Introduction to the physics of multiferroics

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"Models in magnetism: from basics aspects to practical use"
Timisoara september 2009

Summary

Introduction and definitions

The example of $YMnO_3$

Origin of the coupling term Dzyaloshinskii-Moriya

Importance of symmetry

Applications

Some examples

Landau theory and symmetries

The example of $MnWO_4$

Examples are taken in work of Natalia Bellido, Damien Saurel, Kiran Singh and Bohdan Kundys

What is a multiferroic?

Definitions are various: For me in this lecture:

A ferromagnetic and ferroelectric compound. (spontaneous magnetization in zero field and spontaneous polarization in zero field)

It was predicted by P. Curie in 1894 “Les conditions de symétrie nous permettent d’imaginer qu’un corps se polarise magnétiquement lorsqu’on lui applique un champ électrique”

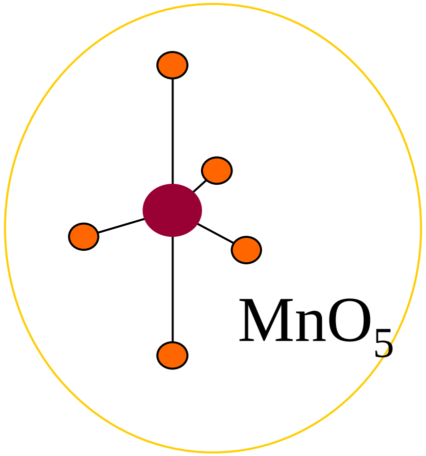
Debye in 1926: magnetoélectric

Landau in 1957

Dzyaloshinskii in 1959 predicts that Cr_2O_3 magnetoelectric

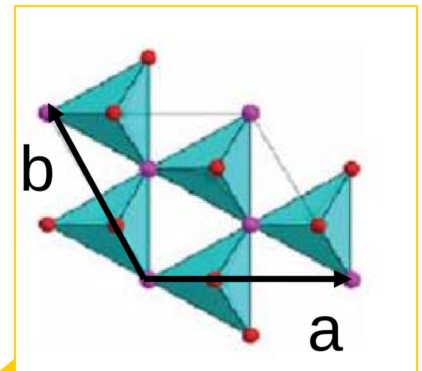
Astrov et al. 1960 E induces M, Folen, Rado Stalker 1961, B induces P.

