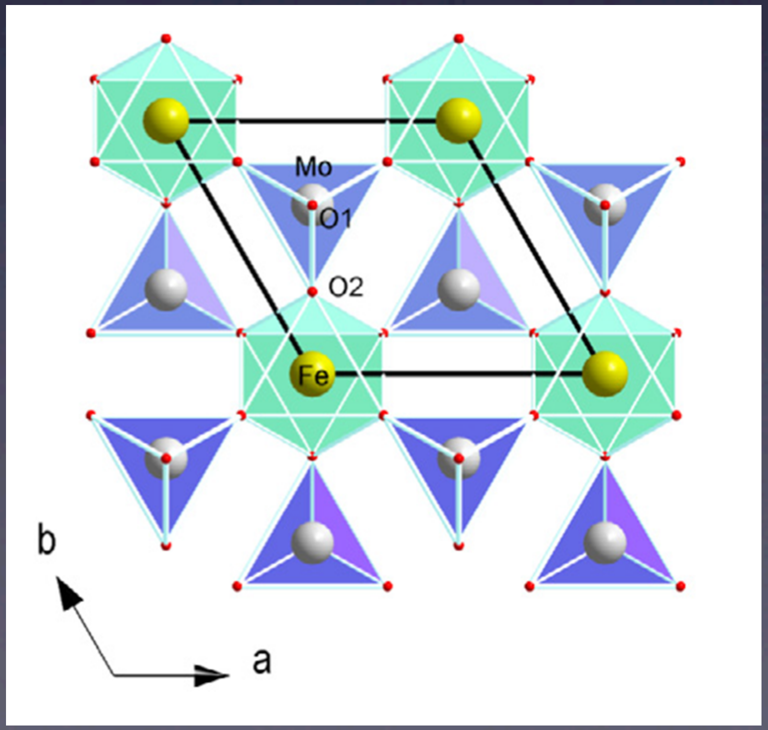
Phys. Rev. Lett. **107**, 137205 (2011)

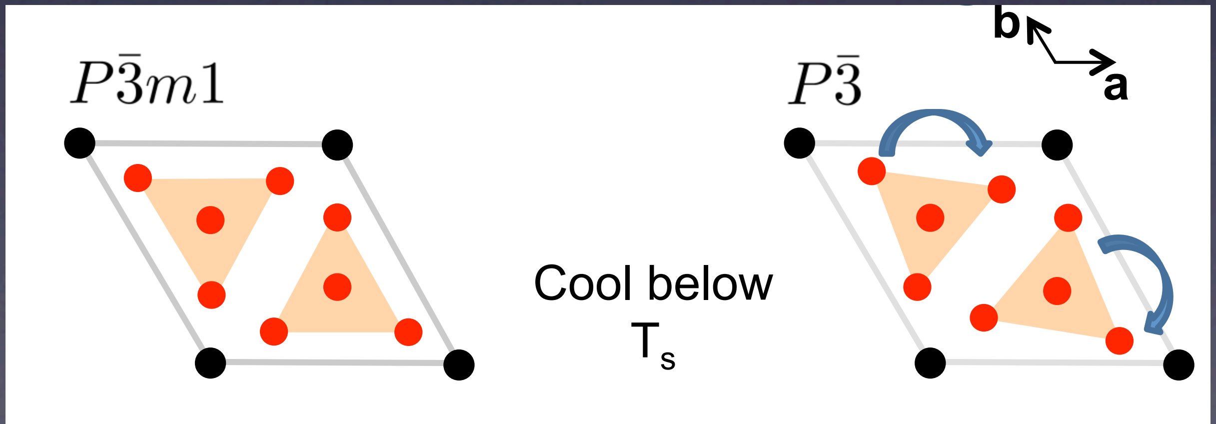
Previously unrecognised: the case of RbFe(Mo4)2



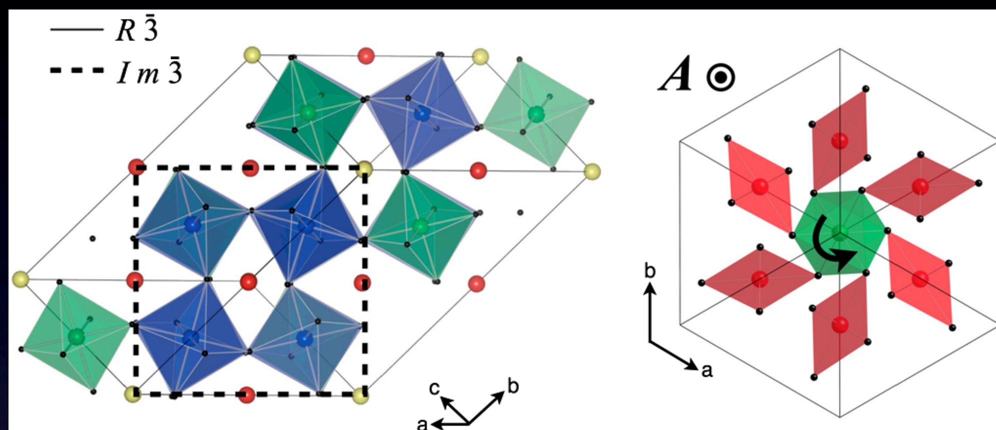
Phys. Rev. Lett. **98**, 267205 (2007)

