Tuning multiferroics under extreme conditions: Effects of high pressure, magnetic fields, and substitutions

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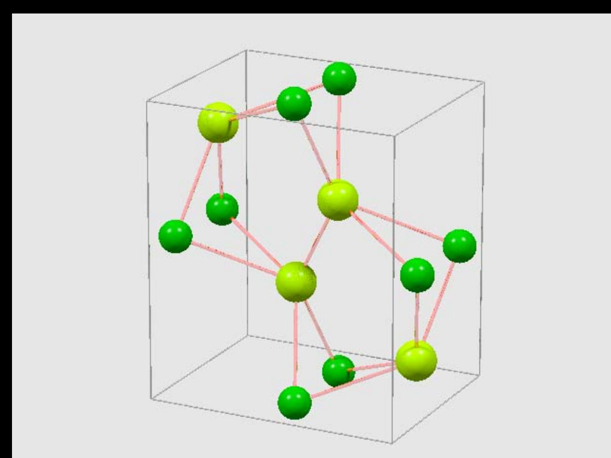

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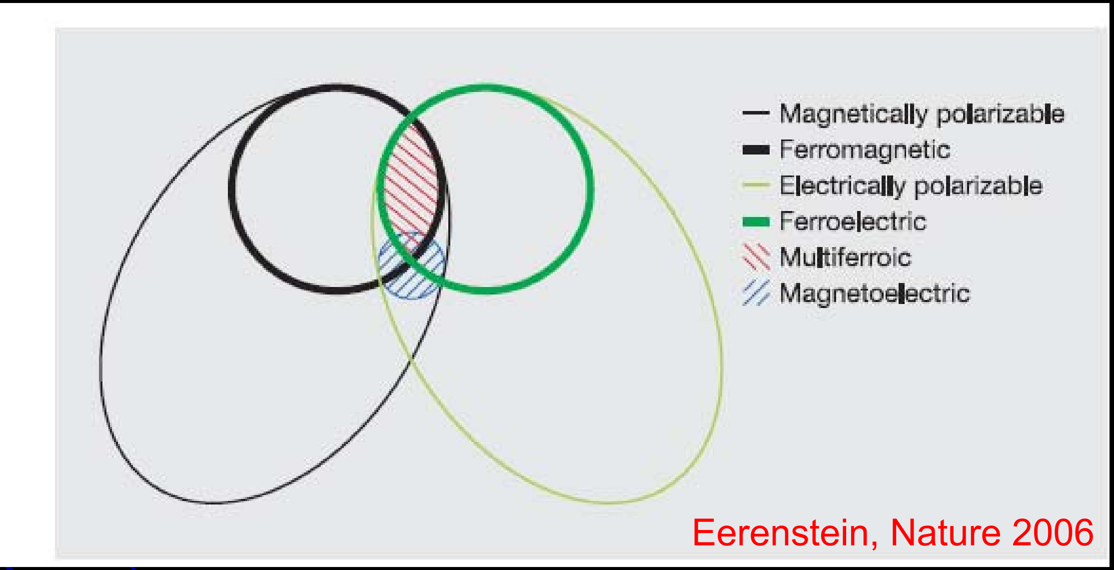
Outline

1) Short introduction: Multiferroics (MF)
2) Helical magnetic order, exchange striction, and double exchange as the source of ferroelectricity
3) The significance of magnetoelastic effects and spin-lattice interaction – how to detect them in MF
4) The effects of high pressure on the MF phases and ferroelectricity
5) Tuning MF properties by ionic substitutions
6) Summary

1. Short introduction: Multiferroics

Multiferroic :

Materials showing magnetic (FM, AFM) and ferroelectric (FE) orders coexisting in some temperature range and a sizable coupling between them.



Materials are rare since two fundamental symmetries have to be broken:

Time reversal symmetry (magnetic order) and
Spatial inversion symmetry (ferroelectric order)

Important role of frustration:

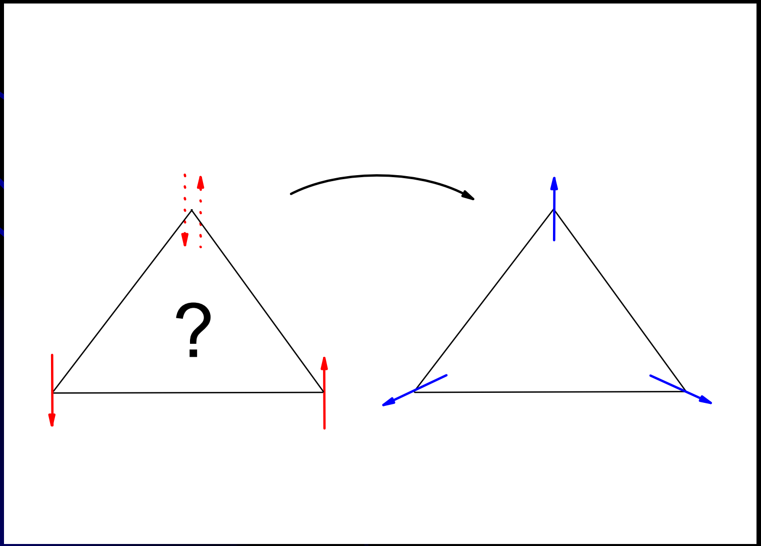
Note:

If Humans get frustrated .....
they often don't know what to do .....
and a small perturbation can change their mood

The same "rules" apply to frustrated physical systems

Examples of frustrated orders:

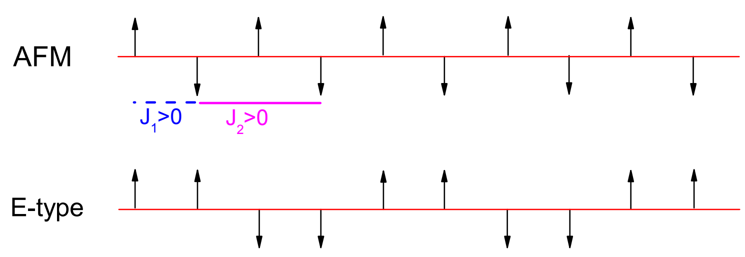
1. Geometric frustration



AFM spins on a triangular lattice are frustrated =>

Noncollinear order, spin rotations, complex phase diagrams ($HoMnO_3$)

2. Frustration due to competing interactions



Ground state energy (Ising limit):

AF: $N (J_2 - J_1)$

E-type: $- N J_2$

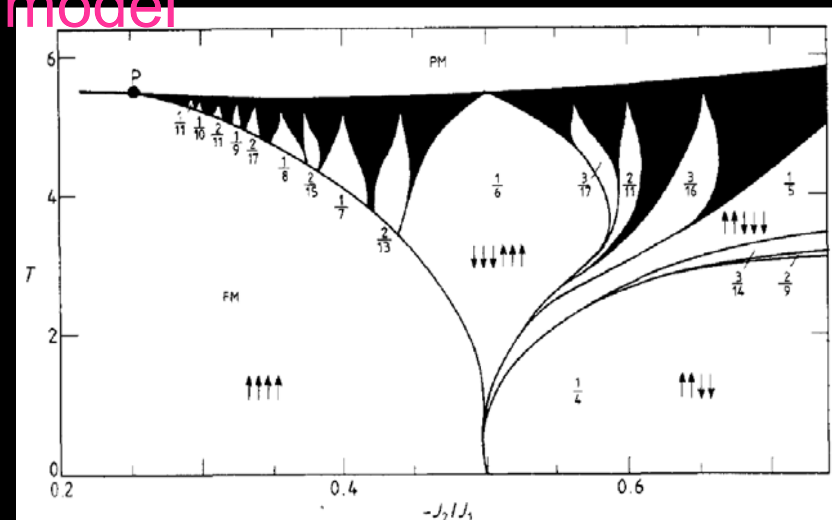
Transition from AF to E-type at $J_1 = 2 J_2$

Same arguments hold for $J_1 < 0$ (FM to E-type)

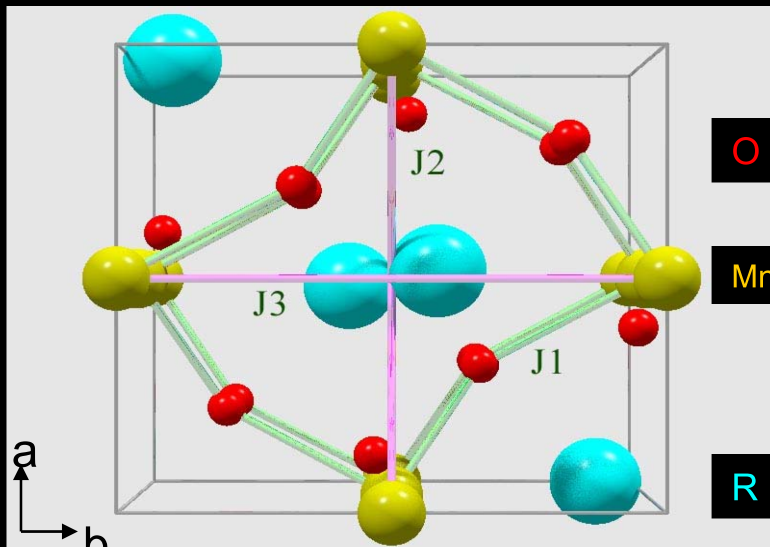
In a simple Ising (Heisenberg) model of spins with AFM/FM first and AFM second neighbor interaction there is frustration and degeneracy near $J_1 = 2J_2$

- This results in a complex phase diagram at T>0 with many commensurate and incommensurate phases

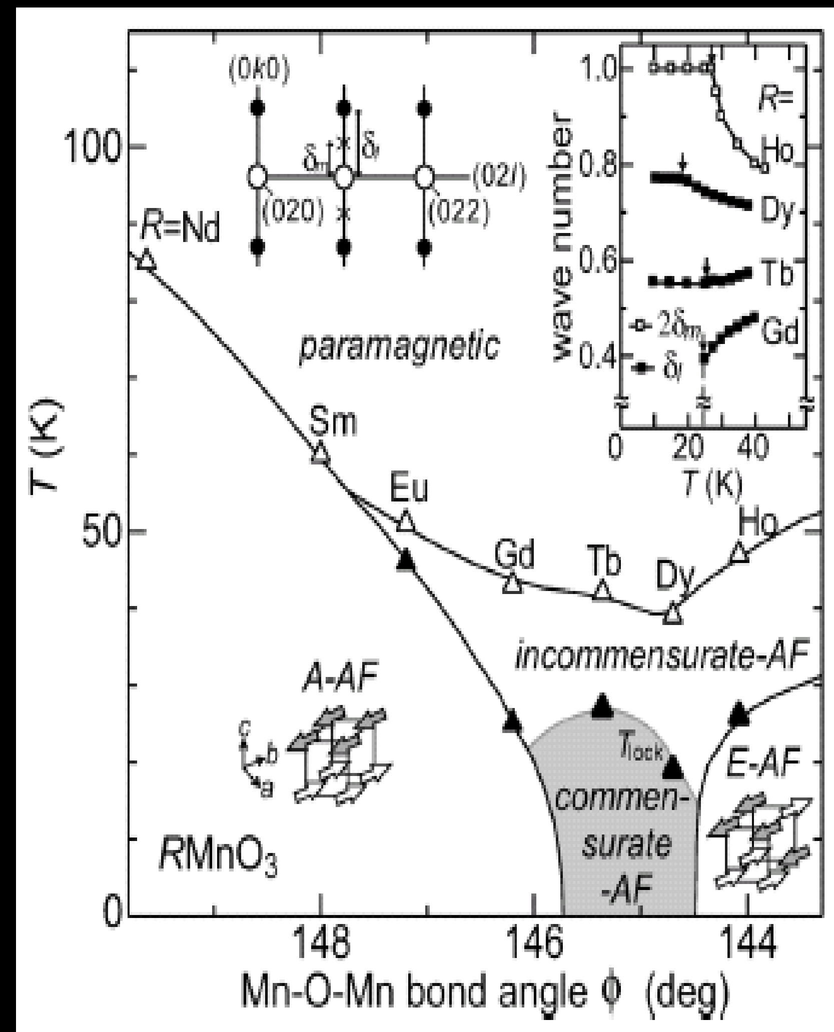
The devil's tree of the Ising model



Competing interactions in $RMnO_3$



Magnetic phase diagram of orthorhombic $RMnO_3$



Superexchange couplings Mn^{3+} - O - Mn^{3+} :

$J_1<0$ (FM) but $J_2>0$ (AFM)

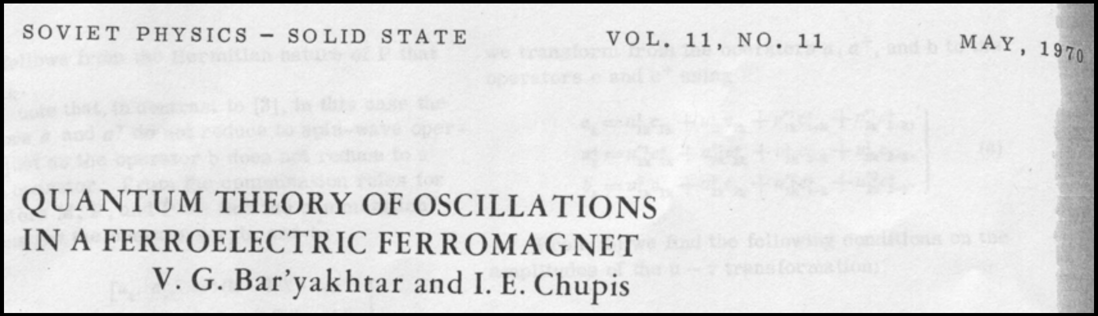
depend on bond angle Φ (Mn-O-Mn), which is controlled by size of R

Frustration and "exotic" phases near Φ ≈ 145 deg

Novel physical effects in multiferroic compounds:

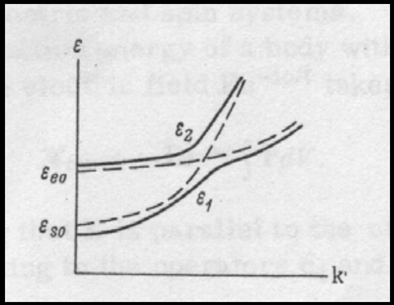
- ✓ Ferroelectricity induced by magnetic orders (e.g. $TbMnO_3$, $Ni_3V_2O_8$, $MnWO_4$)
- ✓ Rotation of FE polarization by 90˚ in magnetic fields ($TbMnO_3$, $MnWO_4$)
- ✓ Complete reversal of FE polarization by magnetic fields ($TbMn_2O_5$)
- ✓ Giant magneto-dielectric effect in $DyMn_2O_5$
  (increase of dielectric constant by more than 100 % in magnetic fields)
- ✓ Ferromagnetic order induced by electric fields ($HoMnO_3$)
- ✓ Complex magnetic phase diagrams with incommensurate and commensurate magnetic structures, lock-in transitions, and multicritical points
- ✓ Experimental discovery of a new excitation - electromagnons
- ✓ . . . . .

Experimental discovery of a new fundamental excitation – The ***electromagnon***


SOVIET PHYSICS – SOLID STATE VOL. 11, NO. 11 MAY, 1970

QUANTUM THEORY OF OSCILLATIONS IN A FERROELECTRIC FERROMAGNET

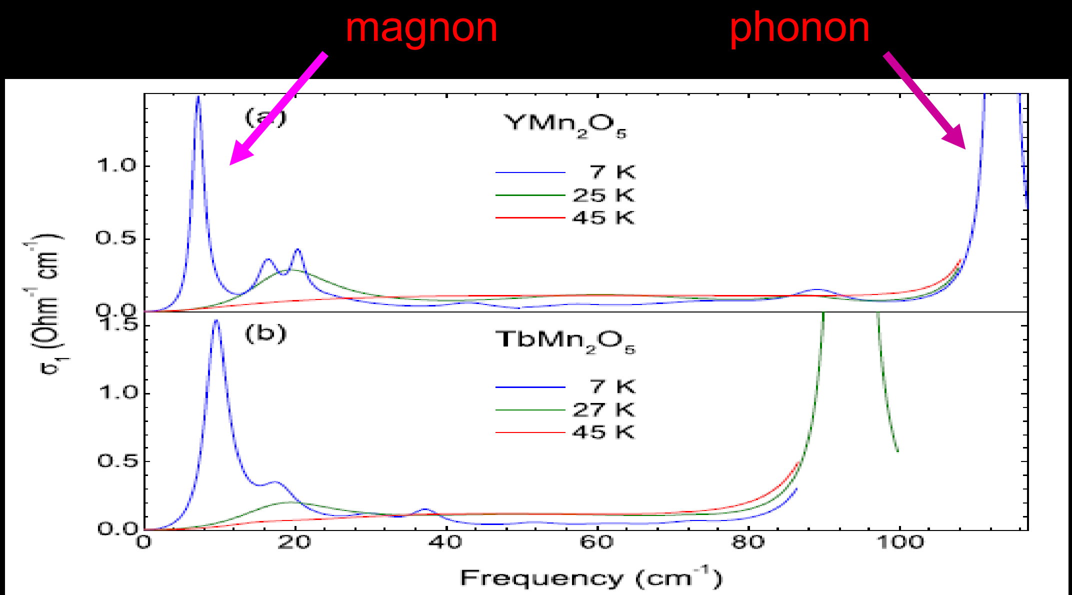
V. G. Bar'yakhtar and I. E. Chupis



Theoretically predicted in 1970: Hybrid excitation of a phonon and a magnon due to strong spin-phonon coupling

➔ Low-energy excitation (10 ... 20 cm^{-1}) predicted in optical experiments (electric field can excite a magnon)

Experimentally confirmed in 2006 in different multi-ferroic compounds:



2. Helical magnetic order, exchange striction, and double exchange as possible sources of FE

Search for common features (magnetic orders) in different MF compounds:
The important role of neutron scattering experiments as the key investigation

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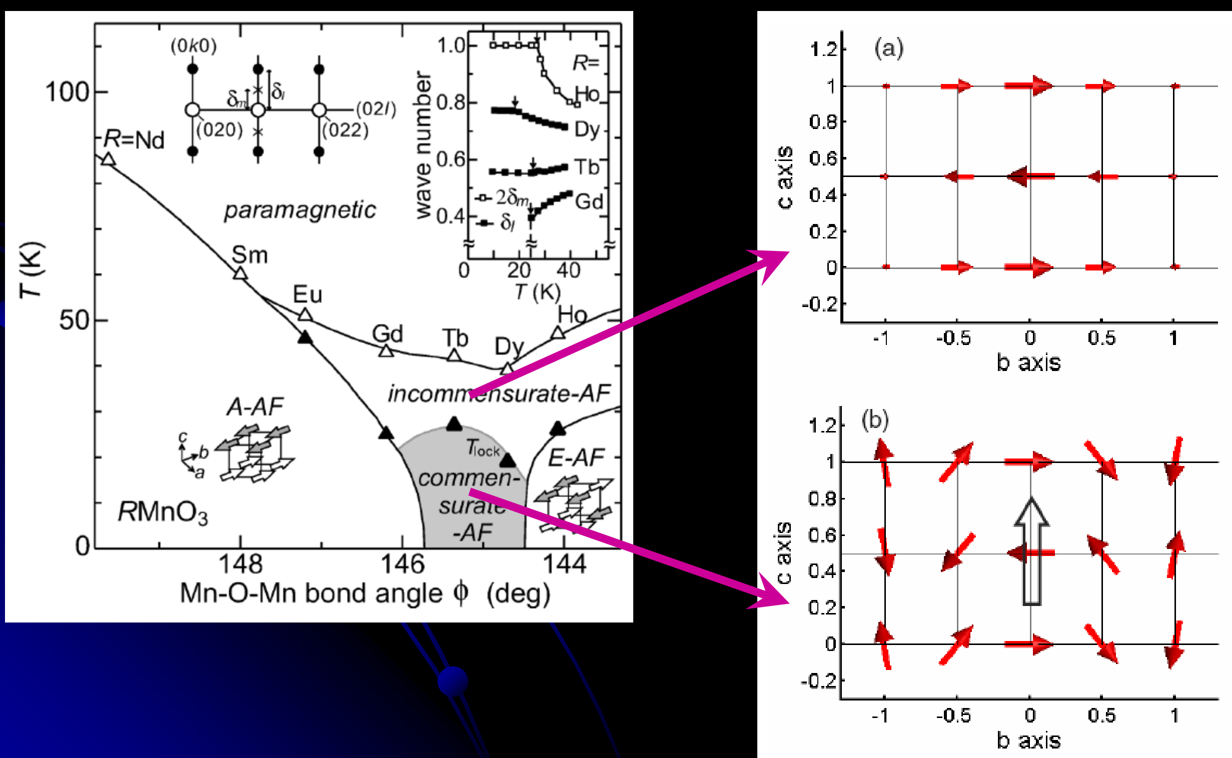
$TbMnO_3$