One example: $YMnO_3$

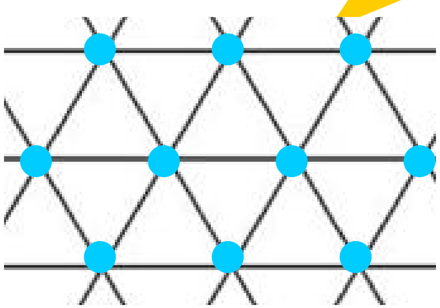


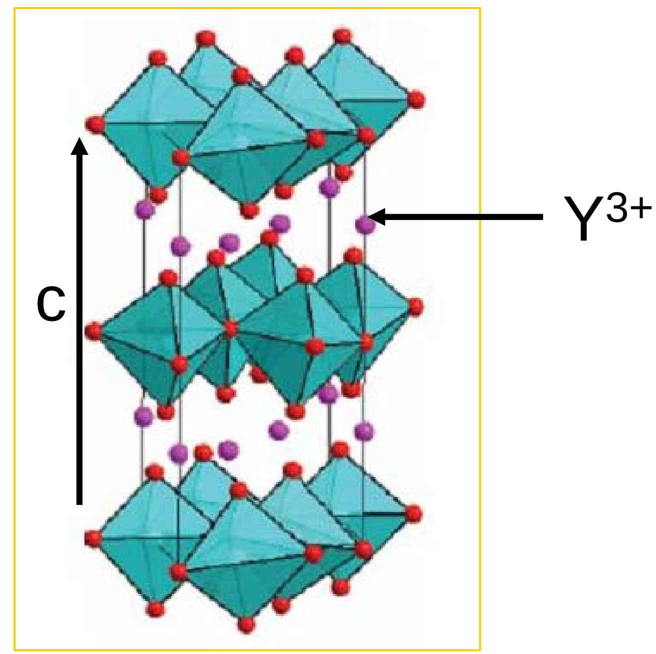
Hexagonal : $P6_3cm$

ferroelectric



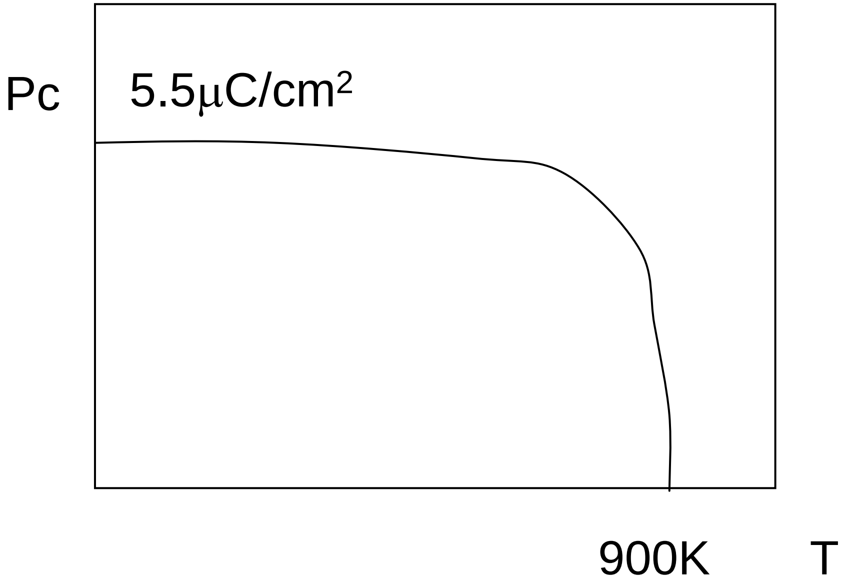
Mn^{3+} S=2

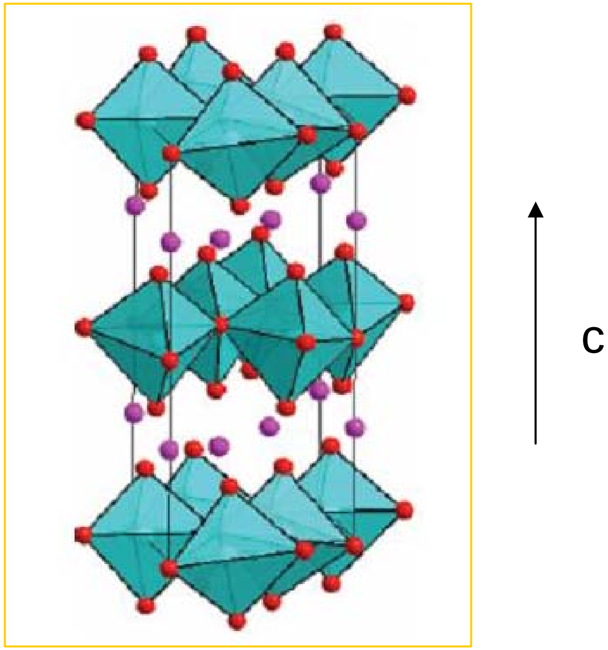




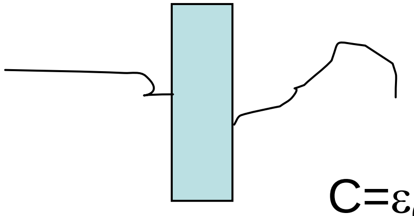
Why this example

- Because is it quite simple in symmetry and interactions
- However, this is rather complex, and if you find it difficult, this is normal, I find it complex.