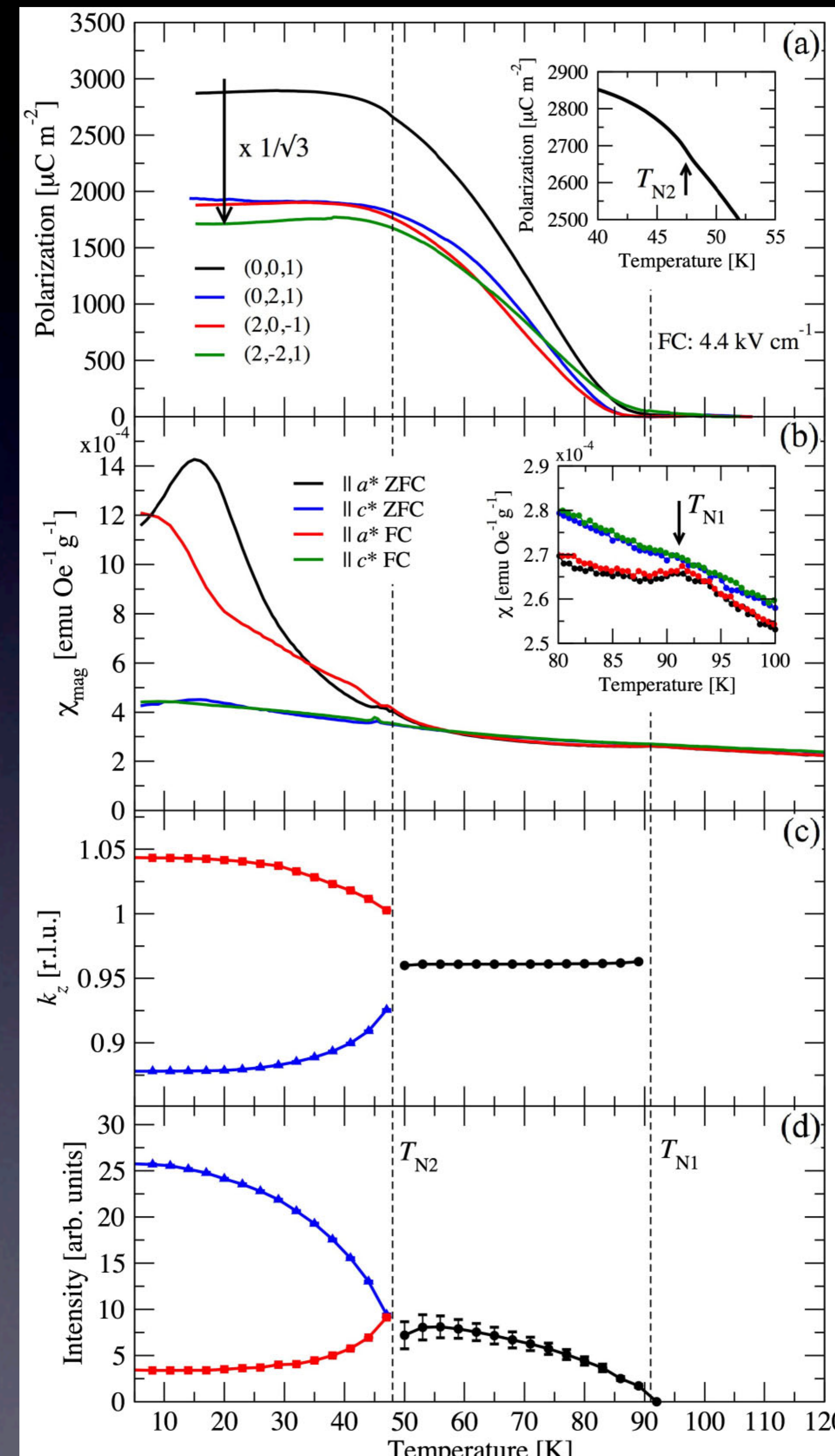






Why is this important ?