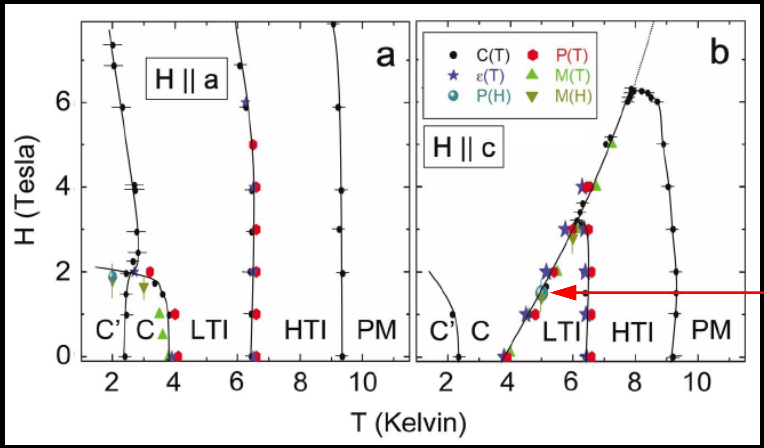
HT IC order ➔

sinusoidal modulation

LT IC order ➔

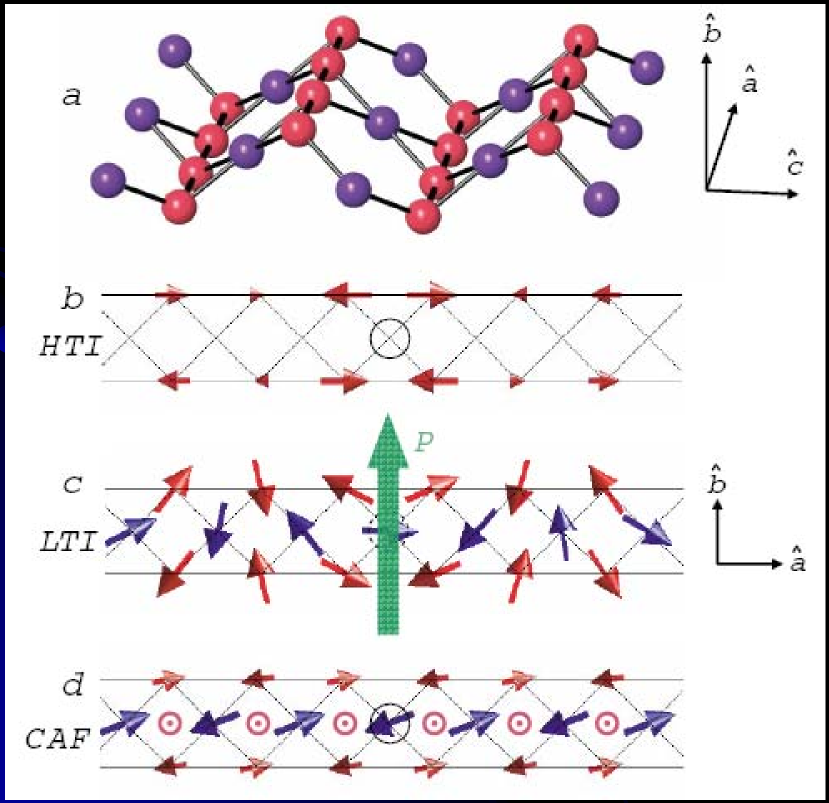
helical (spiral) modulation
(spatial inversion symmetry is broken)

$Ni_3V_2O_8$



Magnetic frustration is due to the geometry (kagome) with AFM exchange

Only LTI phase is ferroelectric !



HT IC order ➔
sinusoidal modulation, inversion symmetry

LT IC order ➔
helical (spiral) modulation, no IS

Commensurate order ➔
sinusoidal modulation, inversion symmetry

$WMnO_4$

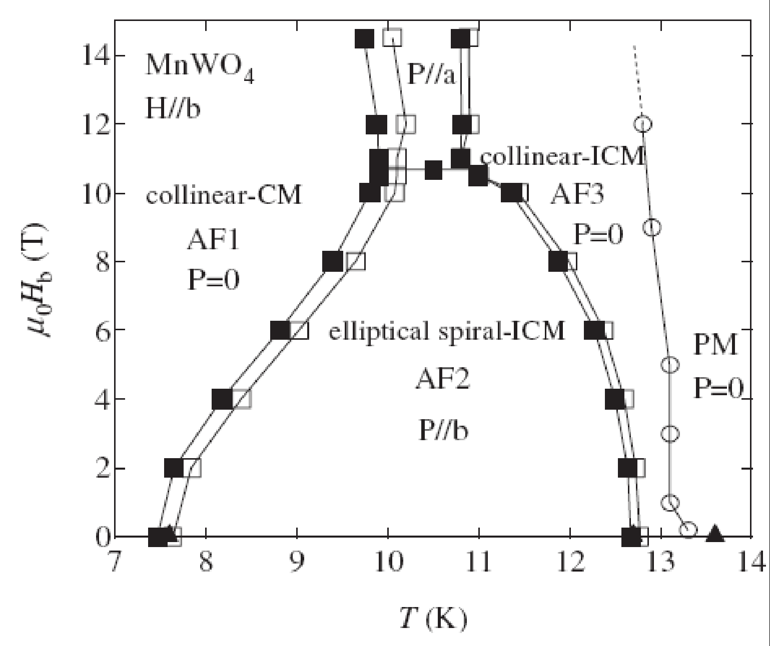
Frustration due to competing intra-chain interactions (FM / AFM)

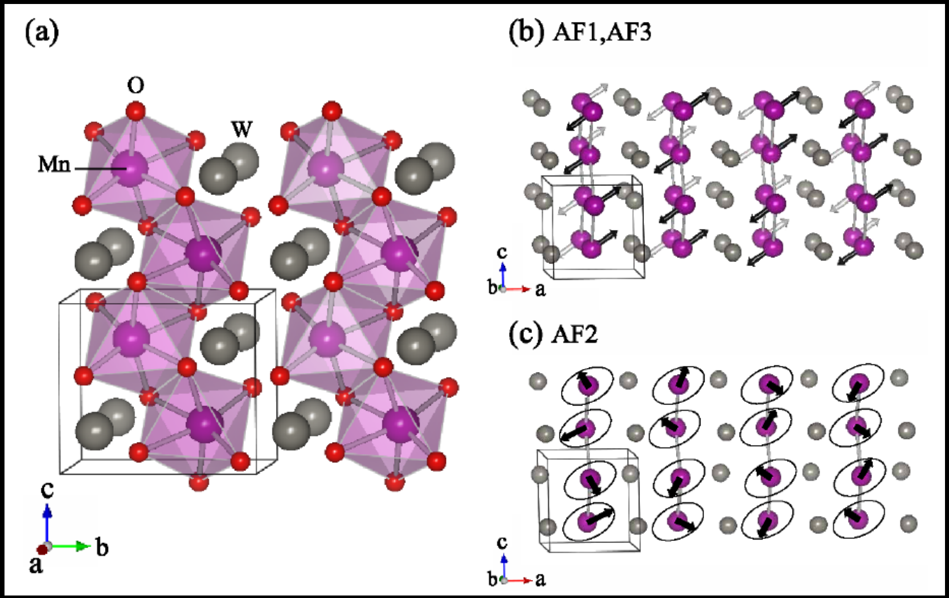
Same phase sequence:

PM → Coll. ICM AF3

→ Helical ICM AF2 (ferroelectric)

→ Coll. CM AF1 (↑ ↑ ↓ ↓)

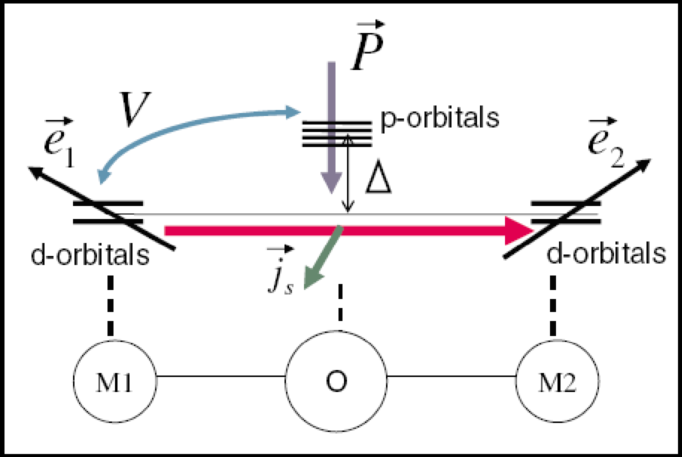




Very different compounds and structures reveal similar phenomena:

Ferroelectricity arising in a spiral magnetic phase ➔ The microscopic origin of FE is the symmetry of the magnetic order (breaking the spatial inversion)

FE polarization induced by non-collinear helical spins



Katsura et al., PRL 2005

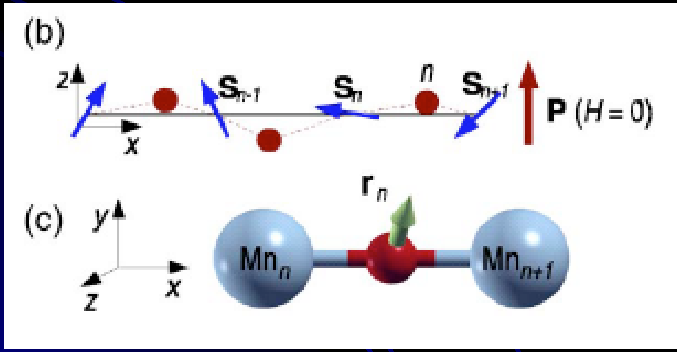
Spin-orbit coupling partially lifts the degeneracy of the Mn^{3+} d-orbitals (t_{2g})

Hopping Mn ↔ O is treated perturbatively in second order

Polarization of electronic orbitals :

$$\vec{P} \sim \vec{e}_{12} \times \left(\vec{e}_1 \times \vec{e}_2\right)$$

spin current



Sergienko/Dagotto, PRB 2006

Considered oxygen displacement at FE transition due to Dzyaloshinskii-Moriya interaction

DM interaction does stabilize the helical spin structure and the oxygen displacements resulting in the FE polarization

Symmetry and Landau theory (Kenzelmann, Mostovoy)

Lowest order coupling $\Phi_{em}(P,M)$ between F
modulation, M, that is invariant upon time re

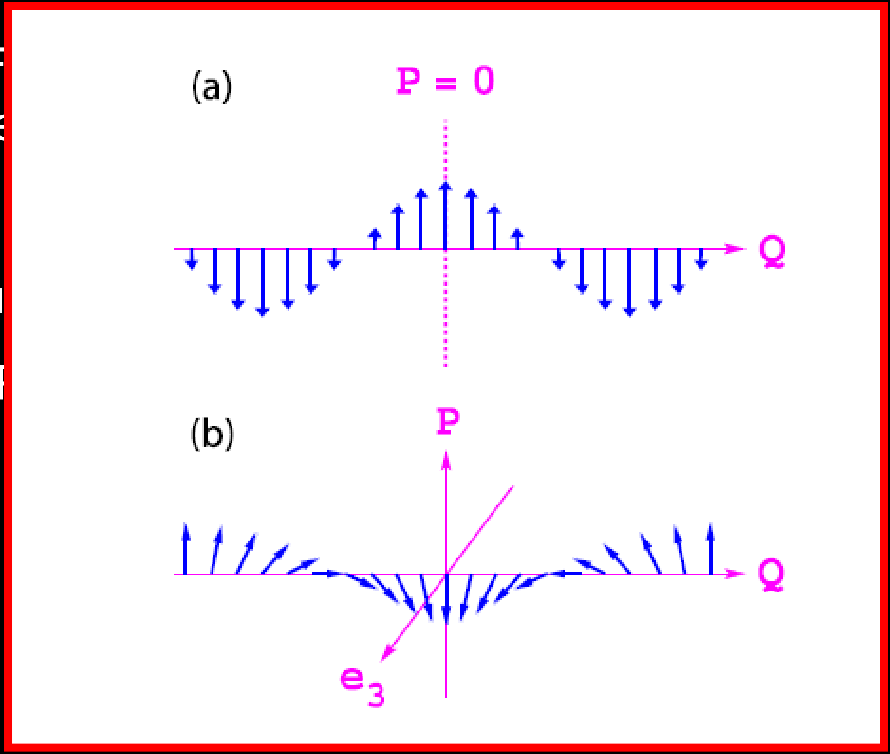
t -> -t : P -> P and M -> -M Φ_{em} qu

x -> -x: P -> -P and M -> M Φ_{em} ~ F

for cubic symmetry: Φ_{em} = const P*

$\Phi_e = P^2/(2\chi_e)$

P = const χ_e [



Spiral magnetic order: $M = m_1\, e_1 \cos(Qx) + m_2\, e_2 \sin(Qx) + m_3 e_3$

Average polarization: $\langle P \rangle = \text{const}\ \chi_e\, m_1\, m_2\, [\, e_3 \times Q\,]$

Sinusoidal magnetic order: m_1 or $m_2 = 0$ => $\langle P \rangle = 0$

FE polarization induced by exchange striction of frustrated spins

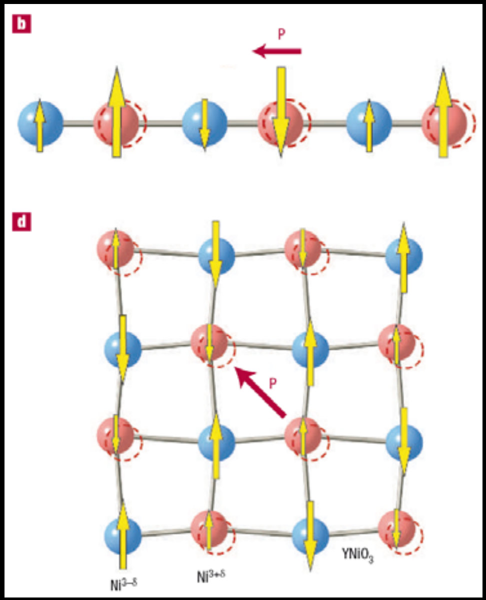
Two frustrated spins tend to separate to reduce magnetic exchange energy

Applies to: E-type (↑↑↓↓) magnetic order due to competing NN and NNN interactions

If the associated ions have different charges => local polarization of the lattice

Can add up to macroscopic polarization and ferroelectricity

No need of non-collinear spin order



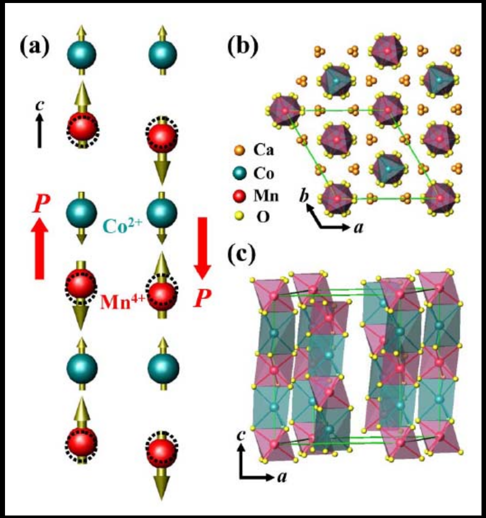
Cheong/Mostovoy, Nature Mat. 2007

Examples:

Ising chain magnet Ca_3CoMnO_6 (Choi et al., PRL 2008)

RMn_2O_5 (*R* = rare earth, Y, Bi)

but not *R*MnO_3 with E-type magnetic order ($HoMnO_3$) - no charge order



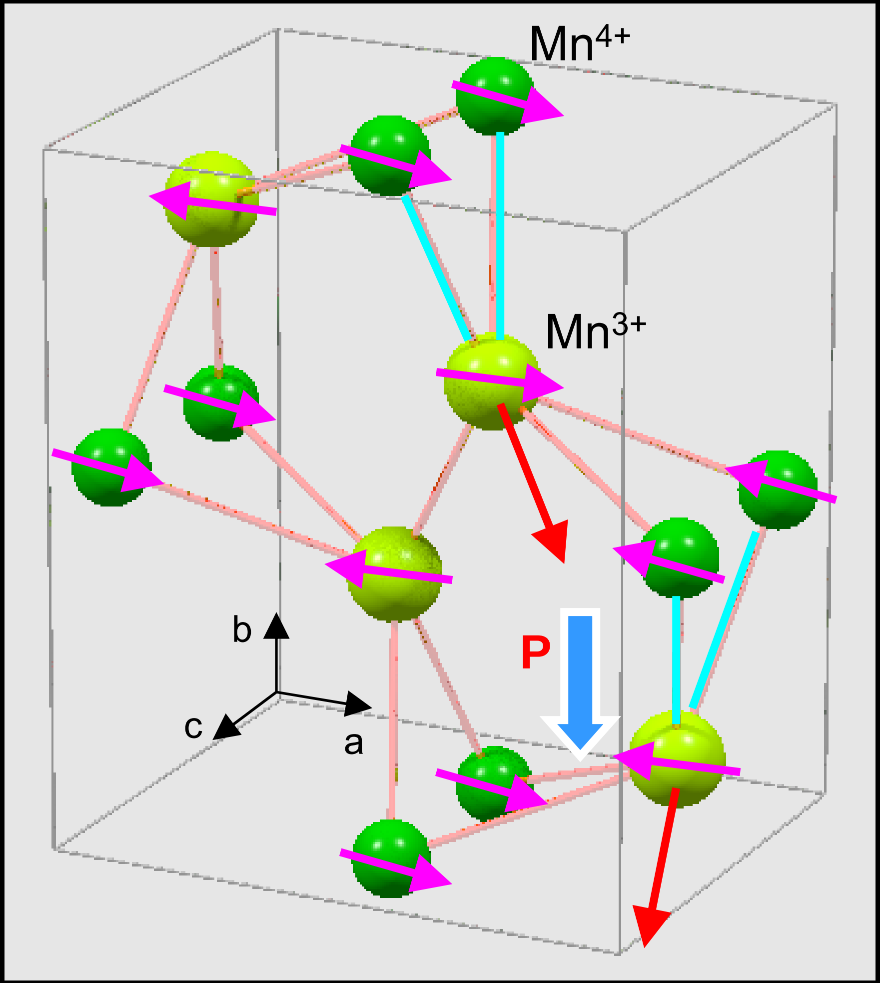
Ferroelectricity due to possible exchange striction effects in RMn_2O_5

Magnetic structure from neutron scattering

Superexchange interactions determine exchange parameters between Mn spins

At least 5 different exchange integrals can be distinguished $\Rightarrow$ Mostly AFM

Ionic displacements relax the magnetic frustration and generate the polarization along the b axis



Ferroelectricity in Multiferroics with E-Type Magnetic Order (Theory – Double exchange model)