Experimental difficulty

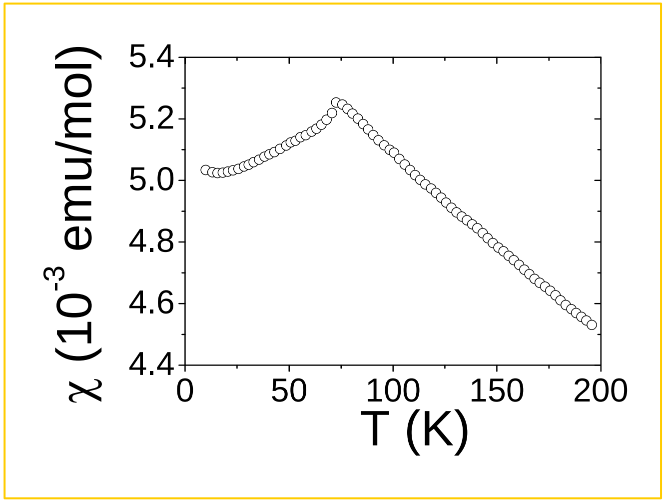


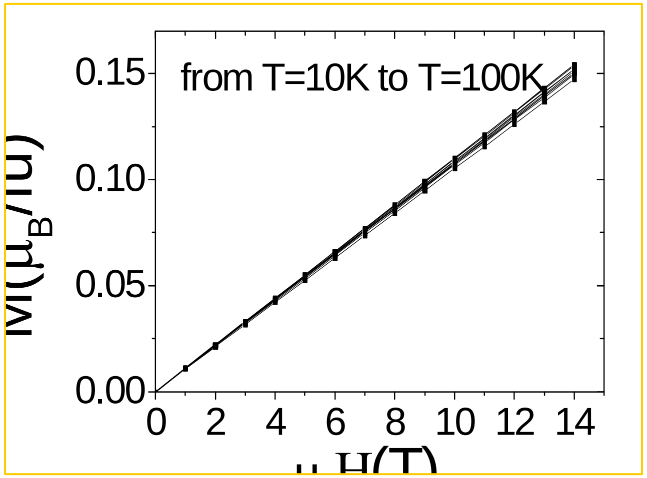
$P=II(t)dt$

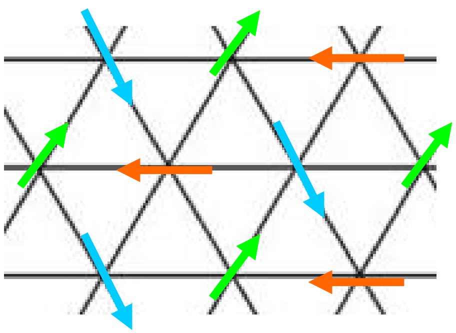
$C=\varepsilon_0\varepsilon S/t$

Antiferromagnetism