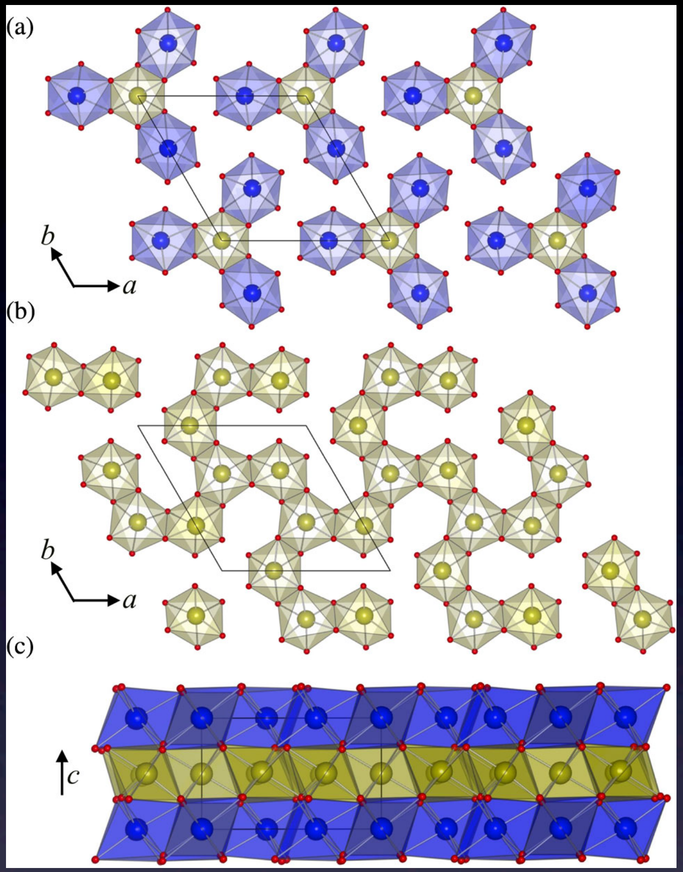
$CaMn_7O_{12}$

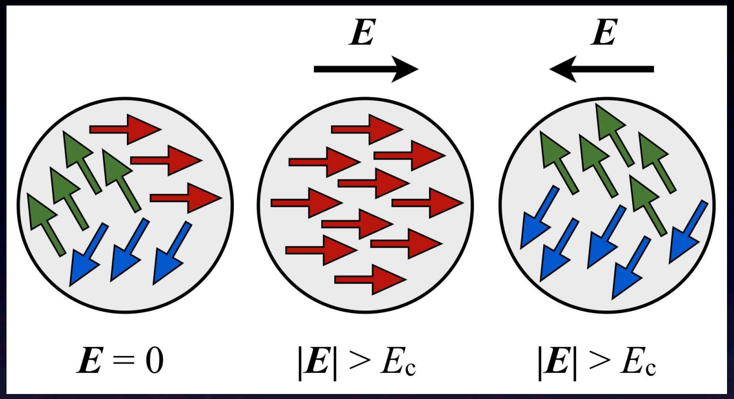
Similar Mechanism

Very large polarisation

Phys. Rev. Lett. **108**, 67201 (2012)

Polar $MnSb_2O_6$



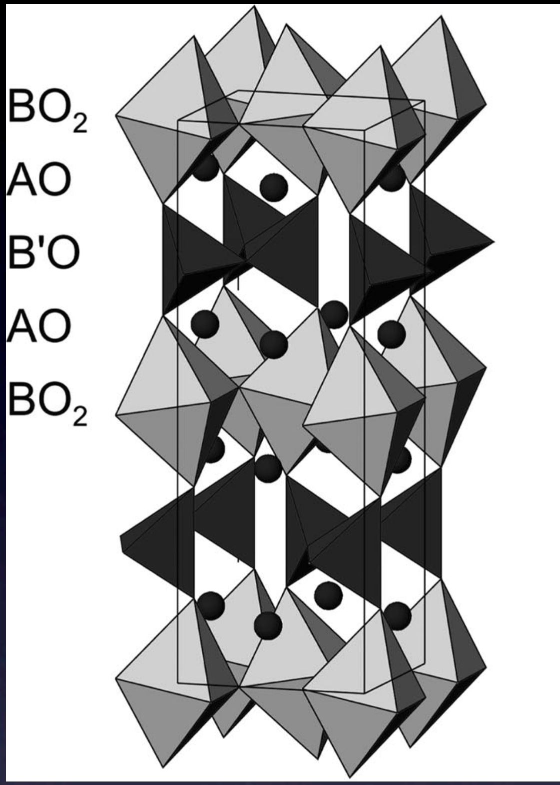


Phys. Rev. Lett. 111 67201 (2013)