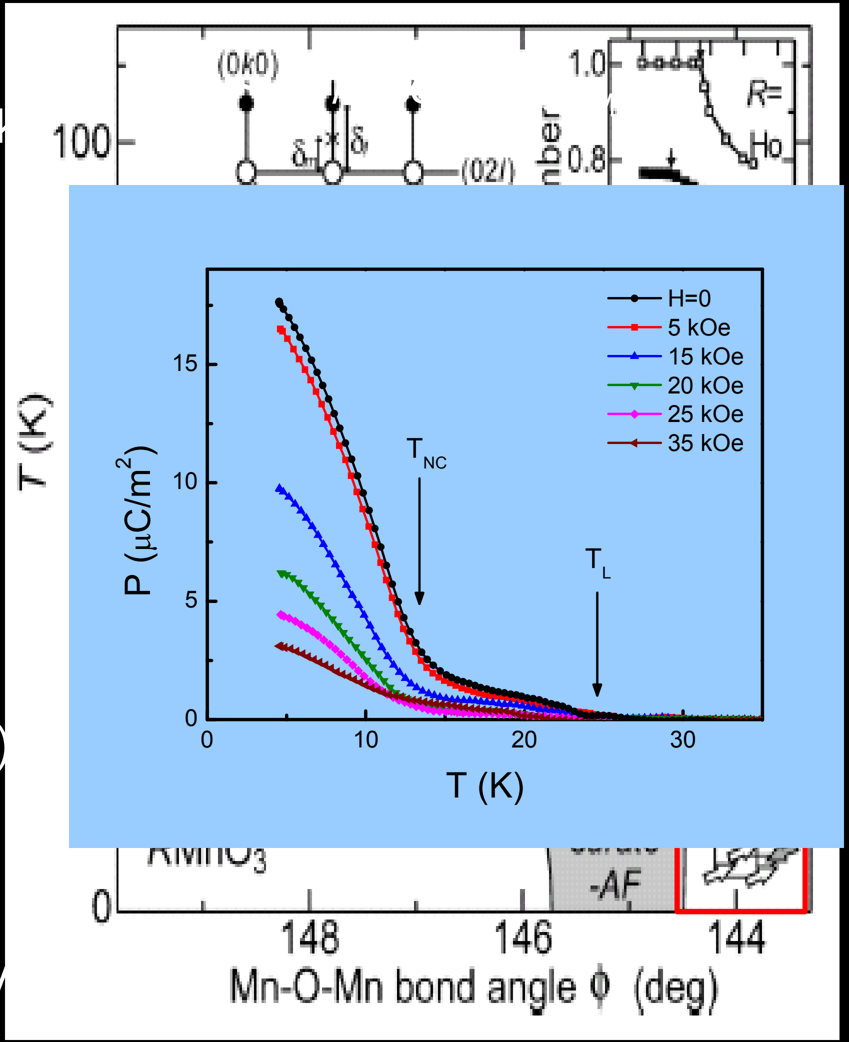
E-type magnetic order in $RMnO_3$: R = Ho

Sergienko/Dagotto, PRL 2006:

"Double-exchange" (virtual) mechanism work against Jahn-Teller distortion in FM spin chains along a-axis

Does not involve DM interaction

Large FE polarization predicted



Problems:

Experimental – only polycrystalline samples can be synthesized (high-pressure synthesis)

Theoretical – predicted polarization is three orders of magnitude larger than measured

Dual nature of FE (electronic + ionic) recently suggested (Picozzi et al., PRL 2007)

2. Magnetoelastic effects and spin-lattice coupling – how to measure these effects ?

In multiferroics the spin-lattice interaction plays a decisive role in mediating the (improper) ferroelectricity induced by magnetic orders

The measurements of the ionic displacements and/or the macroscopic lattice strain is therefore of interest

Scattering experiments (x-ray, neutron) provide the tool to measure displacements on a microscopic level – but often lack the resolution to detect the tiny changes.

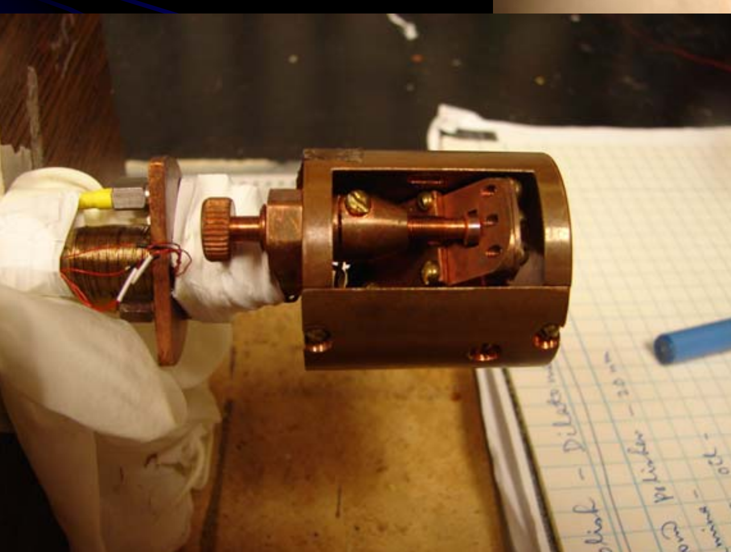
Note: The atomic displacements explaining the experimental values of the FE polarization are as small as 10^{-4} Å .

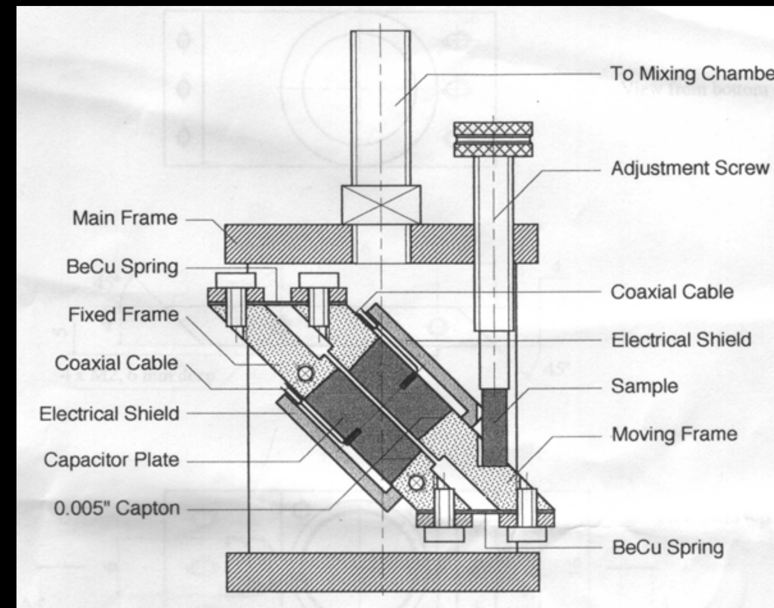
Only a few attempts to derive structural distortions at the magnetic and ferroelectric transitions in multiferroics have been successful.

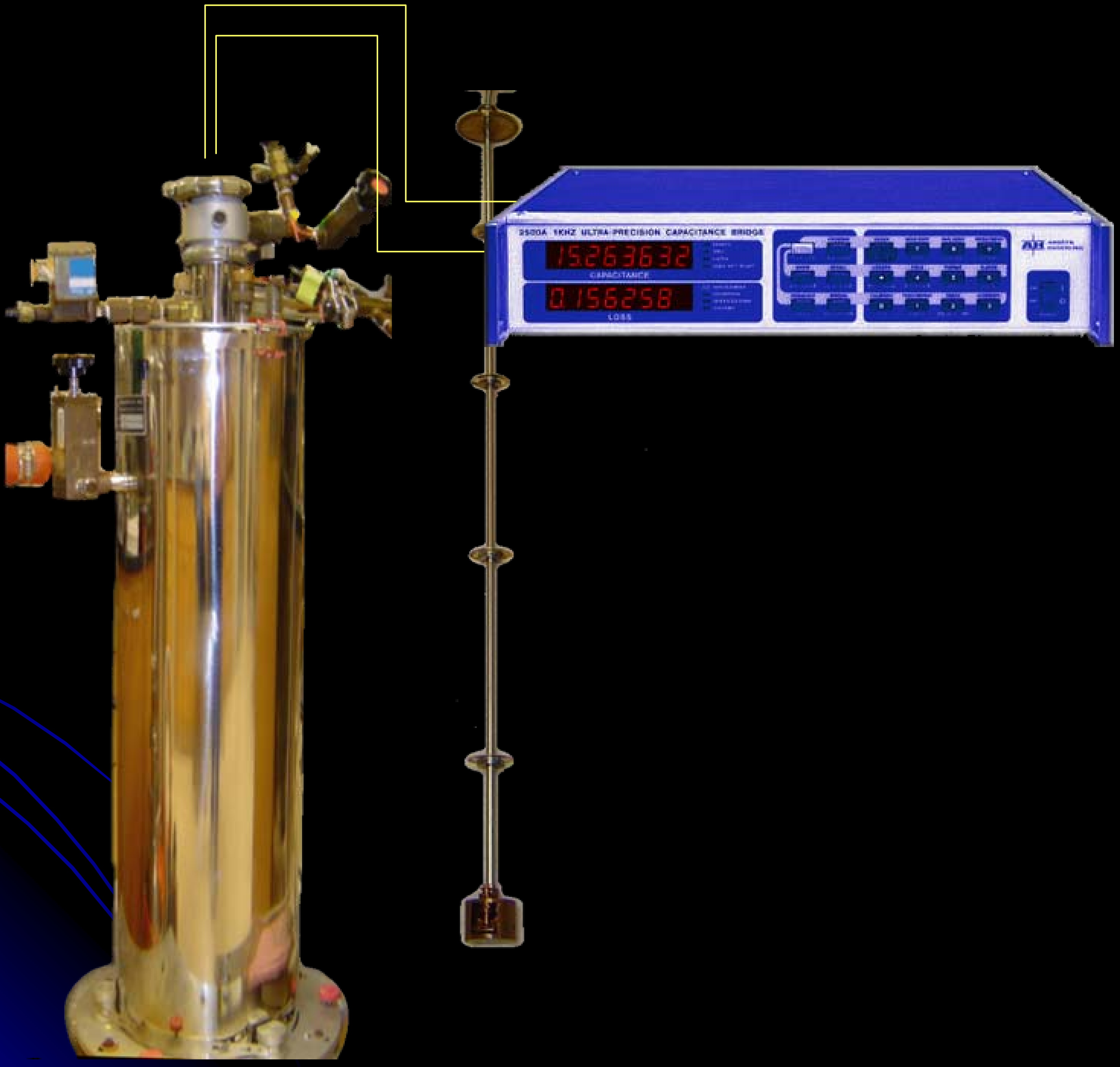
Capacitance dilatometer for high-resolution measurements of lattice strain

(i) Capacitance can be measured with extreme accuracy (~ 10^{-8})

(ii) Measuring the absolute length change of a macroscopic sample can further increase the relative resolution in proper geometry of the device






2500A 1KHZ ULTRA-PRECISION CAPACITANCE BRIDGE
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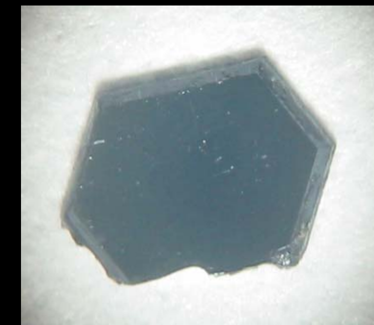
Structural distortions in multiferroic (hex.) $HoMnO_3$

Growth of high-quality single crystals from high-T solution (right) of through a floating zone furnace.

Compound is multiferroic with $T_C > T_N$

Magnetic order on triangular lattice is highly frustrated



Ferro

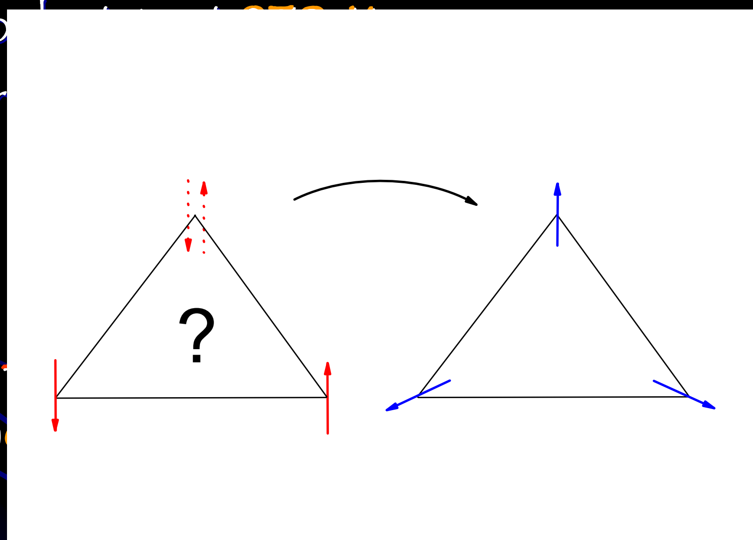
Polar

AFM

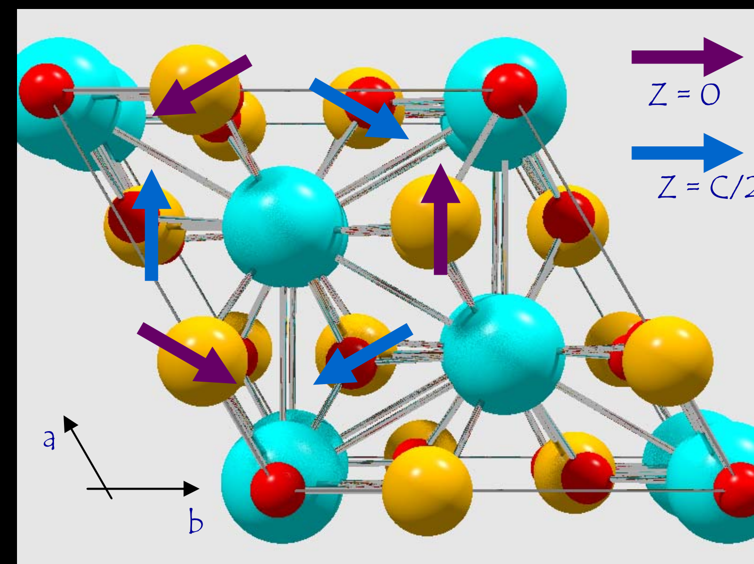
Mn^{3+}

➔ long-

in th

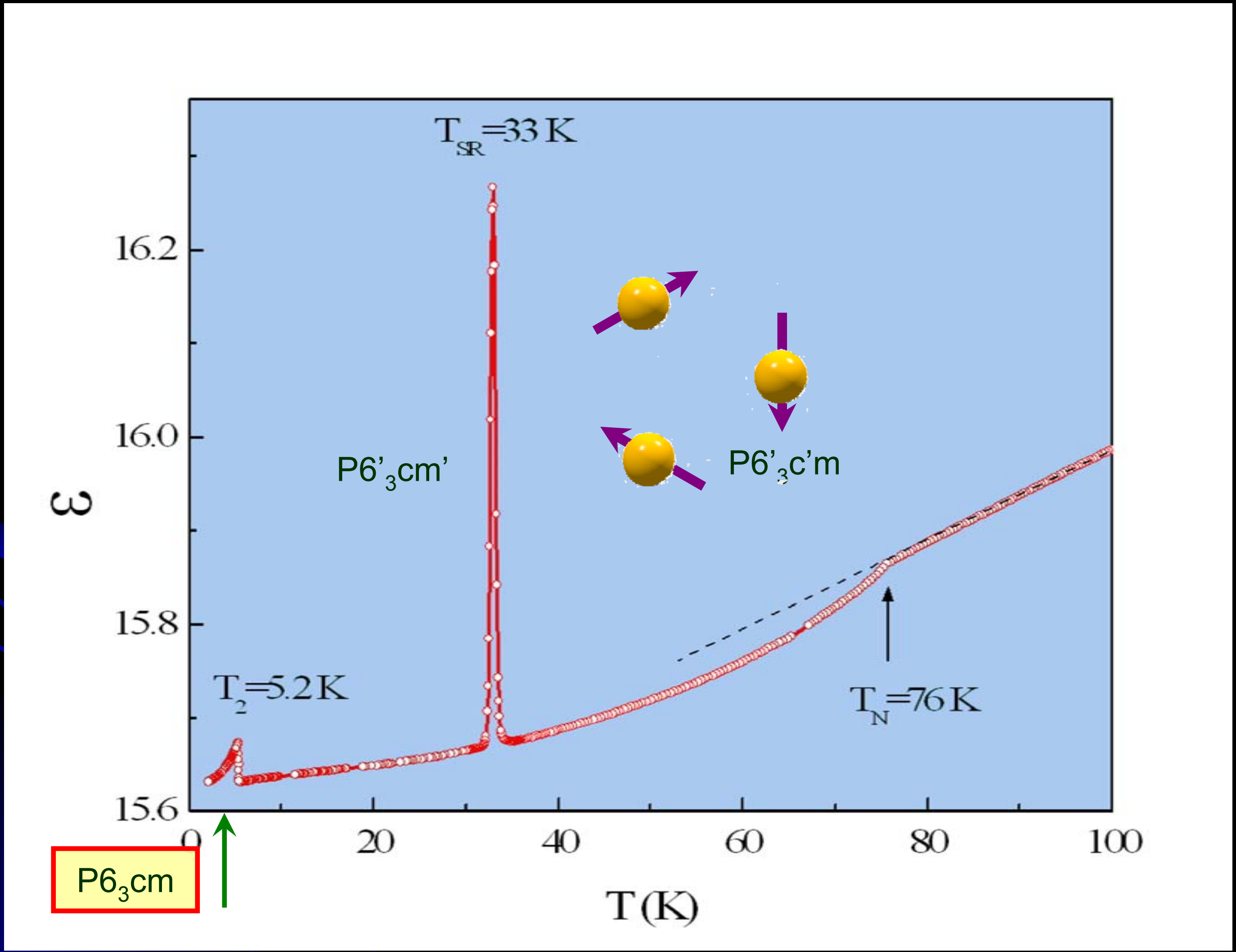


Mn^{3+} moments undergo a spin rotation at T_{SR}=33 K into the $P6'_3cm'$ symmetry