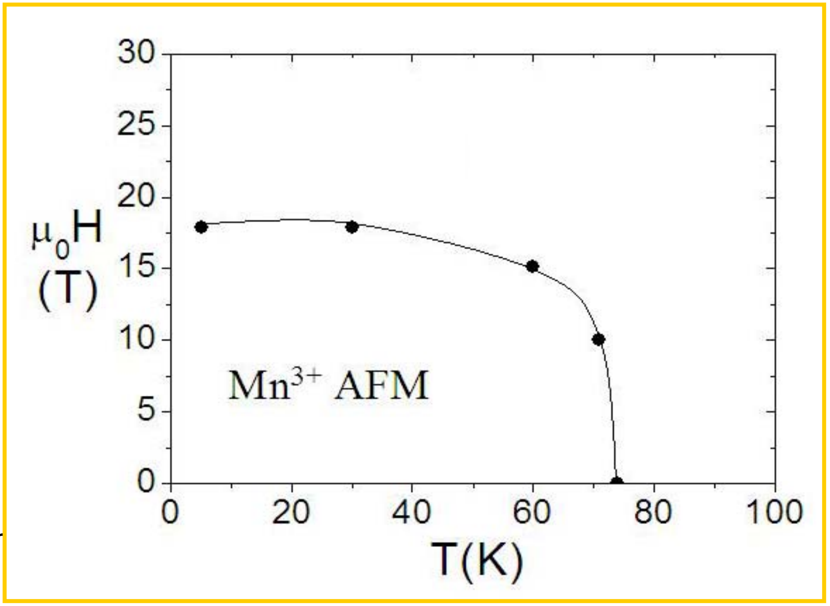
Mn^{3+}



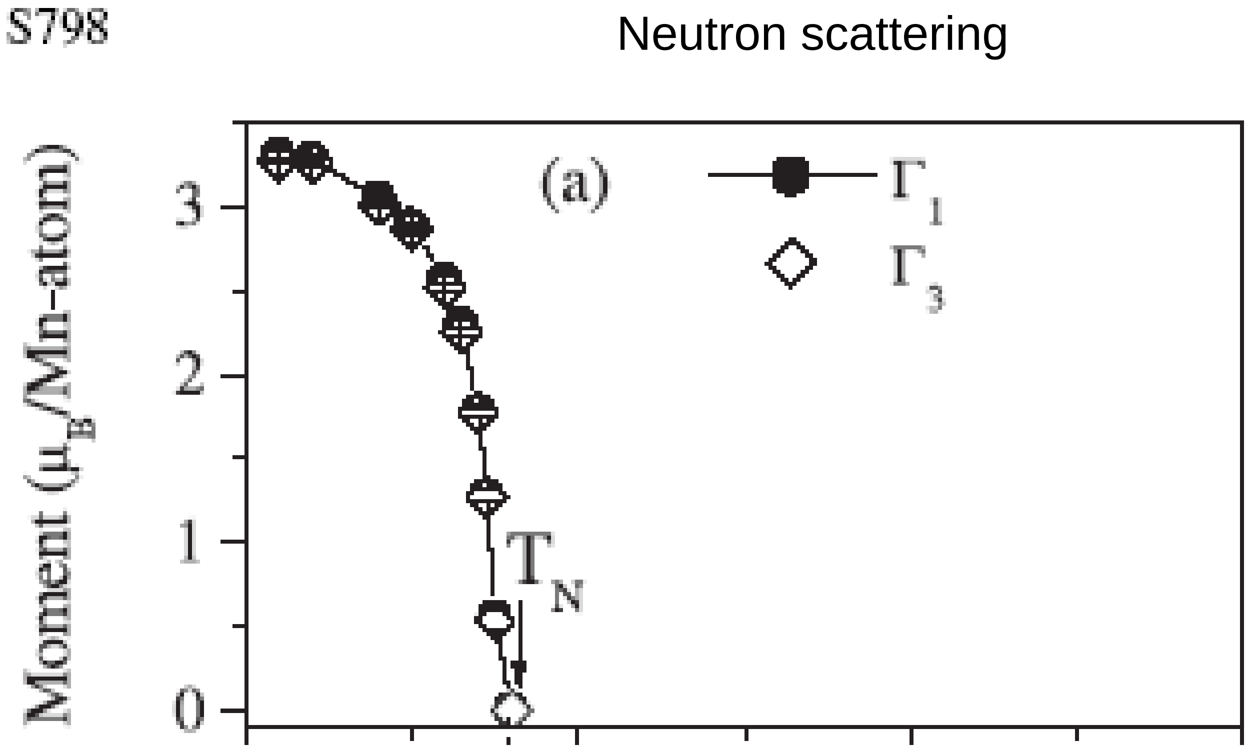




L : alternate magnetization



Neutron scattering

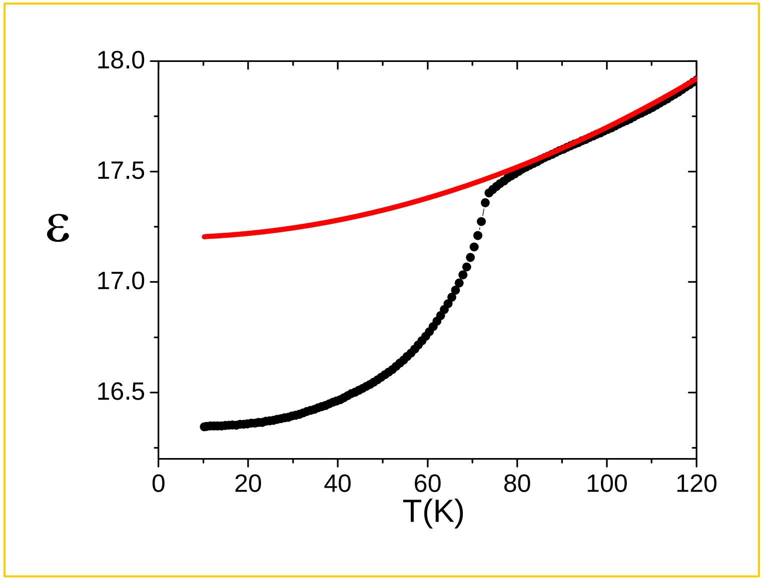


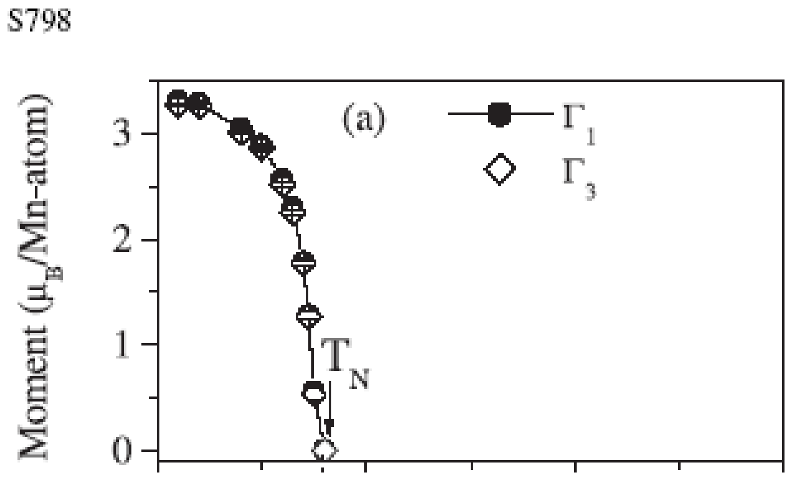