Weakly Polar

Novel ferroelectric switching

$Ca_2Fe_2O_5$



Brownmillerite $A_2BB'O_5$

Alternating Octahedra and tetrahedra

large transition temperatures across the series

Sporadic reports of weak ferromagnetism

Centrosymmetric *Pcnm*

$$a = 5.610\AA$$
$$b = 14.791\AA$$
$$c = 5.425\AA$$

$T_N \sim 725$ K

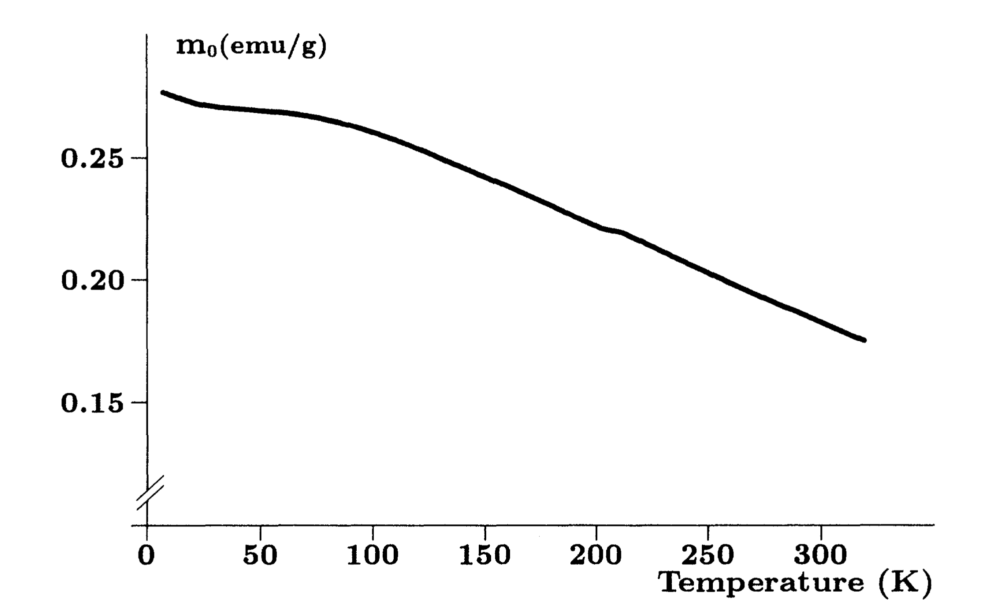
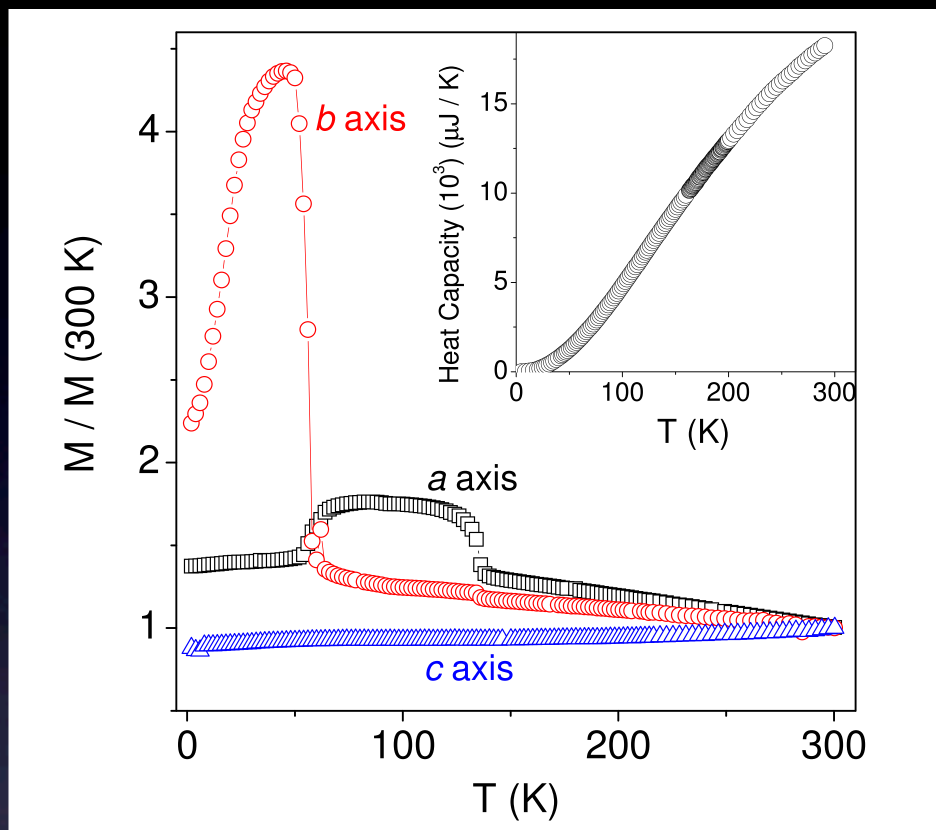
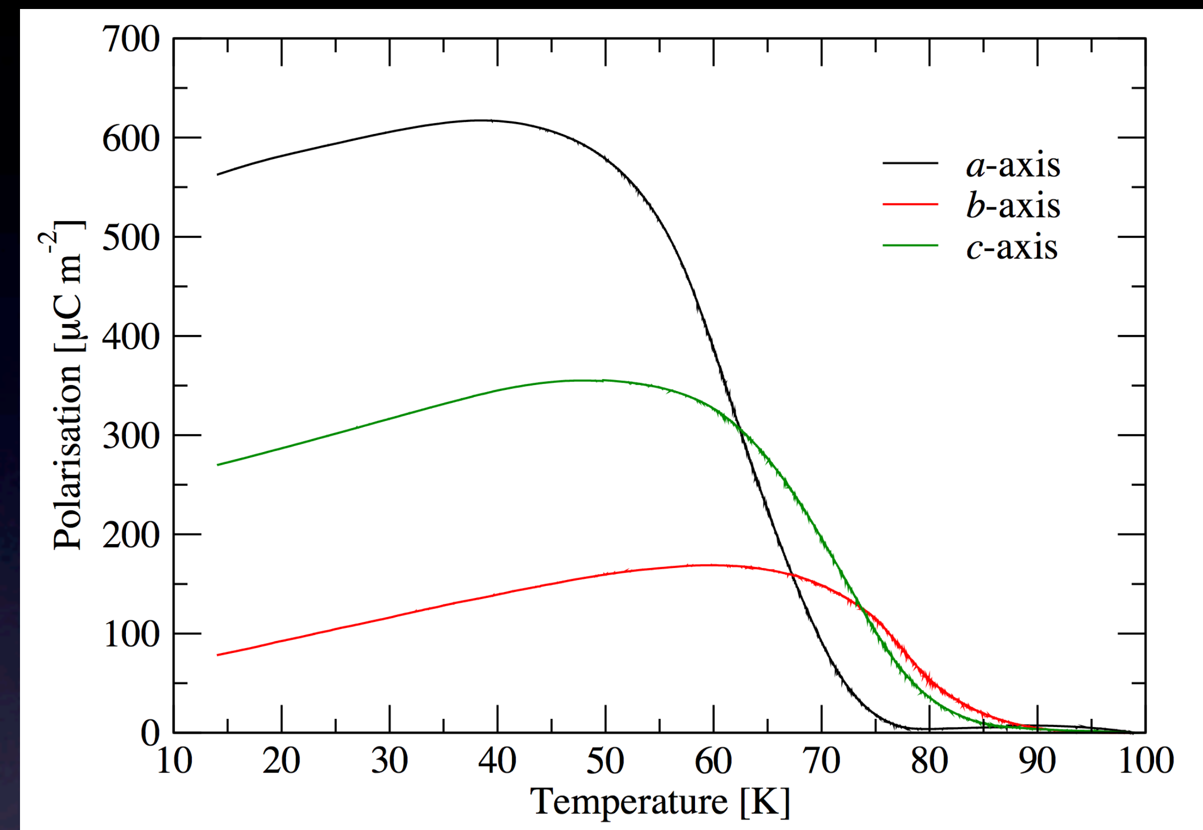