Mn^{3+} moments rotate into the $P6_3cm$ structure at 5 K

Dielectric Anomalies at the Magnetic Transitions of $HoMnO_3$



Dielectric Anomaly at and below T_N

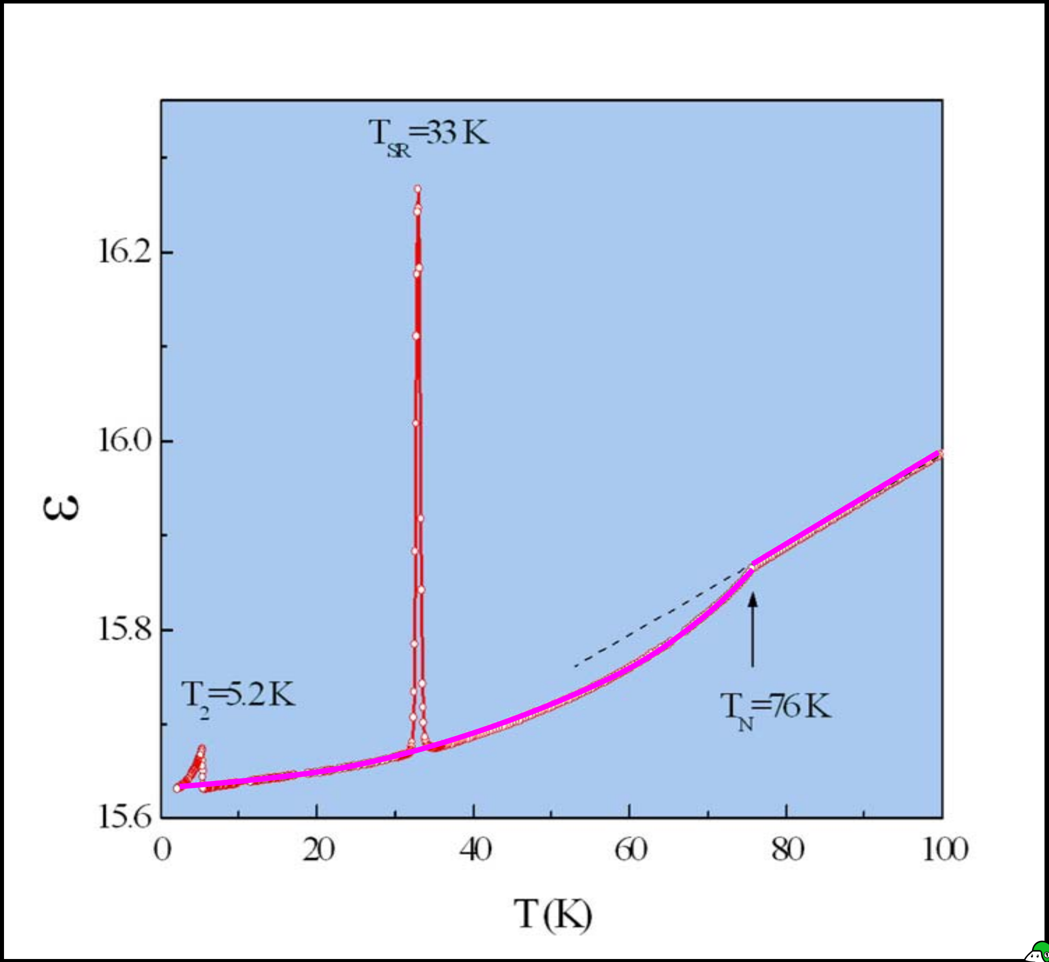
(common to all hexagonal $RMnO_3$)

No direct coupling between c-axis polarization and in-plane magnetization allowed by symmetry

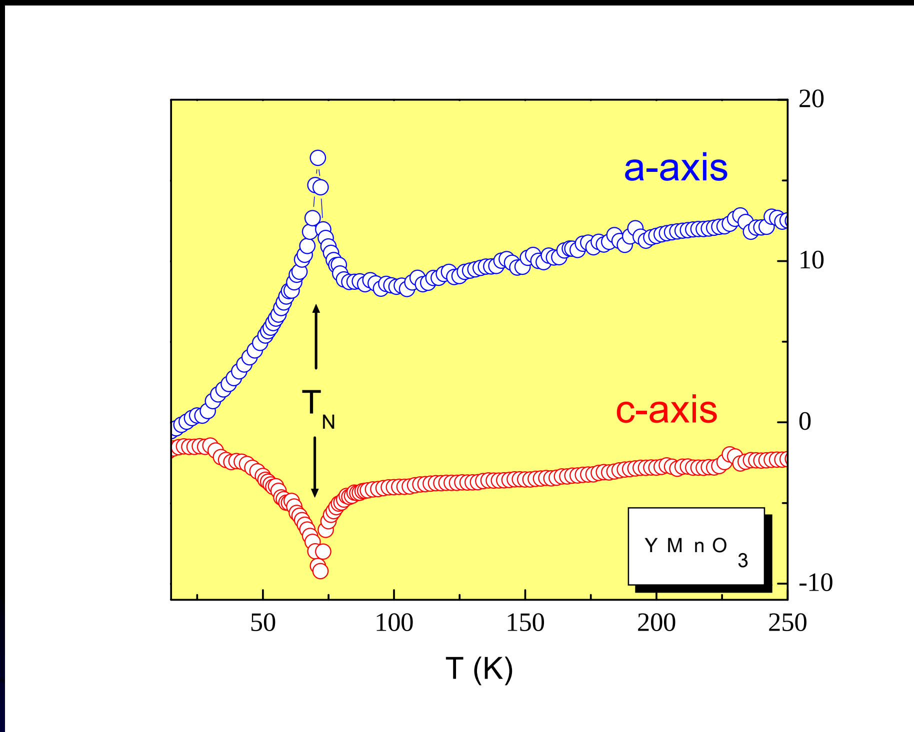
Magneto-dielectric coupling via lattice deformation (magneto-elastic effect)

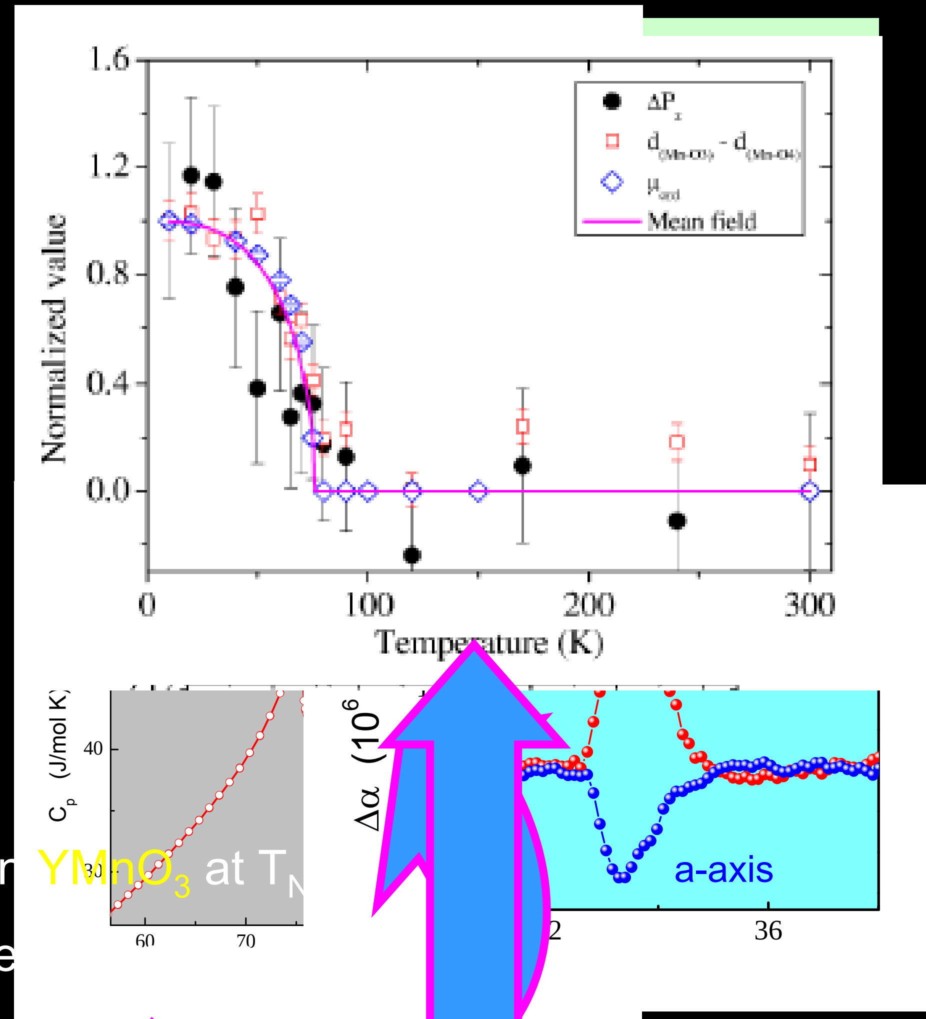
Strong spin-lattice interactions required

Search for structural anomalies or lattice strain



Thermal Expansion Anomalies in $HoMnO_3$ (and $YMnO_3$)





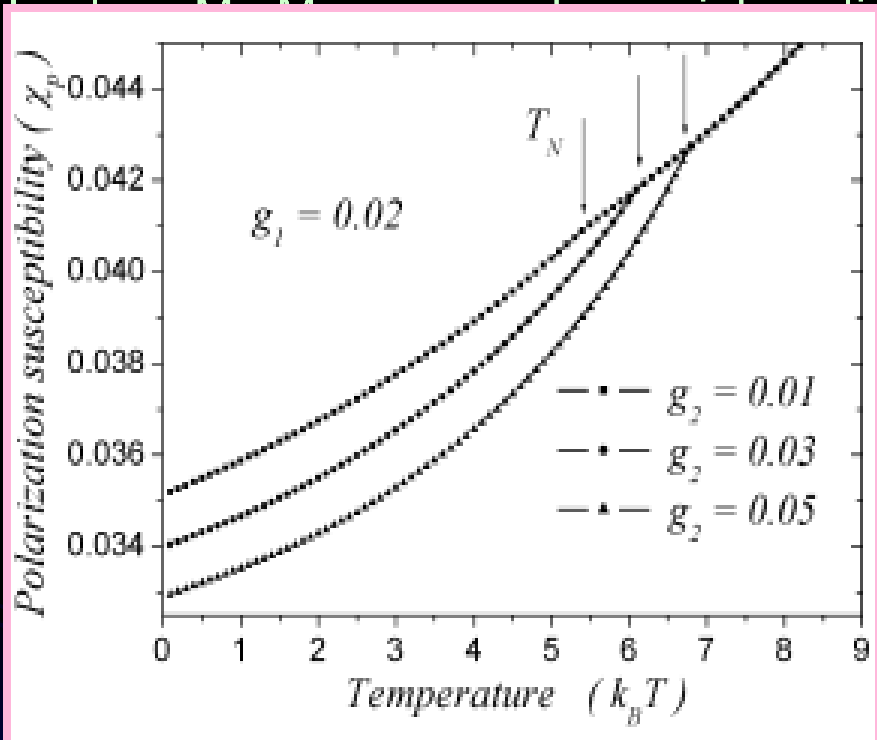
Similar expansion anomalies are also found in $YMnO_3$ at T_N

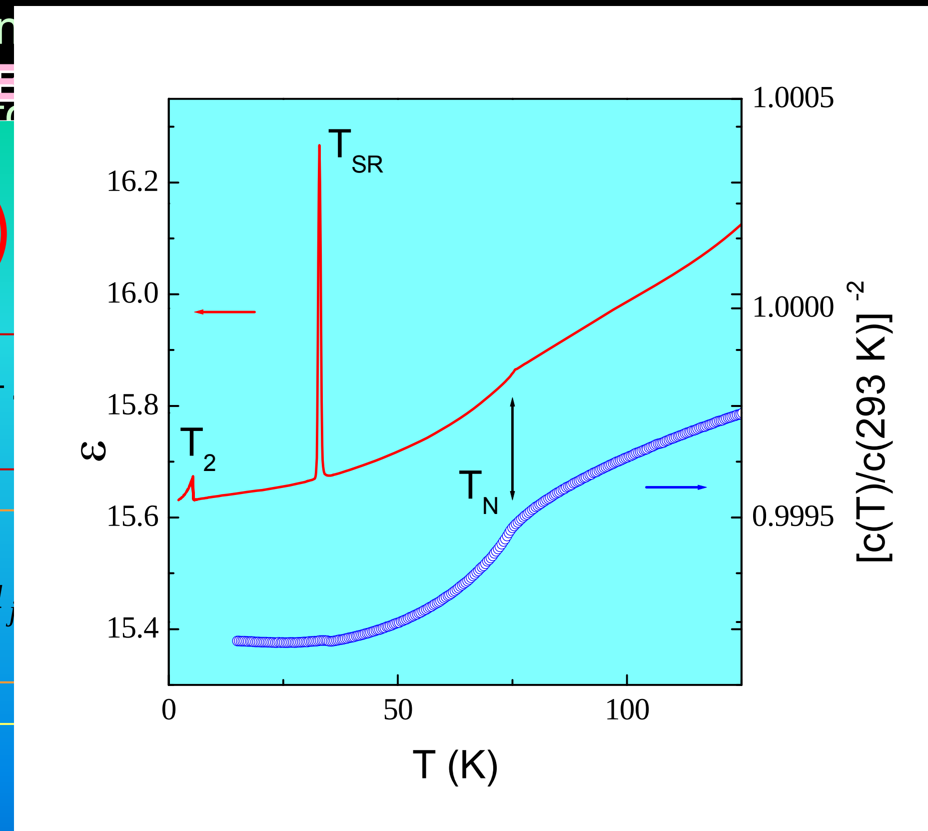
The negative c-axis expansivity appears to be

Recently confirmed by HR neutron scattering (Lee et al., PRB 71, 180413(R) , 2005)

Evidence for increase of FE polarization below T_N

Strong spin-spin and spin-lattice coupling in $RMnO_3$





$$\mathcal{H}^{me} = \sum_{k,\langle i,j\rangle} u_k^2\left(g_1 s_i^z s_j^z + g_2\left(s_i^x s_j^x + s_i^y s_j^y\right)\right)$$

$\varepsilon \sim 1/\langle u_k\rangle^2$ scales with $1/c^2$

C. Zhong and J. Fang *Solid State Comm.* 128, pp449 (2003)

Structural distortions and ferroelectricity in RMn_2O_5

Space group Pbam:

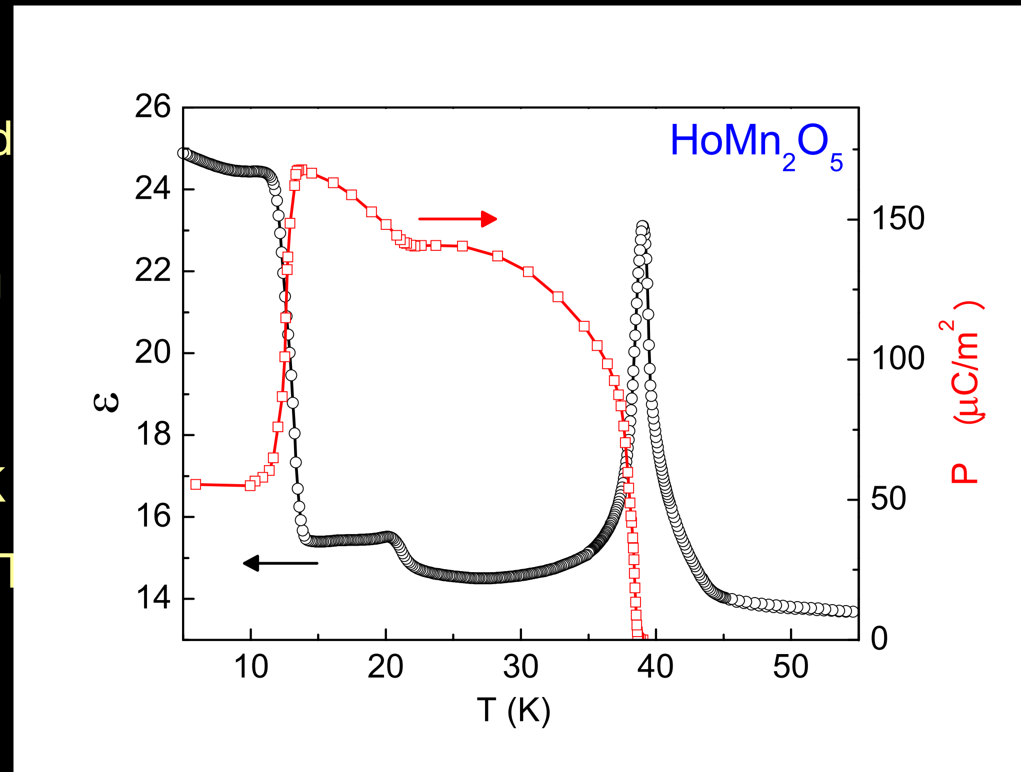
MnO_6 octahedra form ribbons || c and are linked by MnO_5 bi-pyramids

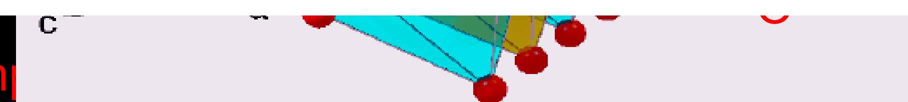
Mainly AFM superexchange coupling between Mn moments

Ferroelectricity arises just below the AFM ordering temperature, $T_N \approx 40$ K

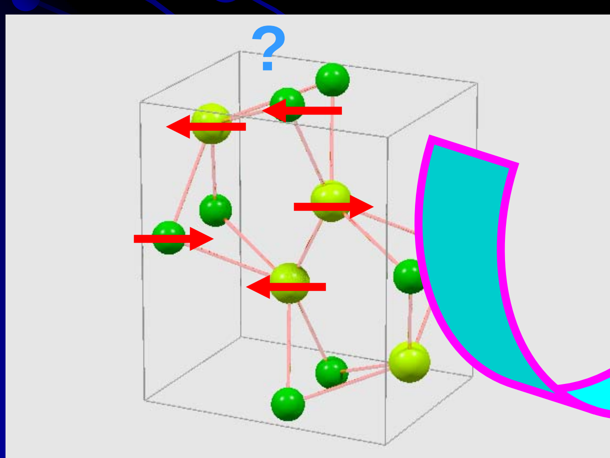
Additional phase transitions at lower T

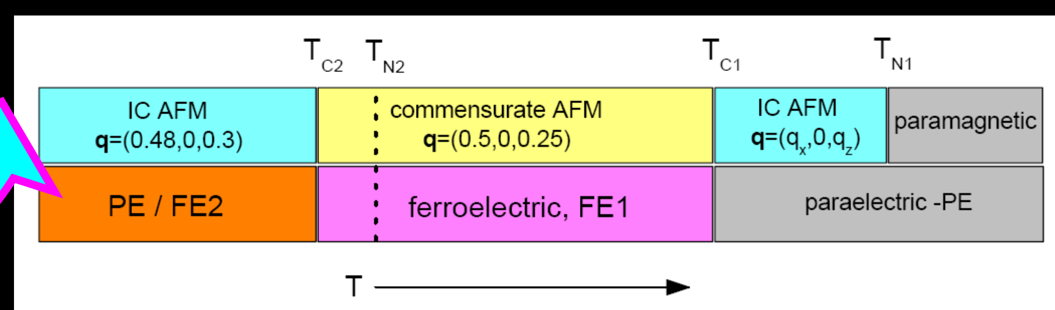
Magnetic frustration among the Mn spins !