Order parameter

$L = \Sigma S_i \exp(2i\pi Qr_i)$

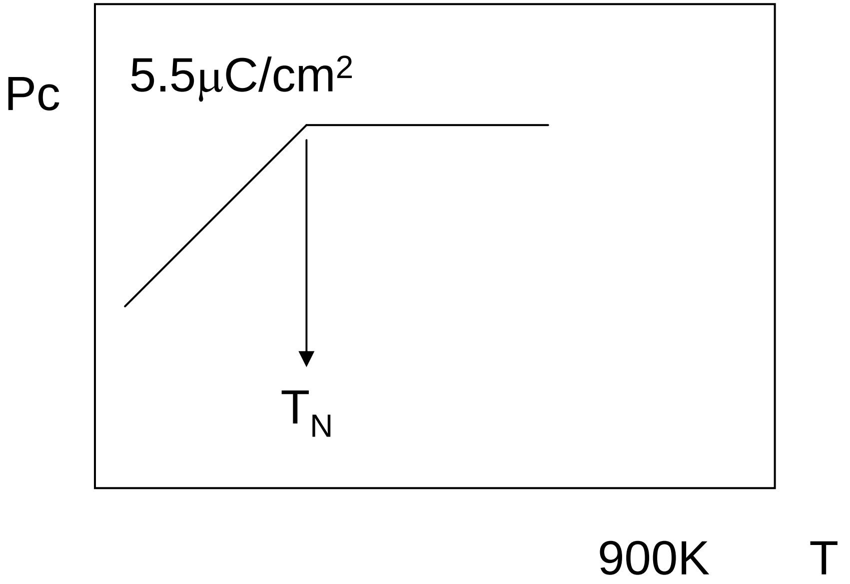
$YMnO_3$ - $\varepsilon(T)$

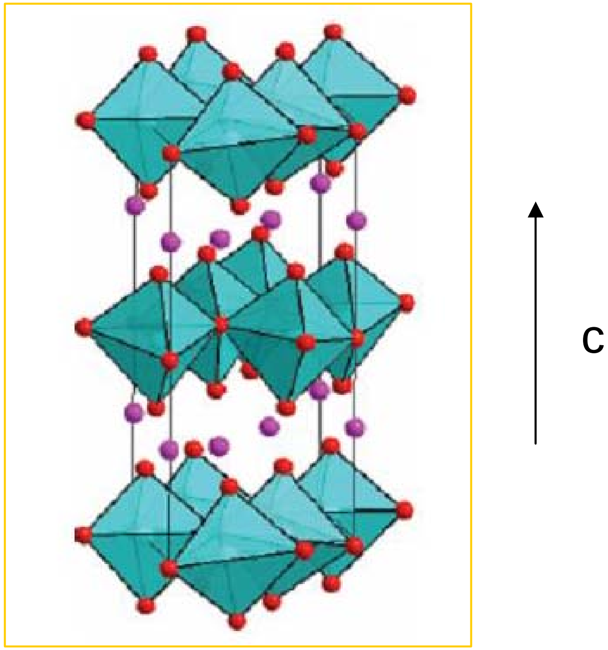
$\varepsilon = 1/\varepsilon_0\, dP/dE$ dielectric constant