FIG. 5. Temperature dependence of the weak ferromagnetic component in $Ca_2Fe_2O_5$.

P. Marchukov, Phys.Rev. B (1993)

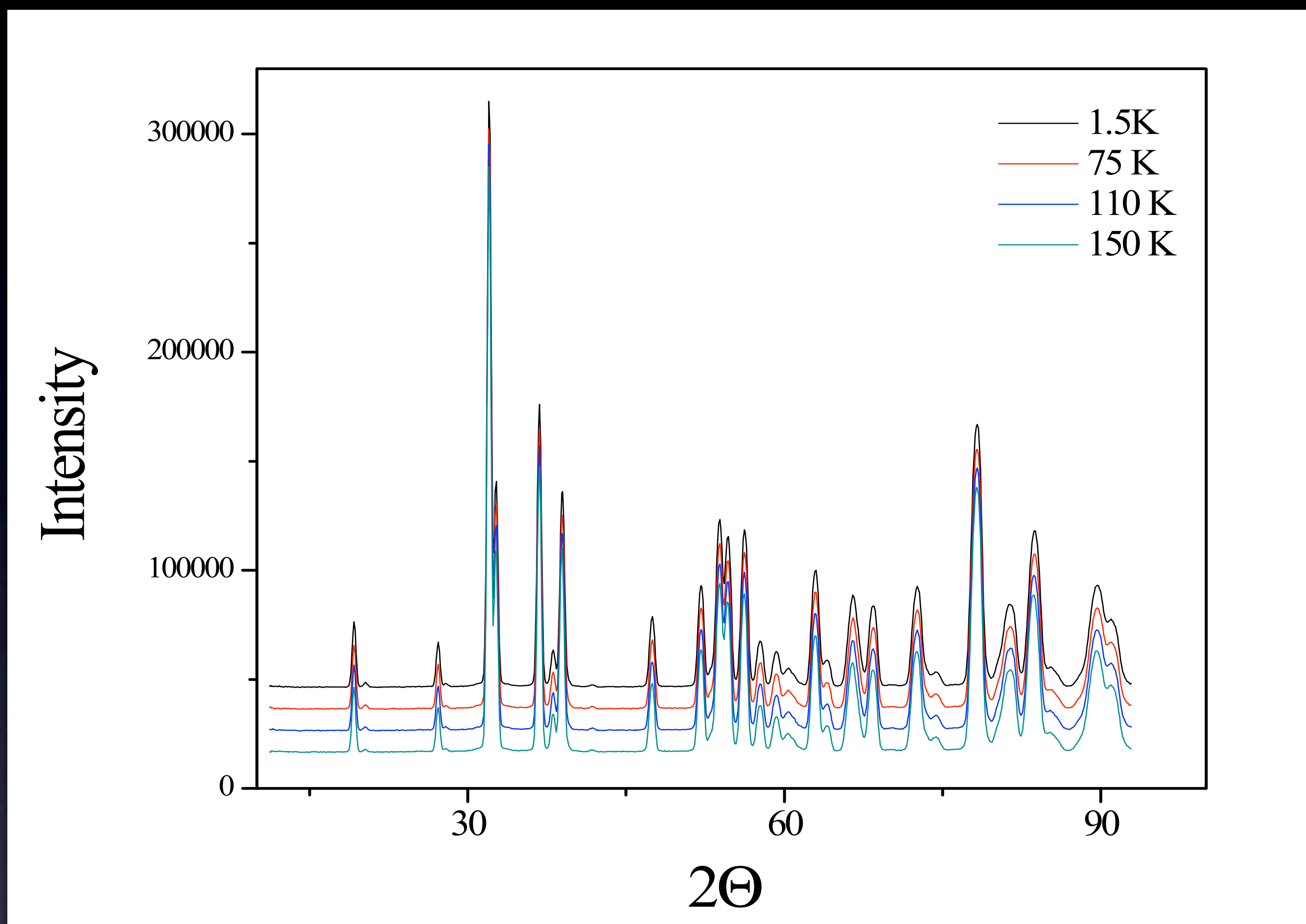
$Ca_2Fe_2O_5$

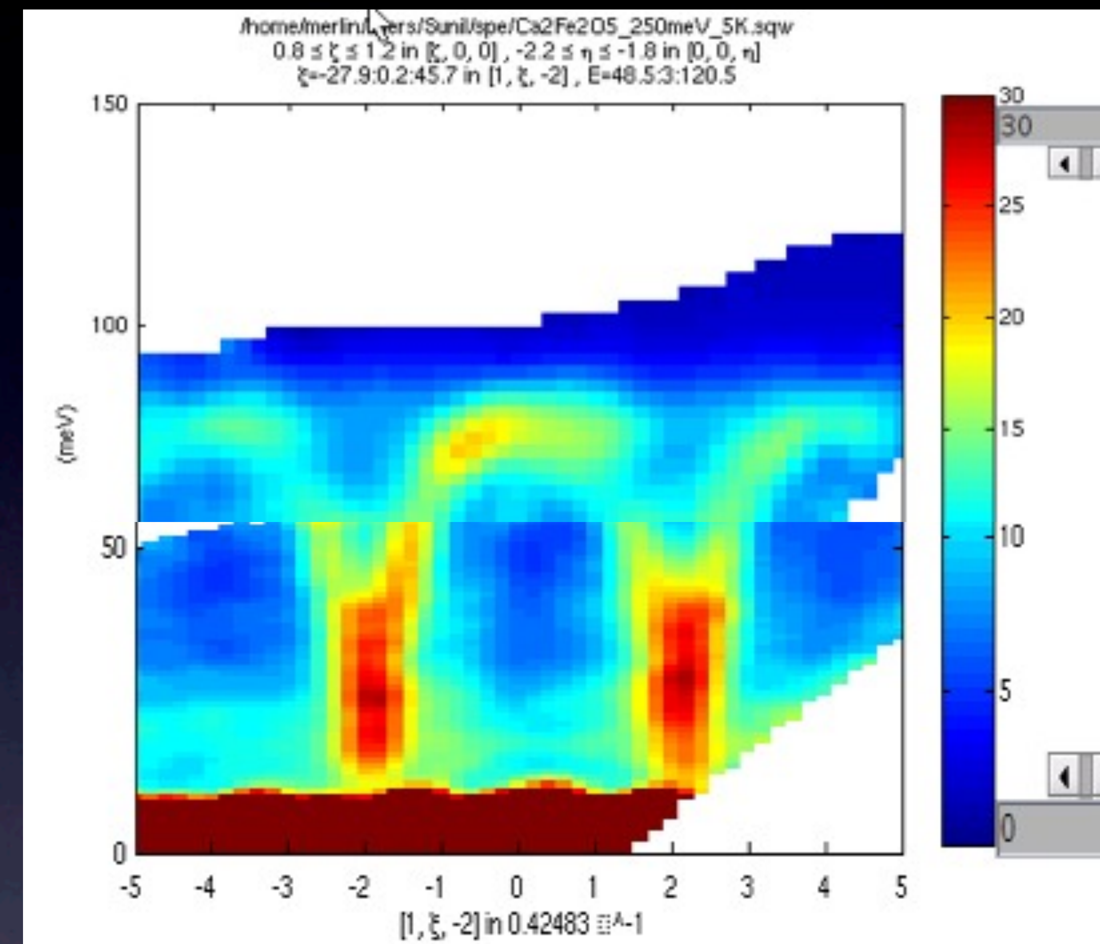




A new multiferroic !