Comp

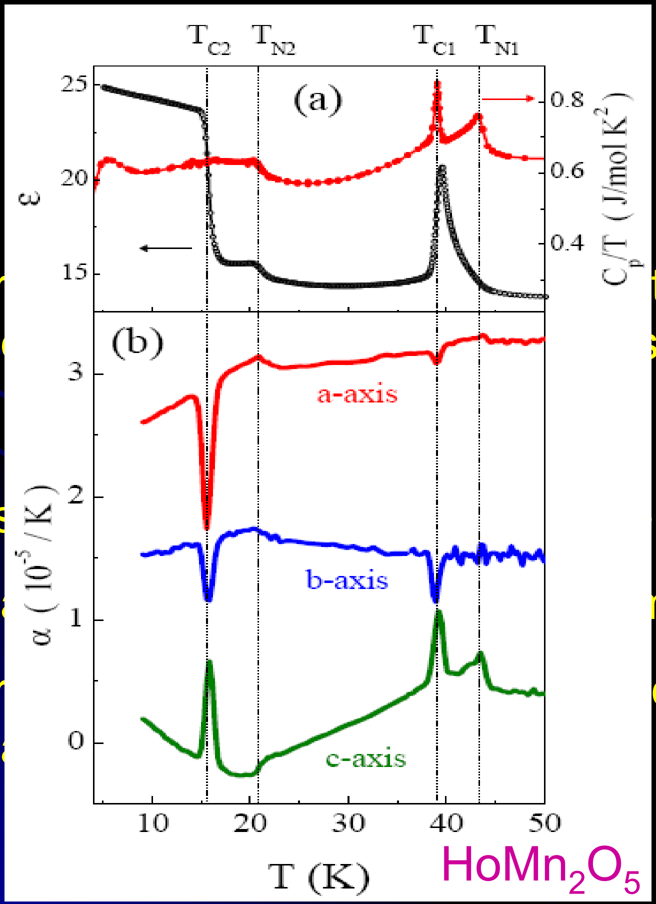


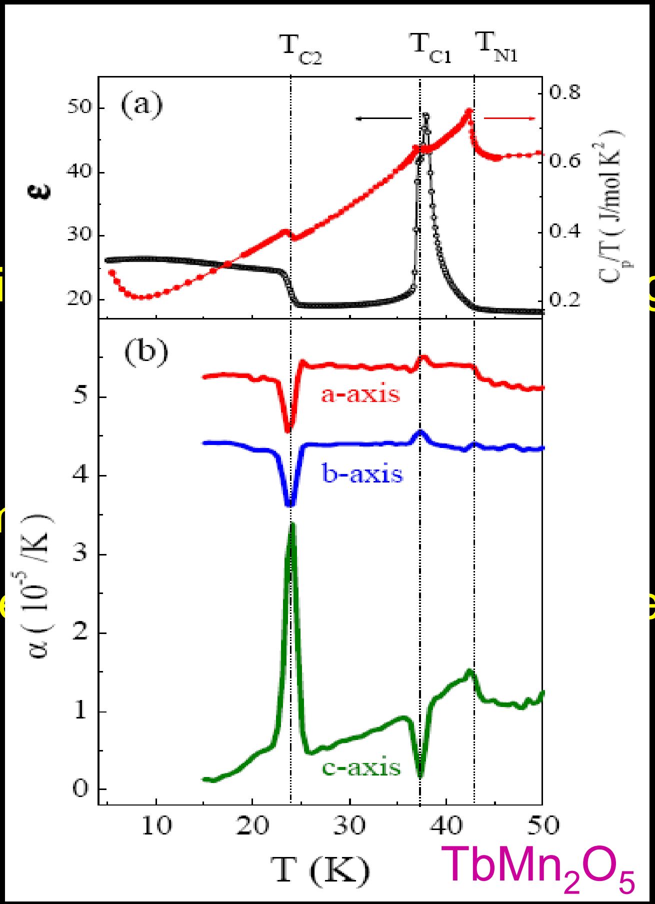


Search for structural anomalies at the FE and AFM transitions

The lattice strain associated with the ferroelectric transitions in RMn_2O_5 was clearly revealed

Largest lattice anomalies at the low-temperature FE transitions
– this is the phase that is most susceptible to perturbations (magnetic field, pressure)





Pr ... the magneti ... g
th ... s

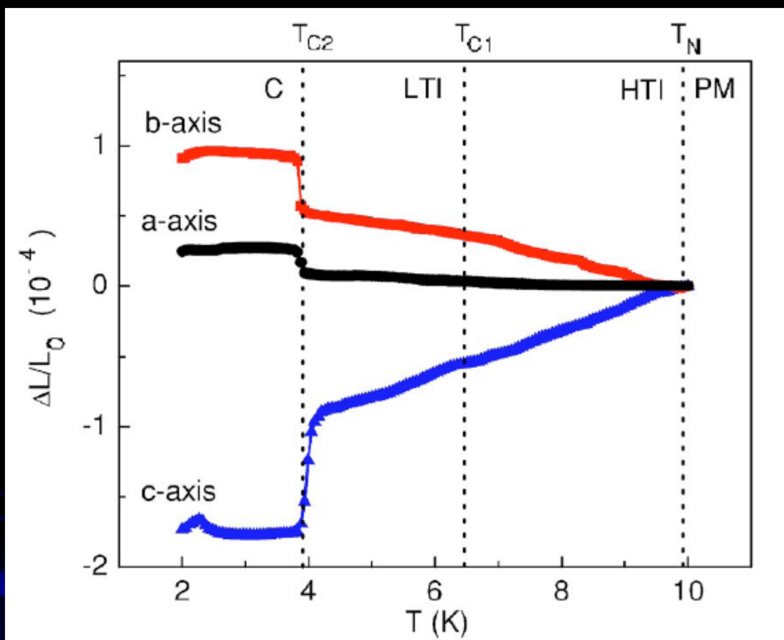
Es ... effects of m

Ma ... nplex magne ... ents

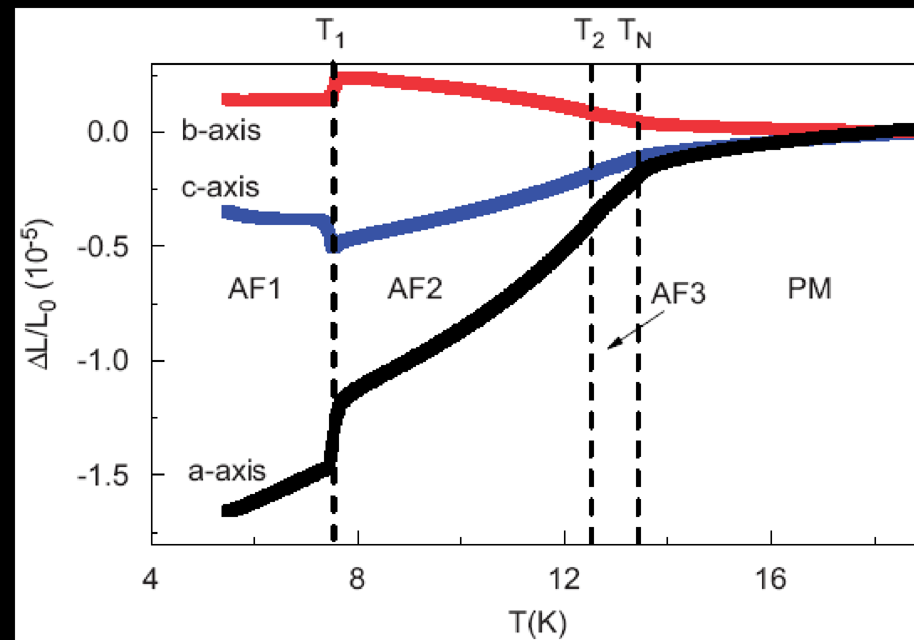
Pr ... c distances ... the
ma

Other multiferroic compounds

$Ni_3V_2O_8$



$MnWO_4$



As with the RMn_2O_5 compounds – the strongest lattice anomalies are at the low-T transition from the ferroelectric to the reentrant paraelectric phase

→ Effects of lattice strain and external pressure are significant at low T's

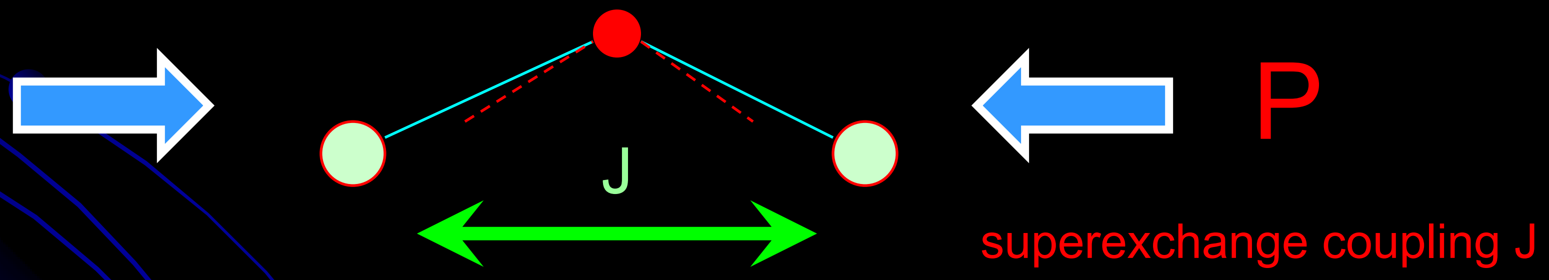
3. The effects of high pressure on the magnetic and ferroelectric phases in multiferroics

The effect of pressure on the magnetic order is fundamentally different from the external magnetic field effects

Magnetic field couples to the moments (spins) and tends to align them

Pressure changes the interatomic distances and bond angles resulting in a control of the exchange coupling constants

For example: 3d – 2p – 3d superexchange coupling strongly depends on the Mn – O – Mn bond angle



The real effects of compression are more complex because of lattice anisotropies and multiple exchange constants affected by pressure

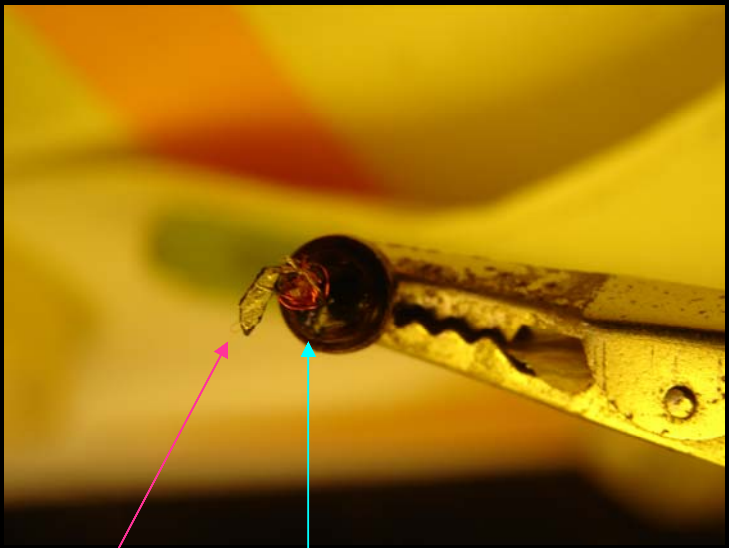
How to measure dielectric properties and ferroelectric polarization under high-pressure conditions :

High-pressure Clamp Cell
($p < 20$ kbar)

Pressure Cell (parts)

Low-temperature probe

Be-Cu cap with wires, sample, and pressure gauge



Sample, lead gauge, thermocouple

- Pressure is changed at RT before each cooling run
- P, T measured inside (Pb manometer, thermocouple)
- T-range: 1.2 K < T < 300 K
- p up to 20 kbar (2 GPa)
- Coaxial wires as close as possible to the sample contacts for dielectric measurements

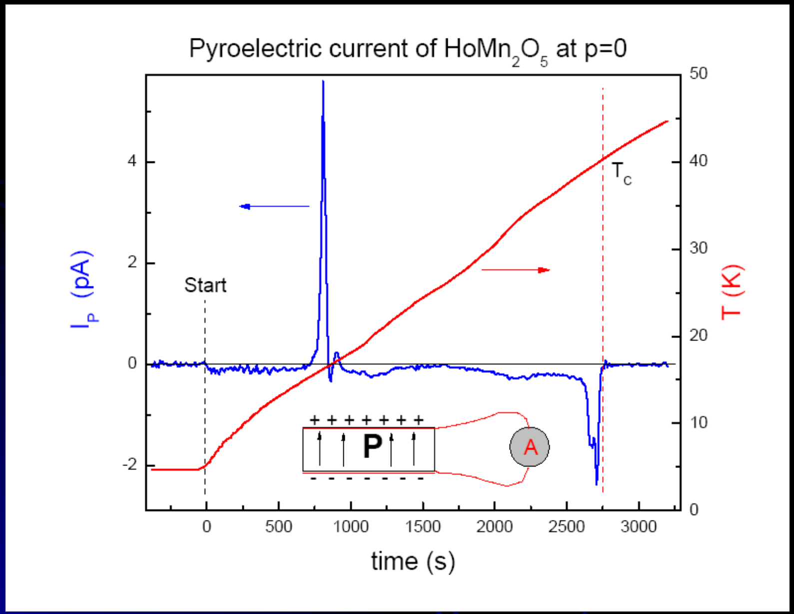
How to measure ferroelectric polarization via the pyroelectric current method :

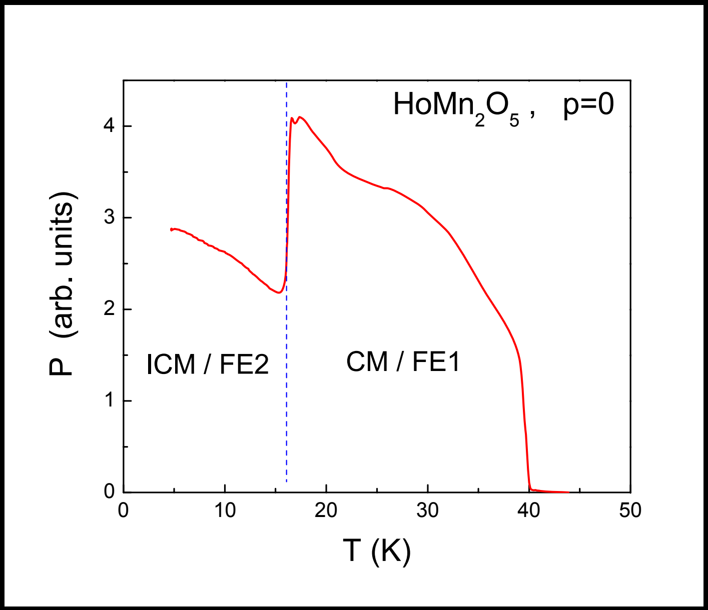
Current across a parallel-plate capacitor

$$i = C\frac{dV}{dt} + A\frac{dP}{dt} + \frac{V}{R}$$

V = constant

R large or V = 0

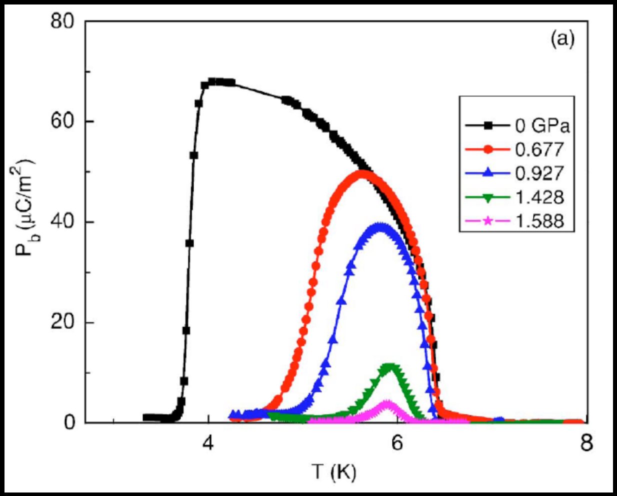


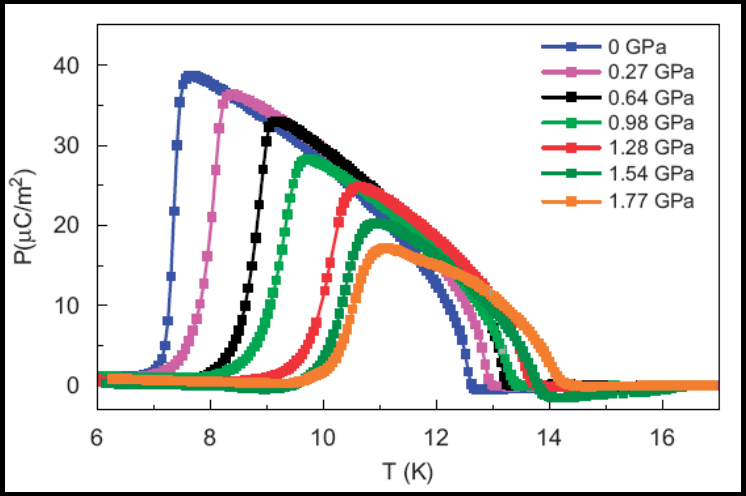


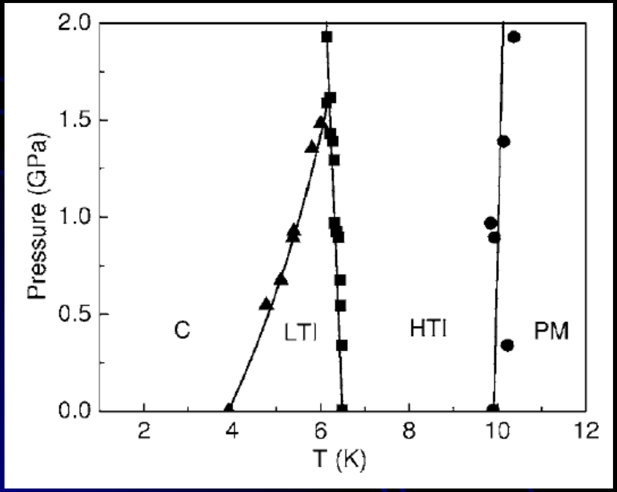
Poling of FE domains needed upon cooling in electric field, measurements of spontaneous polarization upon heating in zero field

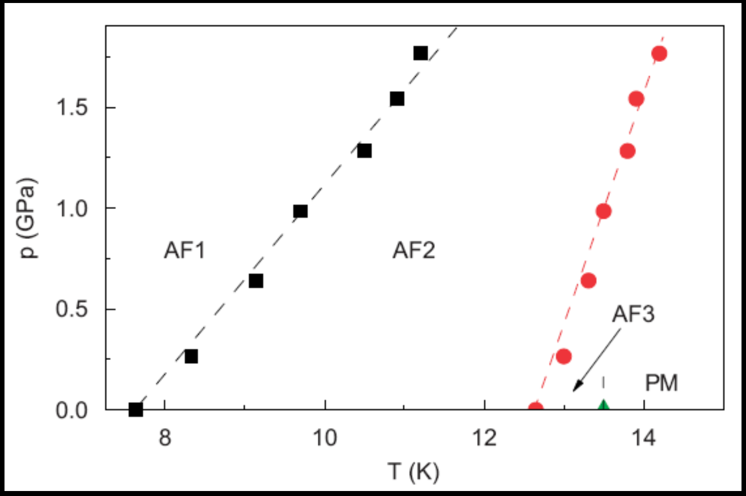
Pressure – temperature phase diagram of $N_3V_2O_8$ and $WMnO_4$

$Ni_3V_2O_8$ | $WMnO_4$









The commensurate (paraelectric) phase is stabilized under pressure and the IC helical (ferroelectric) phase is suppressed

Why does compression favor the low-T commensurate phase in $Ni_3V_2O_8$ and $WMnO_4$?