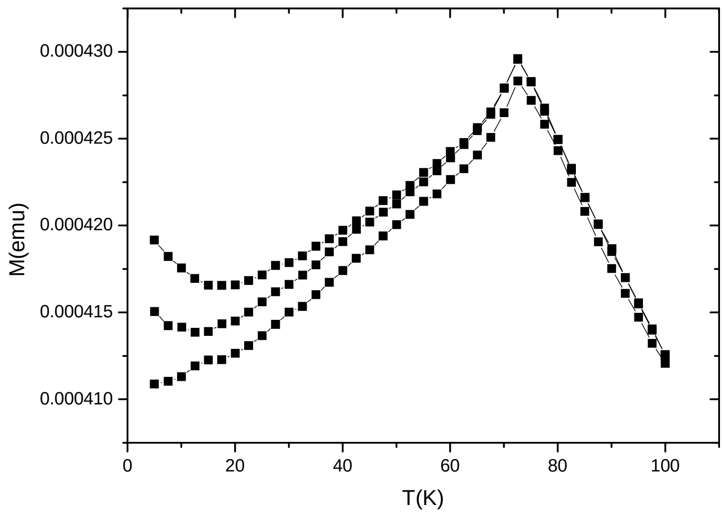


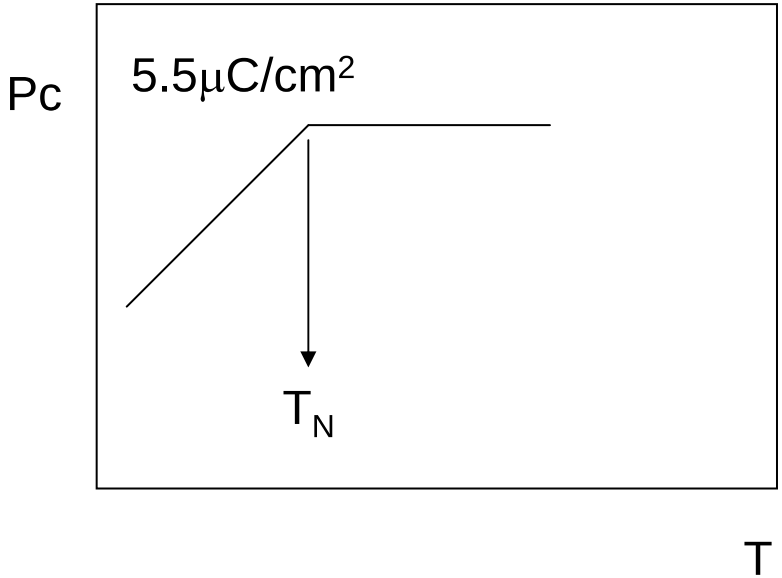


$$\varepsilon \propto -L^2$$


Pc
5.5μC/cm2
T_N
900K
T