$Ca_2Fe_2O_5$





Preliminary neutron diffraction (DMC, SINQ)

No Observable change in magnetic structure

Investigating Spin Waves using inelastic

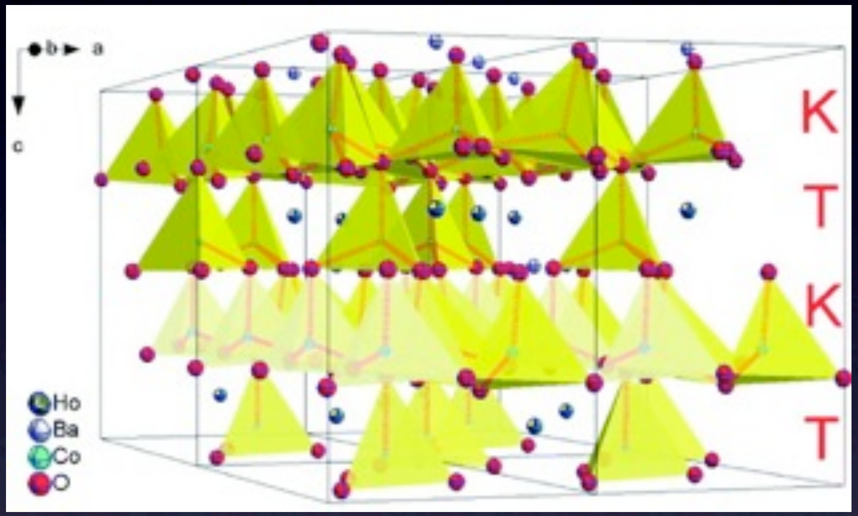
Neutron scattering (MERLIN, ISIS)