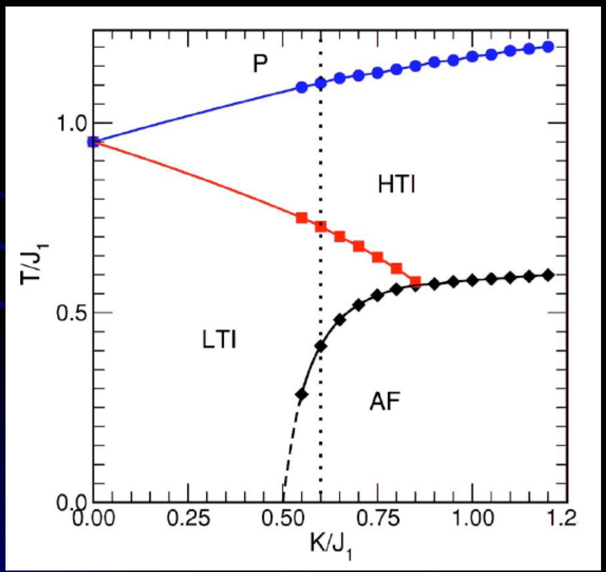
(i) Thermodynamic argument

The low-T CM phase has the smaller volume (from expansion data)

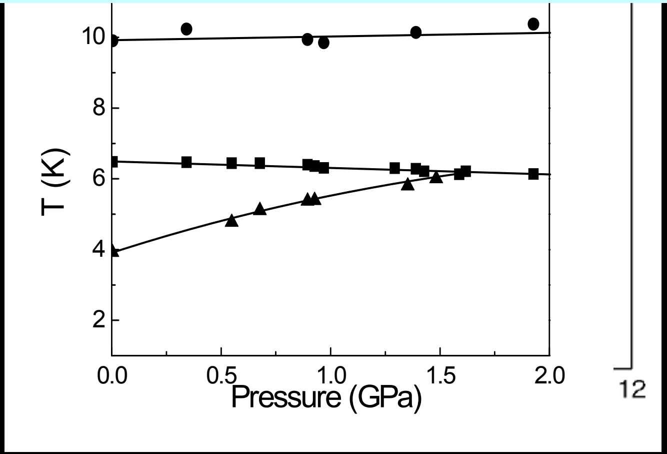
(ii) Microscopic exchange and anisotropy constants

The phase sequence SIN – HEL – CM observed in both compounds has its origin in the competition of exchange interactions and anisotropy

Simple phase diagram, $Ni_3V_2O_8$ (Kenzelmann et al., PRB 2006)

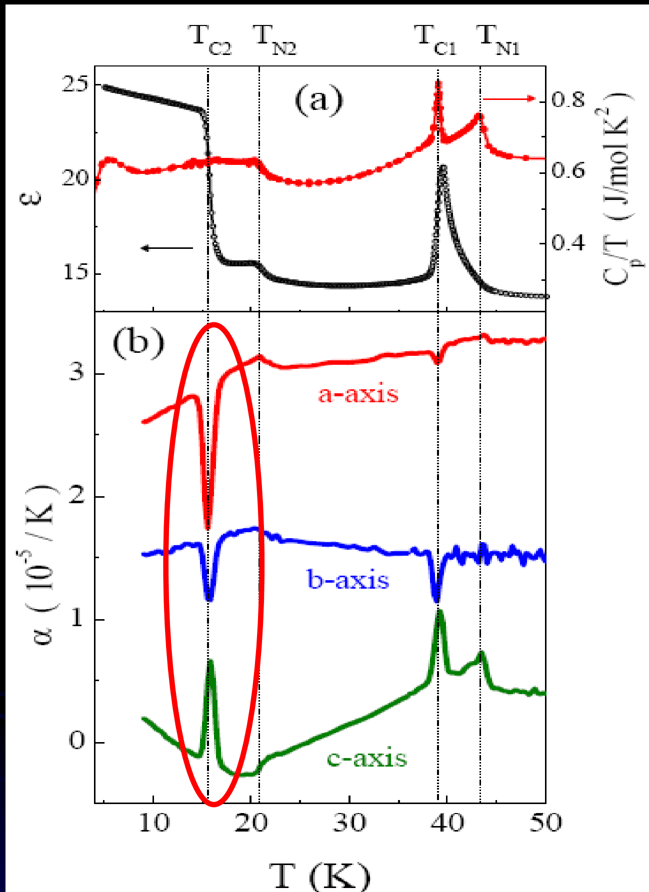


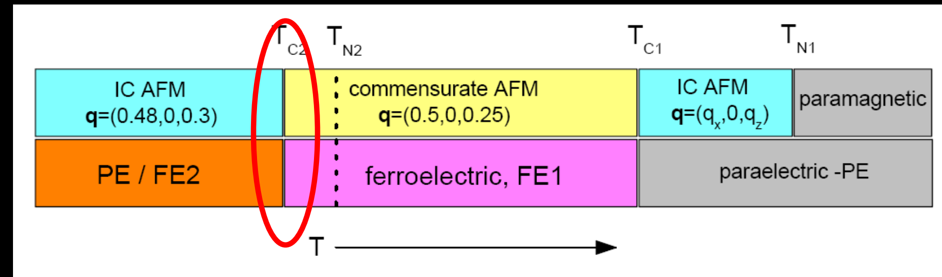
$$H = J_1 \sum_i \vec{S}_i \vec{S}_{i+1} + J_2 \sum_i \vec{S}_i \vec{S}_{i+2} - K \sum_i \left(S_i^z\right)^2$$

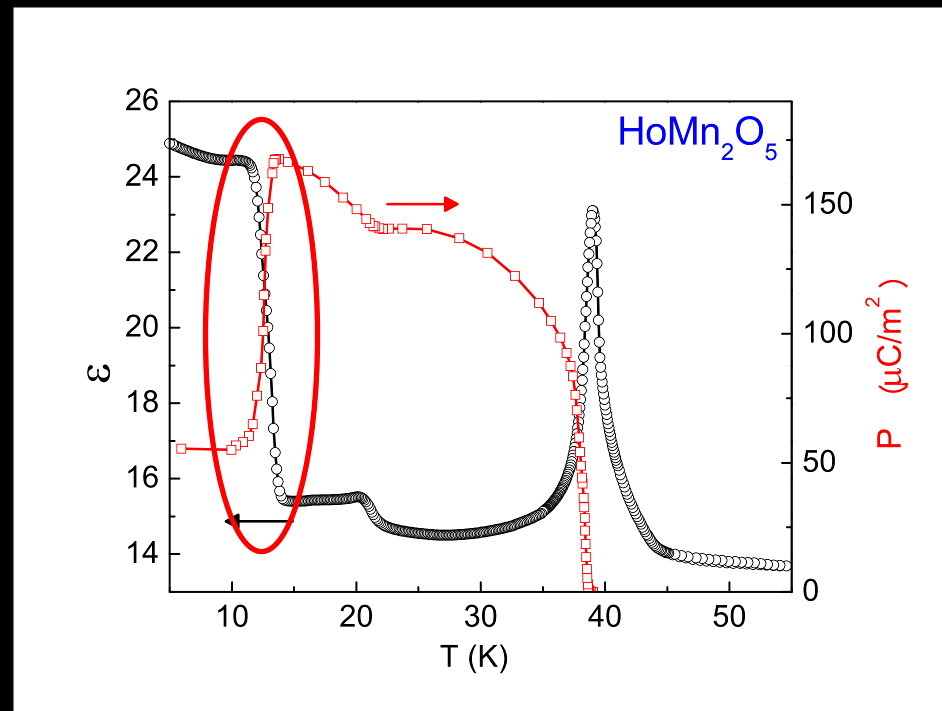


Pressure-induced change of the ratio K/J_1 (?)

Pressure effects on magnetic structure and ferroelectricity of RMn_2O_5





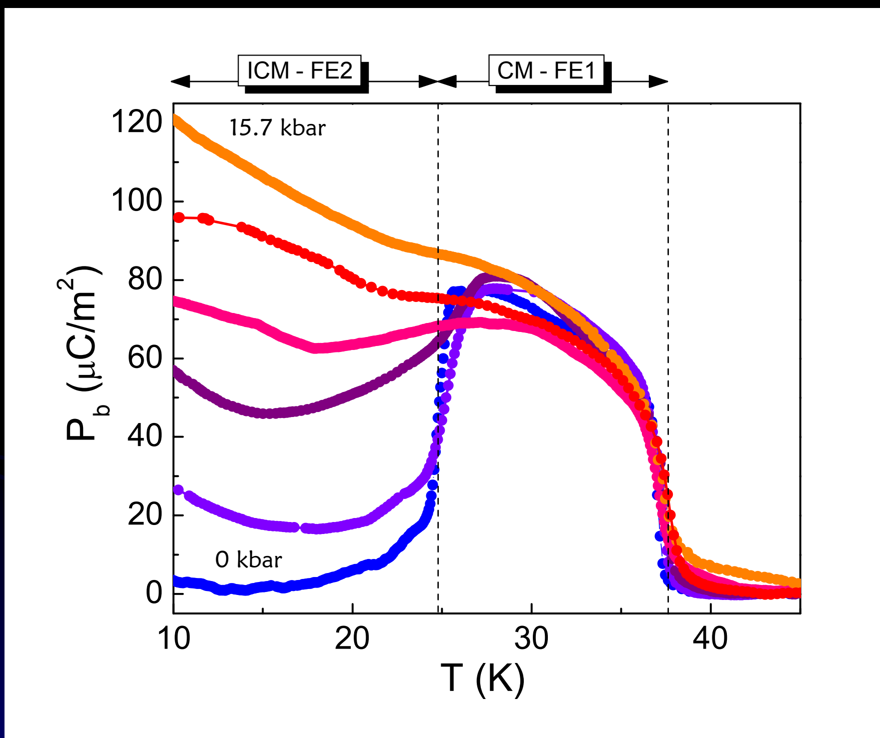


Focus on the low-T transition CM → ICM at T_{C2}
and the pressure effect on the ICM-phase

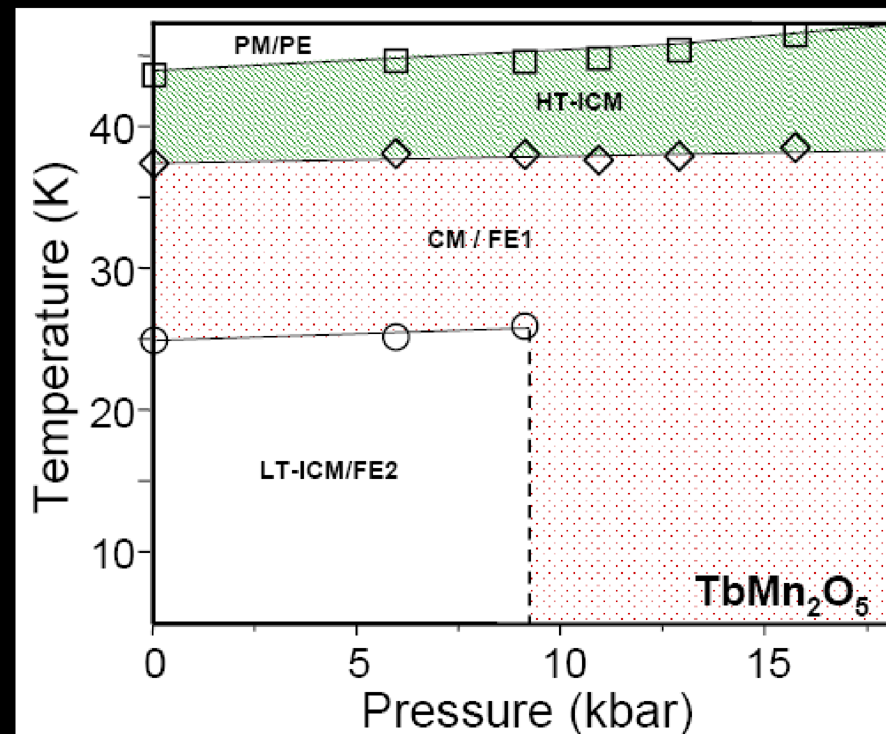
Giant pressure effect on the low-T ferroelectric polarization of $TbMn_2O_5$

$TbMn_2O_5$

Pressure effect on P



P – T phase diagram of $TbMn_2O_5$



C. R. dela Cruz et al., PRB 2007

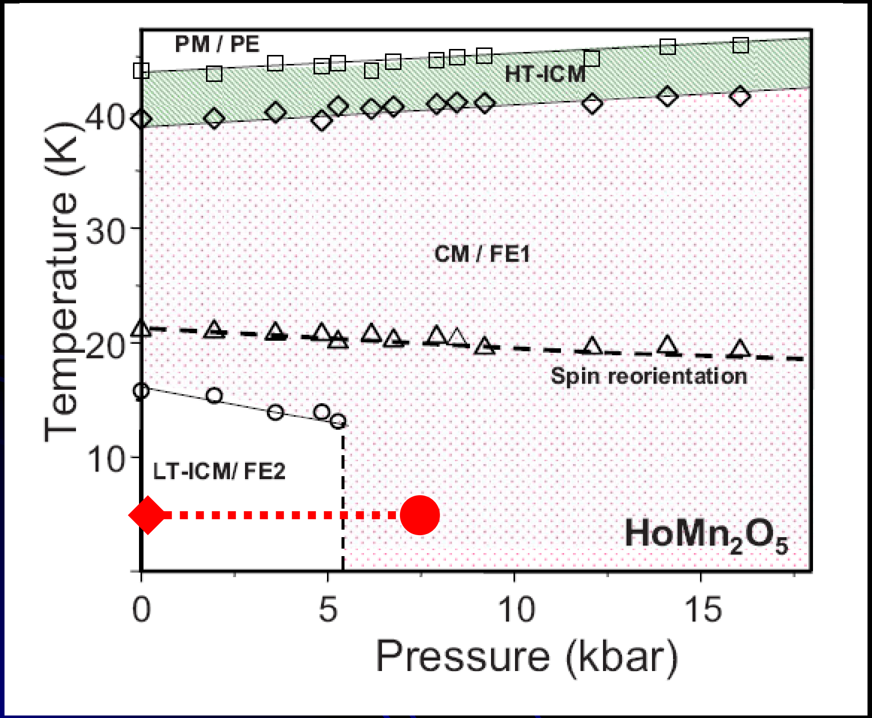
Giant pressure effect on P (> 1300 % @ 15 K)

LT-ICM phase is suppressed at 9 kbar

Control of magnetic order (commensurability) by pressure: $HoMn_2O_5$

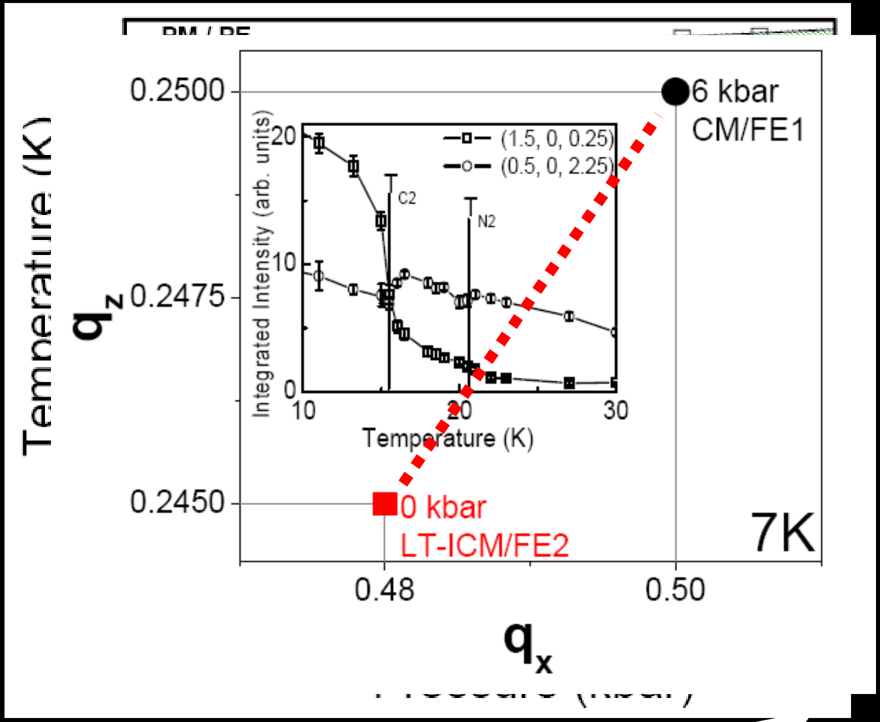
$HoMn_2O_5$

Pressure-induced transition ICM / FE2
→ CM / FE1 phase



C. R. dela Cruz et al., PRB 2007

p – T phase diagram of $HoMn_2O_5$

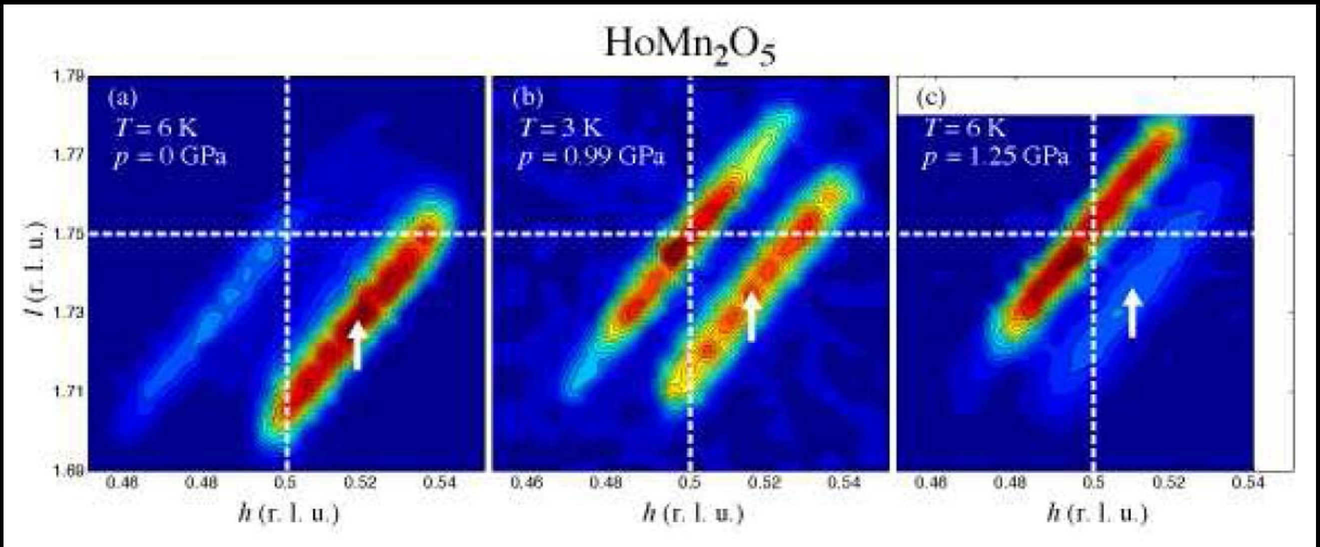


C. R. dela Cruz et al., Physica B 2008

Pressure changes commensurability at low T ➔ Neutron scattering under pressure !