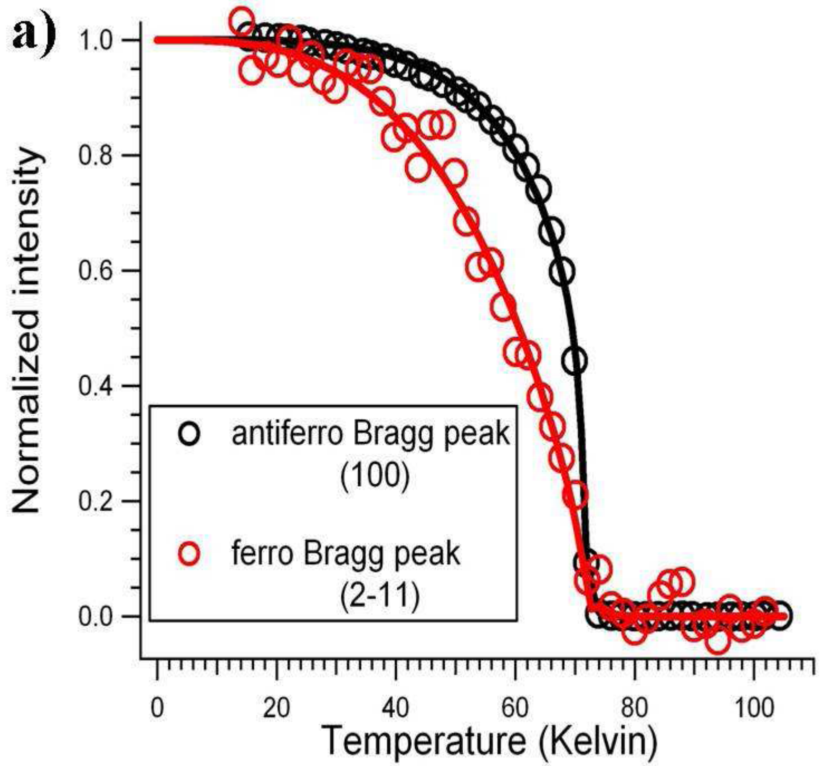

c





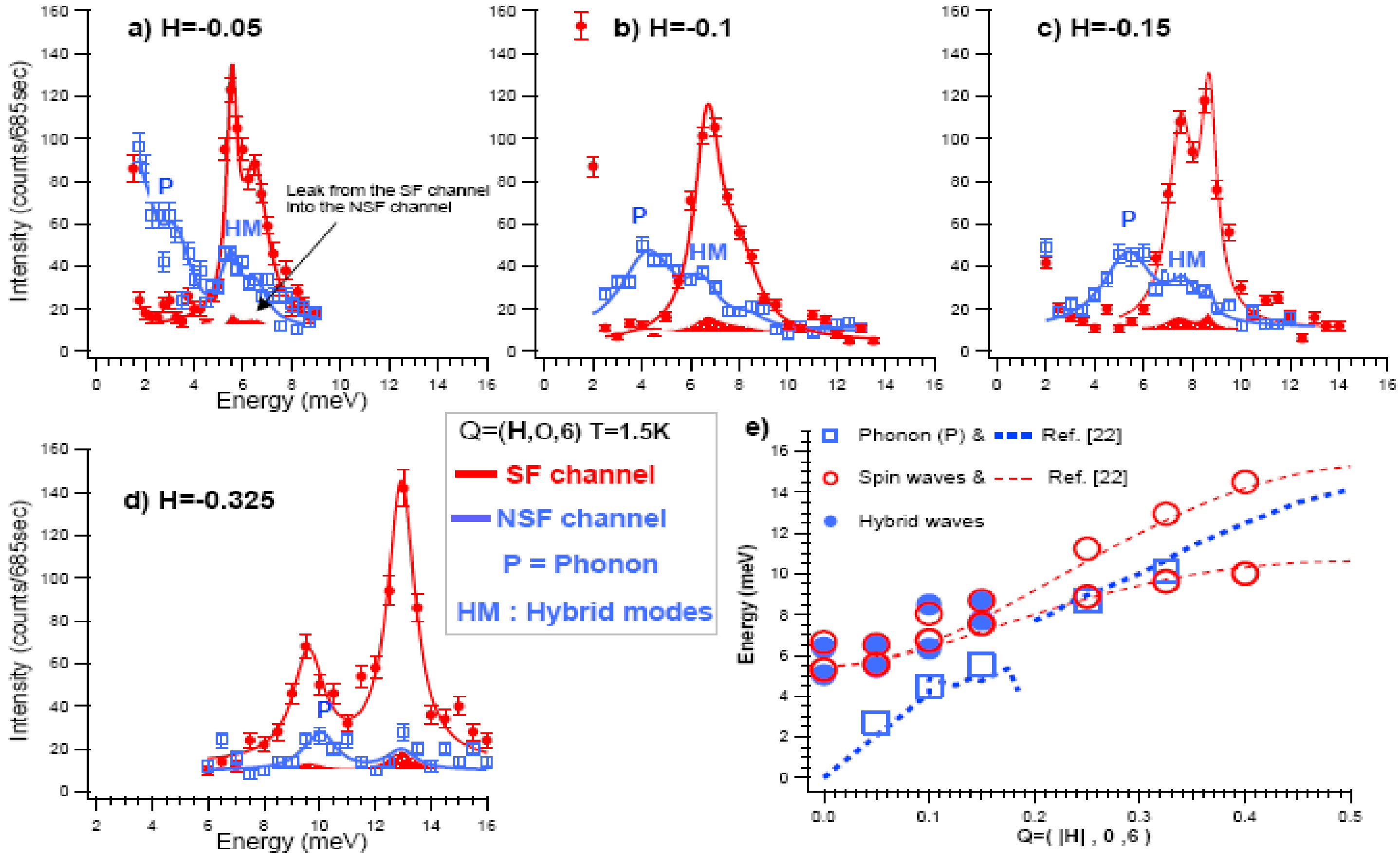
Small ferromagnetic component along c
induced by the ferroelectric component