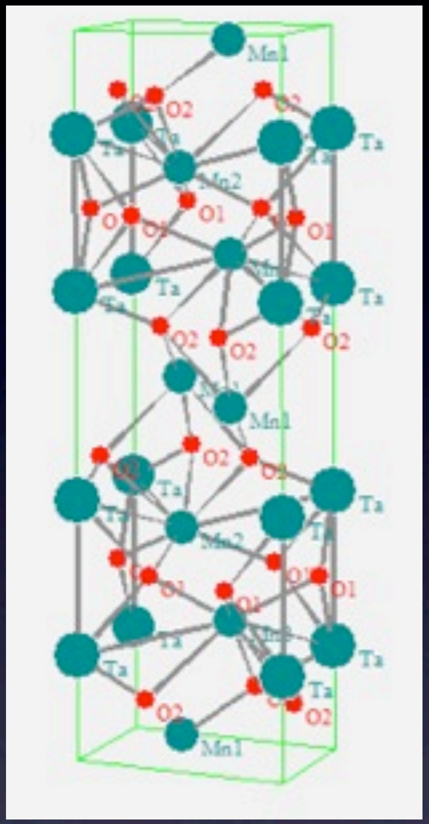
Newer Candidates

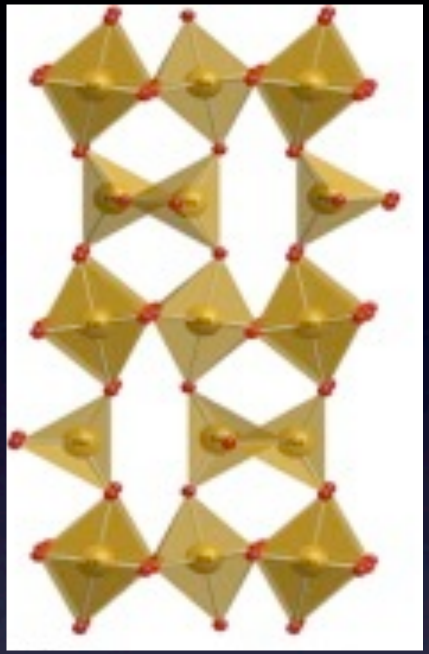
Swedenborgites

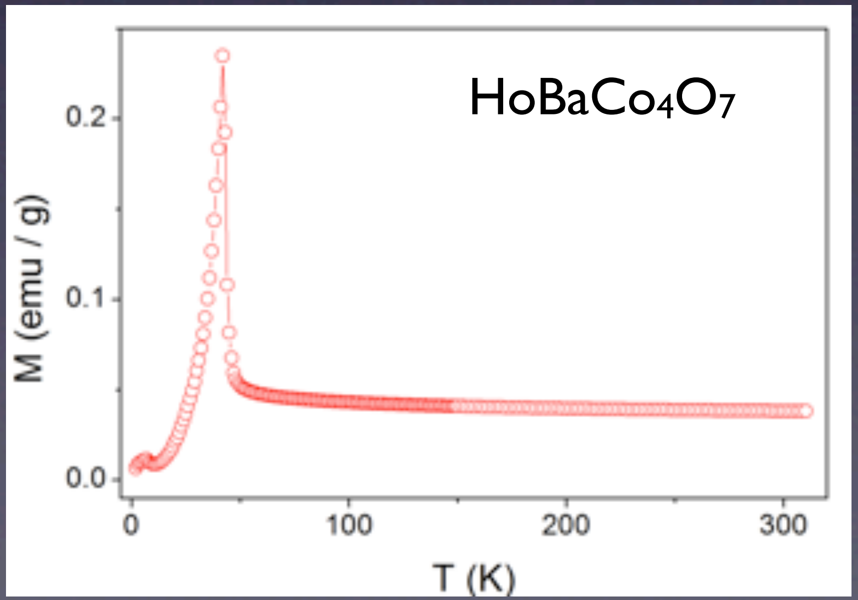
Tantalates

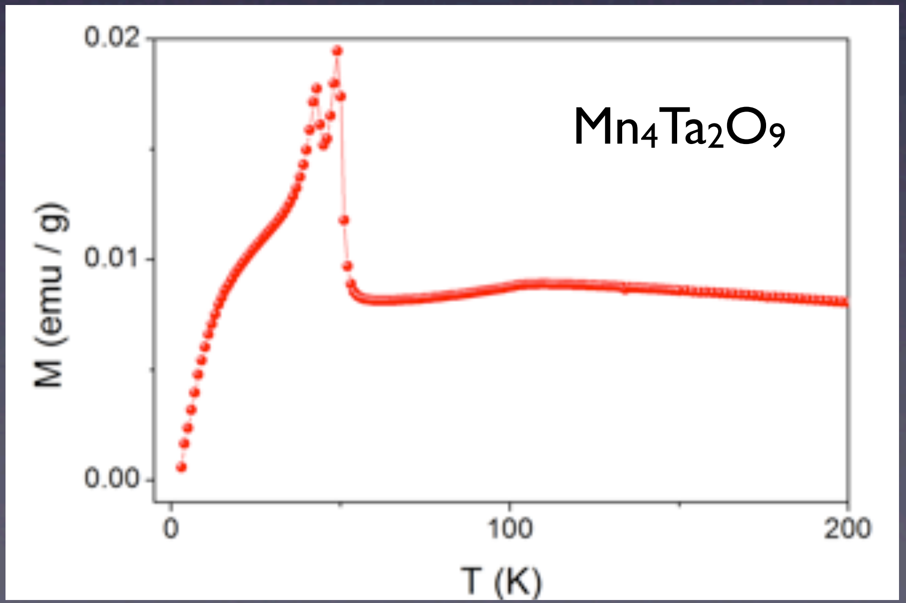
Brownmillerite

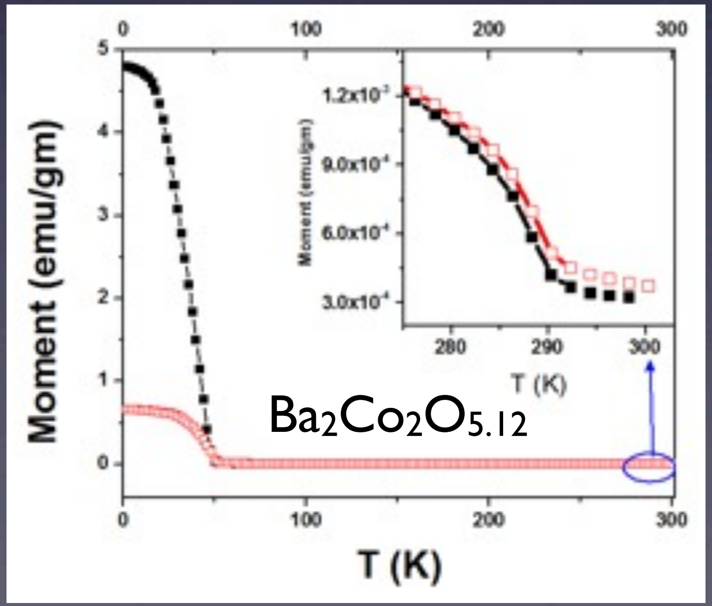












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