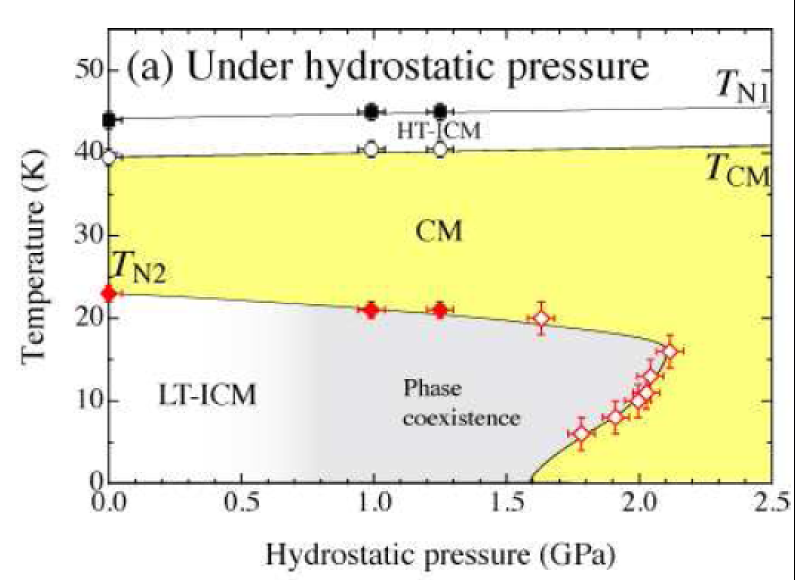
Recently confirmed and extended in the work of Noda's group :

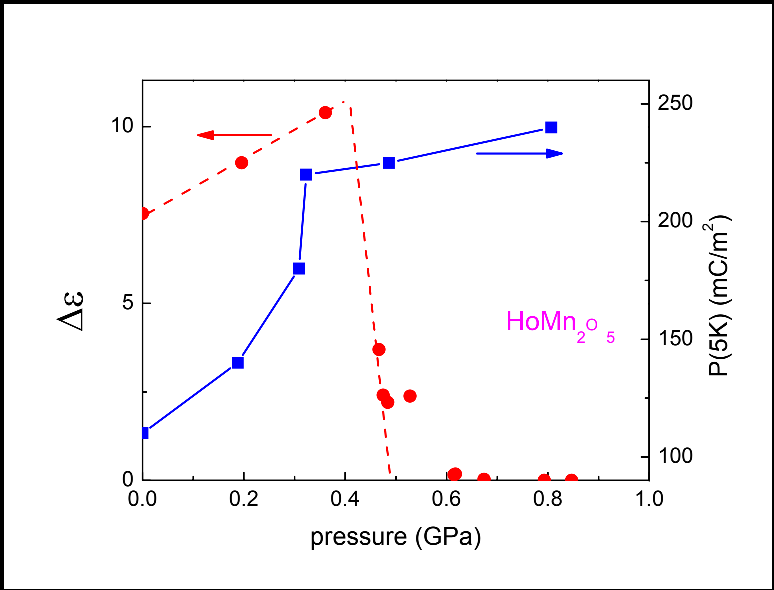
Kimura et al., J. Phys. Soc. Jpn. (2008)



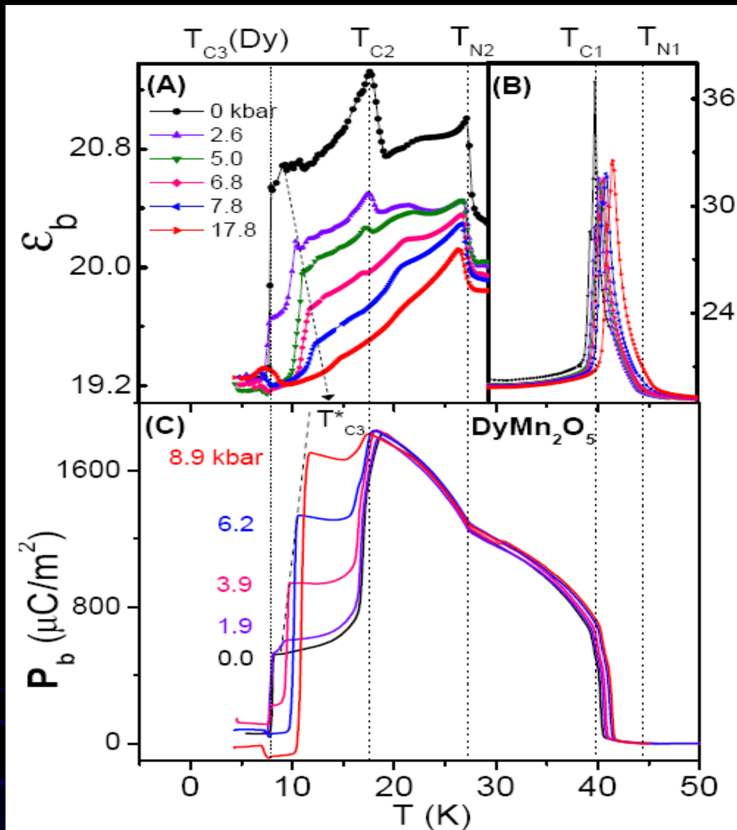
These data reveal phase coexistence of CM and ICM orders.

The higher critical pressures may be sample dependent.

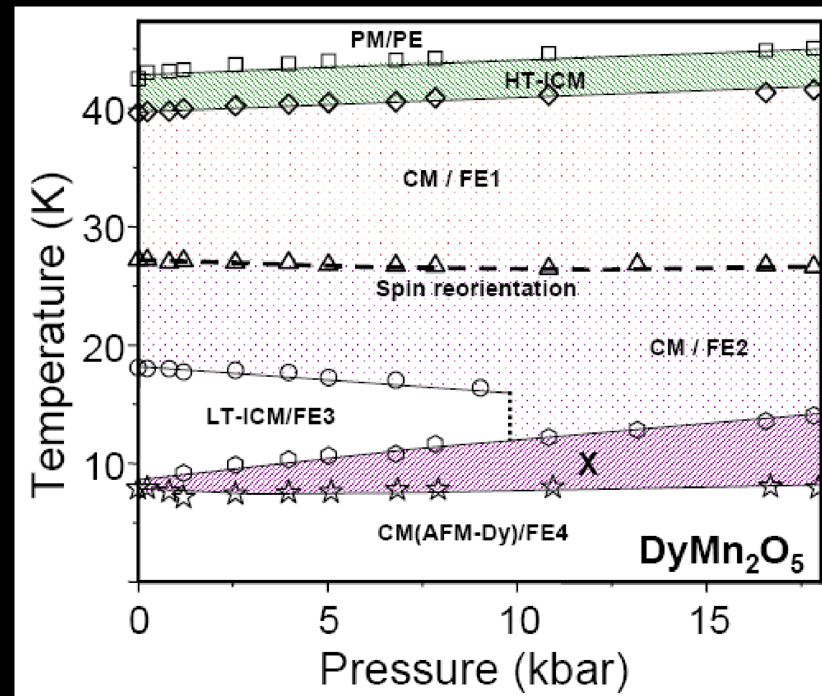




Complex p – T phase diagram of $DyMn_2O_5$



$DyMn_2O_5$



Five phase transitions are visible in distinct changes of ε and P_b

Higher phase complexity, pressure-induced new phase (X – phase)

The “X” phase is found to be paraelectric at high pressure (mixed phase ?)

Magnetic properties still need to be investigated

Pressure-induced polarization reversal in YMn_2O_5

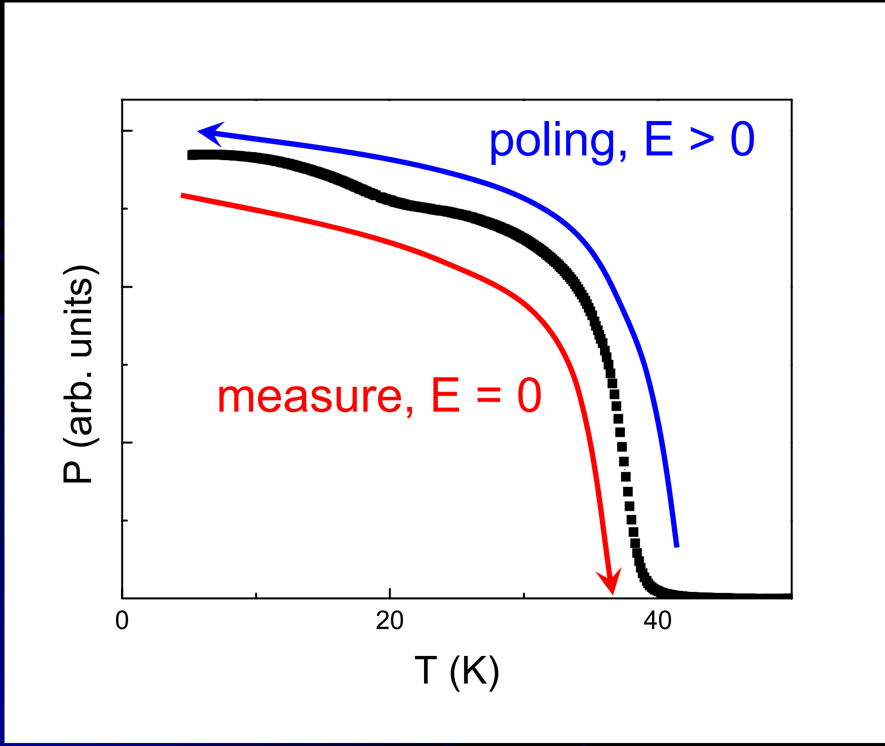
YMn_2O_5 is unique in the RMn_2O_5 family of compounds – it shows a spontaneous sign change of P at T_{c2} (Inomata et al., 1996)

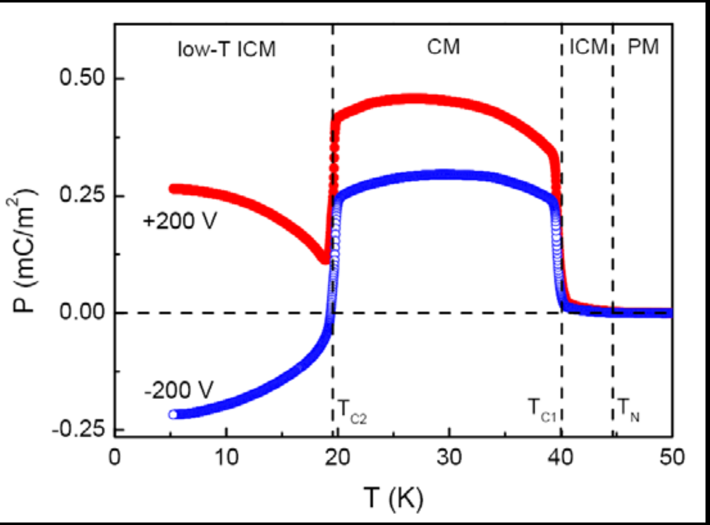
Problem with pyroelectric current measurements:

Poling of FE domains upon cooling is necessary to reveal the intrinsic polarization – measurements are done at E = 0 upon warming

Additional phase transitions may destroy the FE domain alignment !

This can give rise to spurious effects or incorrect results



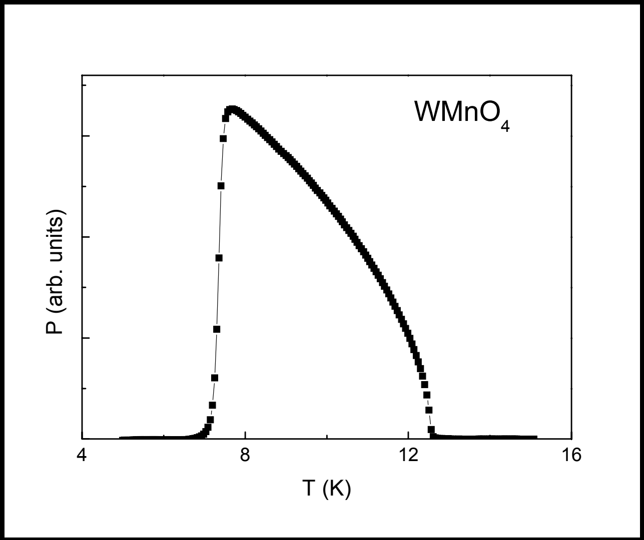


Poling to 5 K, ± 200 V

In multiferroics with a paraelectric low-T phase pyroelectric current measurements can be conducted with a poling field applied, e.g. $WMnO_4$

However, this is not possible if P reverses sign

How to maintain the FE domain alignment for current measurements if the intrinsic polarization changes sign ?



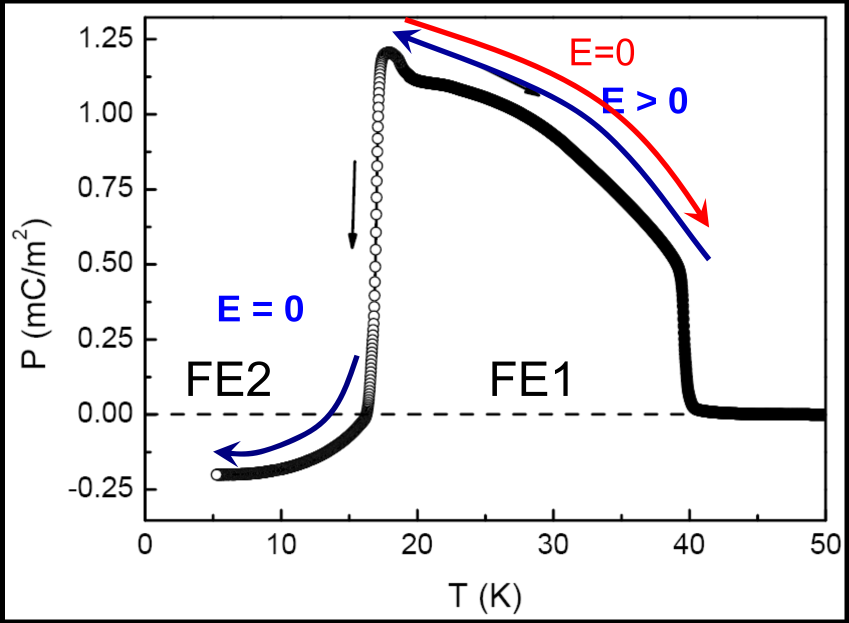
Experimental protocol to measure P(T) in YMn_2O_5 in both FE phases

(i) Poling in E > 0 to max of P (T_{C2}, FE1)

(ii) Measure in E = 0 upon warming
→ Polarization of the FE1 phase

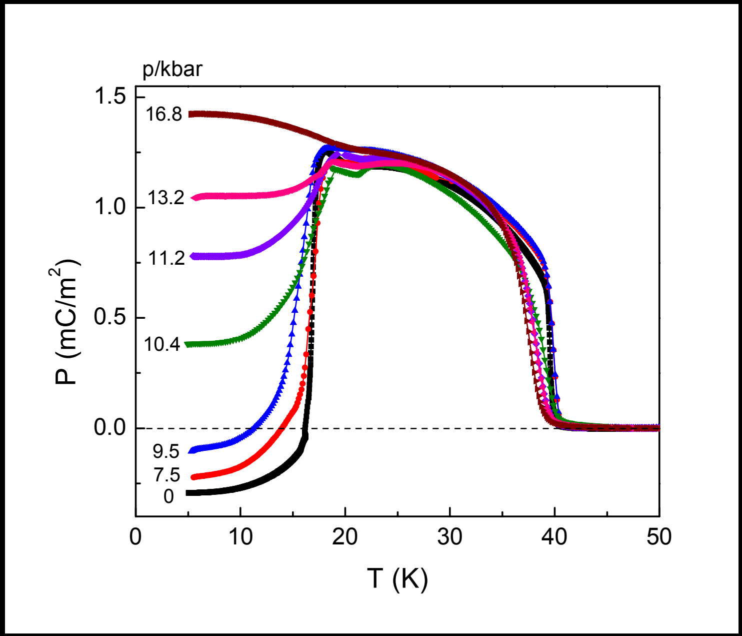
(iii) Repeat step (i)

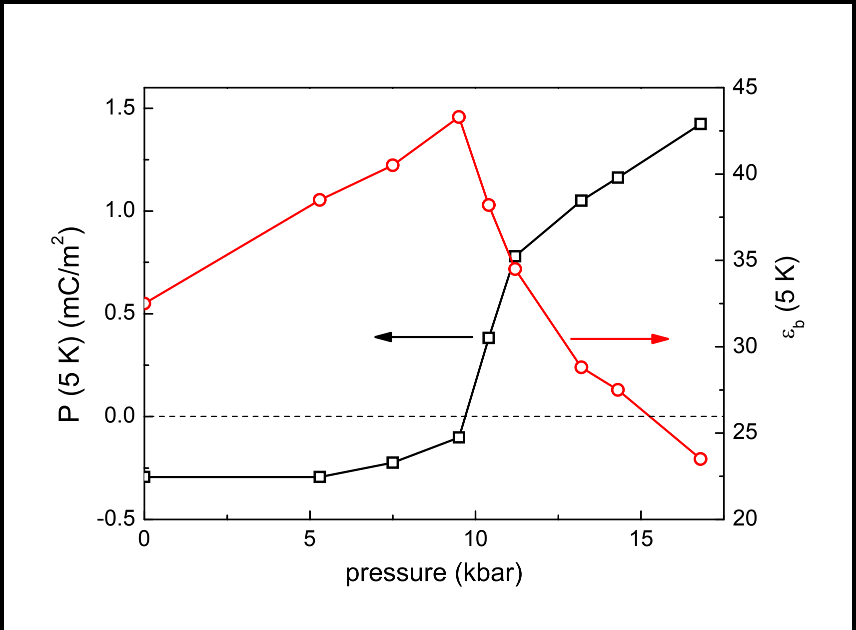
(iv) Measure in E = 0 upon cooling
→ Polarization of the FE2 phase



Pressure effects in YMn_2O_5

R. P. Chaudhury et al., PRB 2008





The FE polarization of the low-T ICM phase is completely reversed by pressure near p_{C1} ~ 10 kbar.

Above p_{C2} ~ 14 kbar the low-T ICM is transformed into the CM phase

The FE polarization reaches its maximum in the p-induced CM phase at the lowest temperature.

Understanding the pressure effects in RMn_2O_5

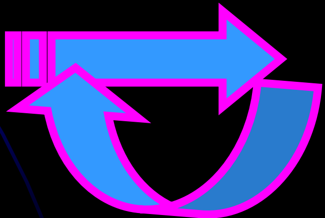
Frustration and exchange striction as the origin of ferroelectricity

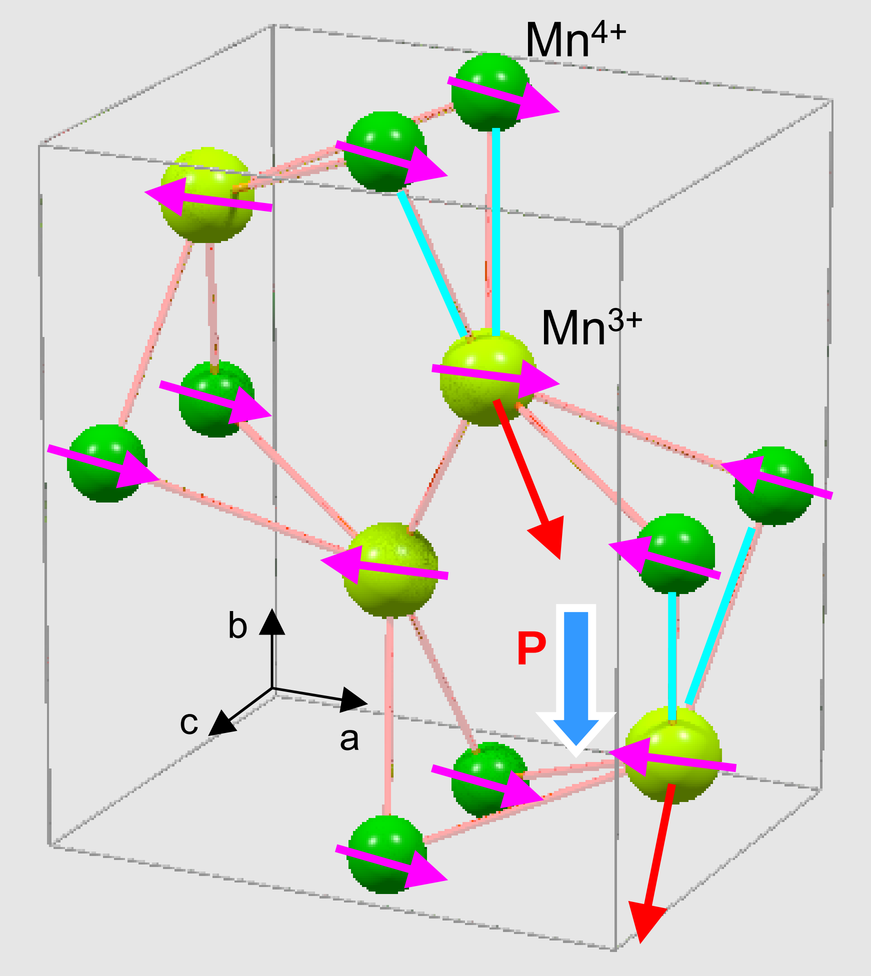
Superexchange interactions determine exchange parameters between Mn spins

At least 5 different exchange integrals can be distinguished $\Rightarrow$ Mostly AFM

Ionic displacements relax the magnetic frustration and generate the polarization along the b axis

Magnetic structure from neutron scattering





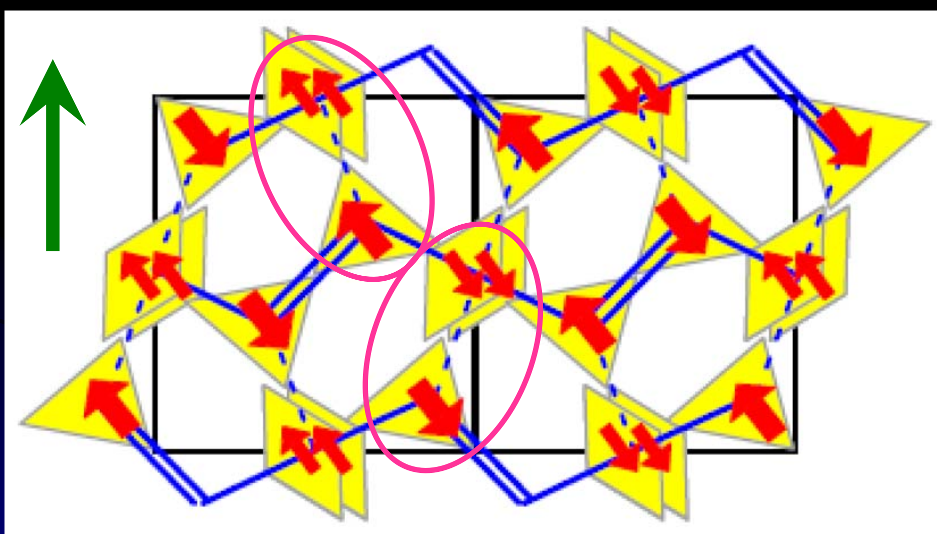
AFM / FE domains in the CM phase of RMn_2O_5

Mn^{4+} and Mn^{3+} form AFM zigzag chains along the a-axis.

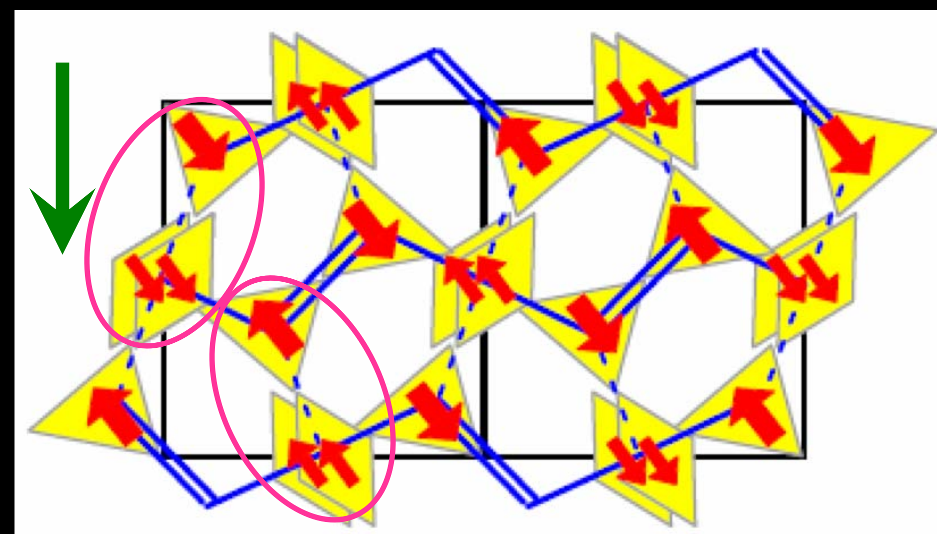
The spins of adjacent chains are frustrated in every second pair.

The macroscopic polarization adds up along the b-axis

The opposite FE domain results from the reversal of spins of every second chain (or phase shift by one lattice constant).



Domain 1: $P > 0$

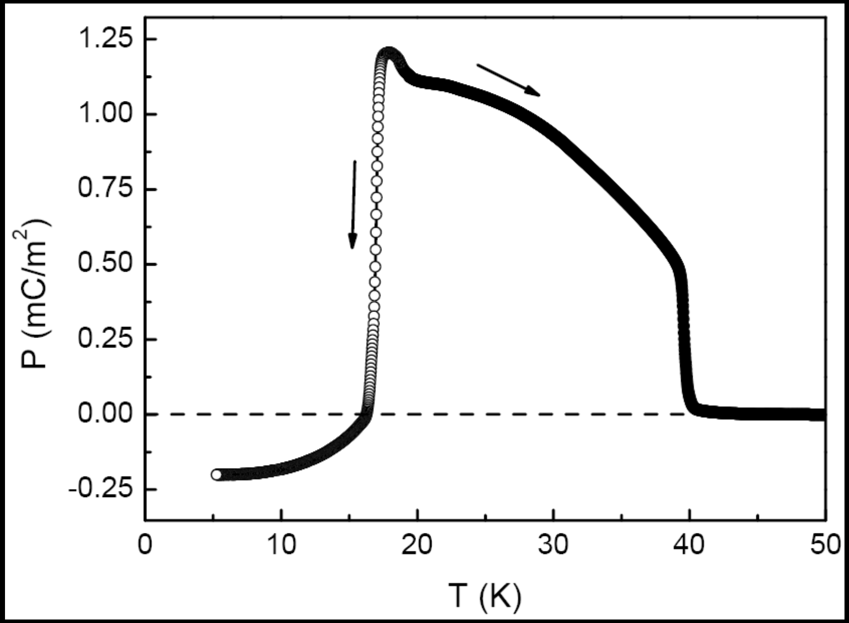


Domain 2: $P < 0$

The magnitude and sign of P depend on the relative phase of the magnetic modulation between two adjacent chains

Chapon et al. (PRL 2006) explained the sign change of P at T_{C2} with a change of phase angle φ between the magnetic orders of adjacent chains

$$P^{\mathrm{ICM}} = 4C\vec{S}_3 \cdot \vec{S}_4 \cos(2\pi(\tfrac{1}{4}+\delta_z)z')\cos(2\pi\delta_x(\tfrac{1}{2}-x)) \times \cos(\epsilon)\sin(\varphi),$$

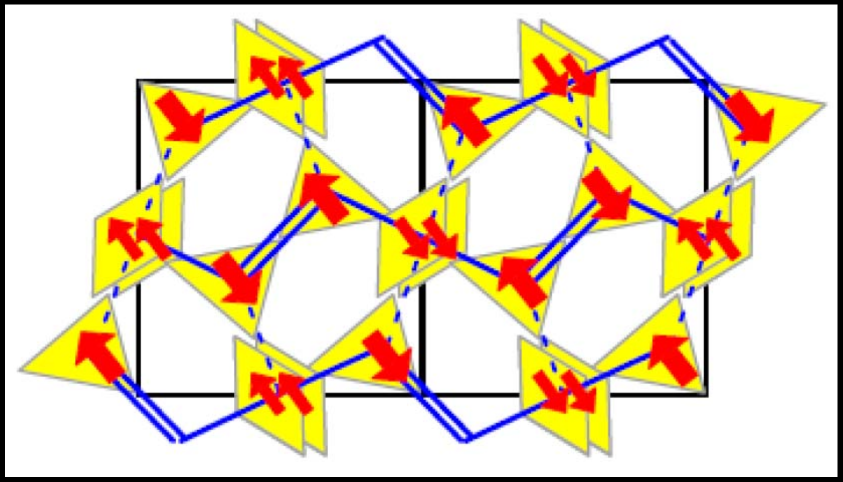


Magnetic structure changes at T_{C2} :

(i) The relative angle between spin vectors of neighboring chains increases from ~ 0 to 40° reducing the magnetic coupling between them

(ii) The phase of the magnetic modulation between adjacent chains increases, reducing and eventually reversing the polarization

(iii) The CM magnetic order unlocks and becomes incommensurate again



The observed pressure effects can now be understood as:

Decreasing the phase difference of magnetic modulation of adjacent chains → reversal of FE polarization at 10 kbar

Transition from the ICM to the CM phase at higher pressure

5. Tuning MF properties by ionic substitutions

Replacement of magnetic ions by other (magnetic or non-magnetic) ions can have a large effect on the physics of frustrated (multiferroic) systems through

(i) Introducing magnetic moments of different size

(ii) Change of exchange coupling constants between different ions

(iii) Change of crystalline anisotropy

(iv) Introducing disorder among the magnetic ions

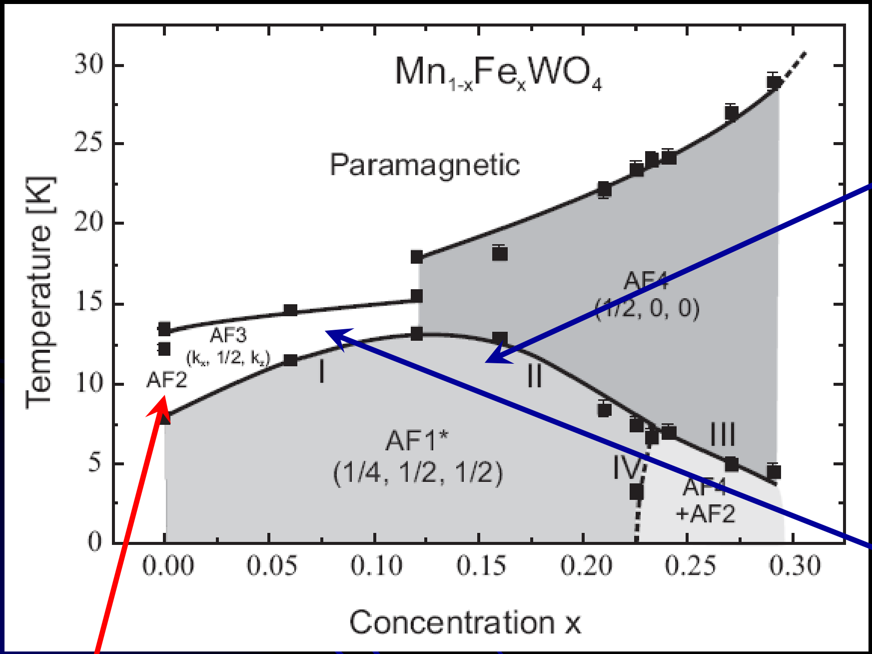
Since MF systems are very fragile (remember: many magnetic states/orders are close in energy) small amounts of substitutions usually result in big effects !

Example 1: $WMnO_4$

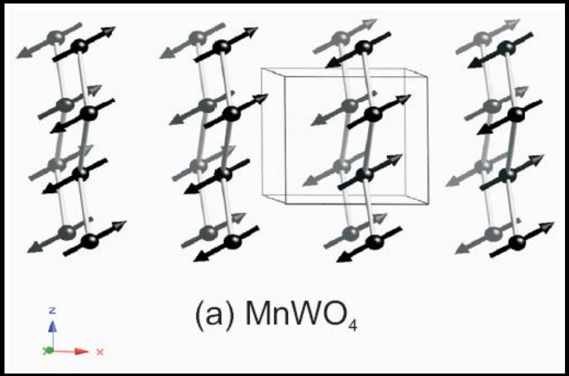
In $MnWO_4$ the Mn^{2+} - ion can be replaced by Fe^{2+} :

Tuning of magnetic exchange and anisotropy in $Mn_{1-x}Fe_xWO_4$ possible

Phase diagram from neutron scattering



Ground state: AF1 – Phase (E-type), PE

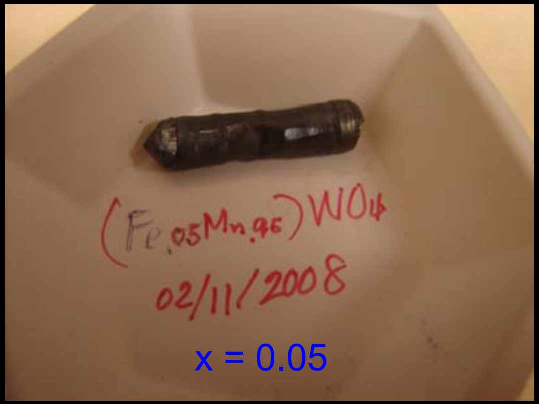


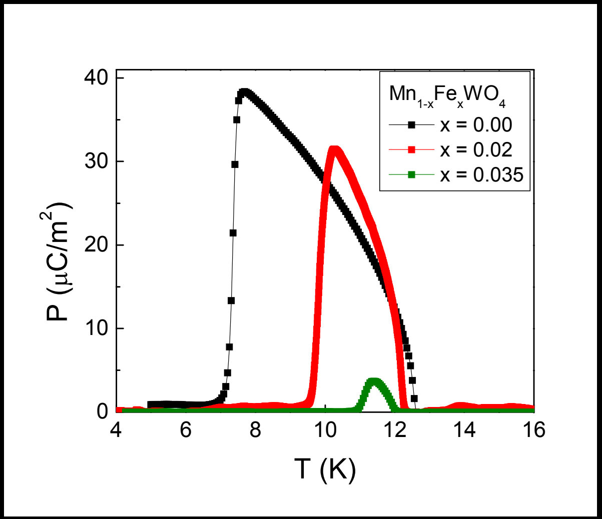
AF3 – Phase:
IC collinear (sinusoidal), PE

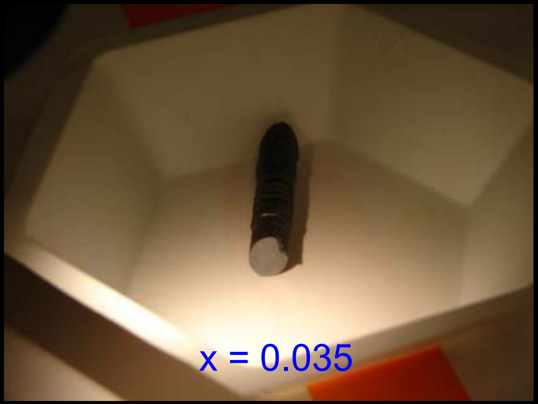
AF2 – Phase (x=0) :
IC non-collinear (helical), FE

Does ferroelectricity exist for $x > 0$?

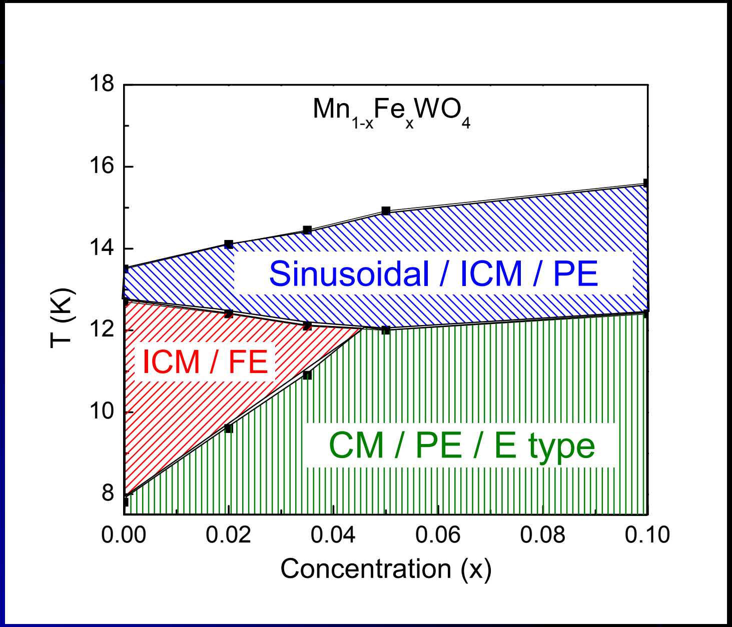
Growth of a series of large single crystals with x_{Fe} = 0.25, 0.1, 0.05, 0.035, 0.02







Phase diagram

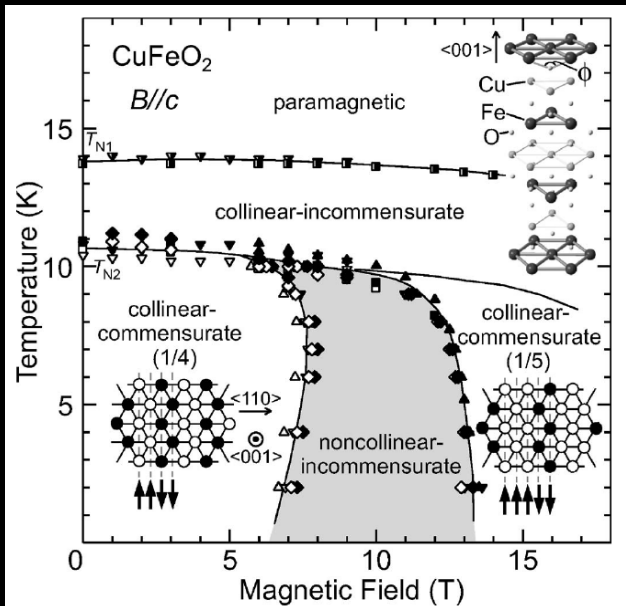


The ferroelectric (helical) phase is completely suppressed by Fe substitution as low as 4 %

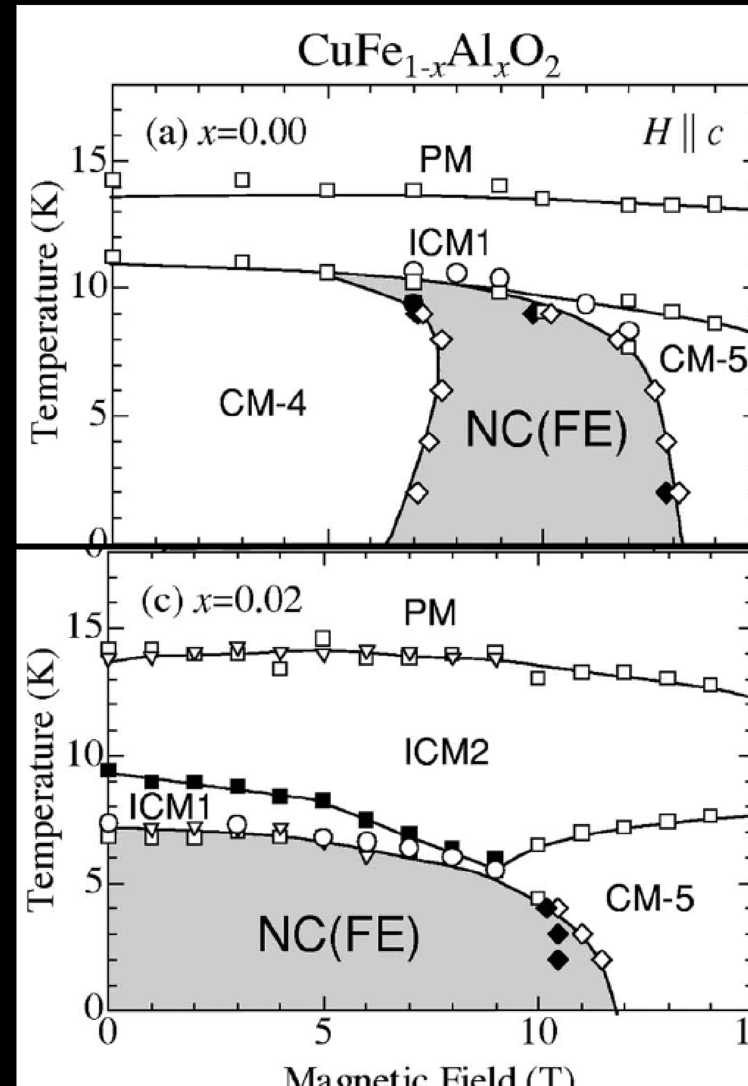
For x > 0.04 the transition from the ICM collinear (sinusoidal) phase proceeds directly into the commensurate (E-type) phase, both phases are paraelectric.

Confirmed by neutron scattering experiments.

Example 2: $CuFeO_2$



T. Kimura et al., PRB 2006



S. Seki et al., PRB 2007

$CuFeO_2$ is paraelectric at H=0 with a magnetic transition from a ICM< sinusoidal structure to the E-type ↑↑↓↓ magnetic order.

Replacing Fe by 2 % Al stabilizes the non-collinear (helical) magnetic order and ferroelectricity

Note the sensitivity of the E-type ground state !

Acknowledgements

Many students and collaborators have contributed to the success of our work on multiferroic materials:

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