L order parameter
P non zero everywhere, secondary
M third order



They don't vary in the same way.

Pailhes et al., 2009



After Pailhes et al.

Hybrid modes

questions

- $YMnO_3$ is ferromagnetic (?) below T_N!
  - This was already published by Bertaut

PROPRIETES MAGNETIQUES ET STRUCTURES
DU MANGANITE D'YTTRIUM

E. F. BERTAUT, R. PAUTHENET et M. MERCIER
Laboratoire d'Electrostatique et de Physique du Métal,
Centre d'Etudes Nucléaires de Grenoble

Recu le 18 septembre 1963

Dans une lettre précédente [1], deux modèles de structures magnétiques "en triangles" également compatibles avec les données de diffraction neutronique ont été proposés pour $MnYO_3$.

Dans la présente lettre, nous étudions ses propriétés magnétiques. En particulier un faible ferromagnétisme parasite observé nous permettra de préciser le modèle de structure.

Propriétés magnétiques

La variation de l'aimantation spécifique σ en fonction du champ magnétique interne H_i est mesurée entre 4.2°K et l'ambiante par la méthode d'extraction axiale.

Aux températures $T > 130$°K, l'inverse de la

Aux températures T inférieures à environ 50°K, l'aimantation décrit un cycle d'hystérèse dont la branche descendante peut être représentée par:

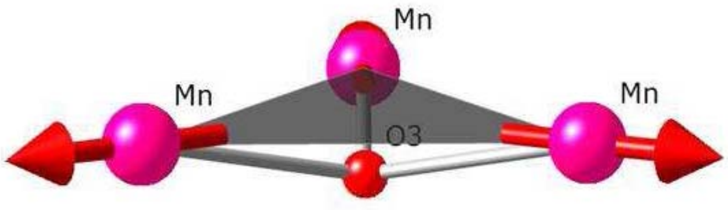
$$\sigma = \sigma_0 + \chi_m H_i .$$

Des courbes expérimentales, on déduit en fonction de T, la susceptibilité χ_m, le faible ferromagnétisme σ_0; l'aimantation rémanente σ_r, le champ coercitif H_c. A $T = 46$°K, σ_0, σ_r et H_c disparaissent; en même temps $1/\chi_m$ présente un minimum d'ailleurs peu prononcé. $T_N = 46$°K présente donc la température de Néel au-dessous de laquelle les spins s'ordonnent "en triangles" [1]. H_c croît rapidement lorsque la température décroît [$H_c(20.4°K) = 1000$ Oe]; [$H_c(4.2°K) = 3640$ Oe]. A $T = 4.2$°K,

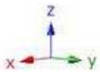
questions

- $YMnO_3$ is ferromagnetic (?) below T_N!
- What is the origin of the coupling? Why there is an effect on polarization?
  - Two steps
    - The microscopic coupling (exchange, LS coupling)
    - The long range ordering (symmetry)
  - Both are difficult

Origin of the coupling term

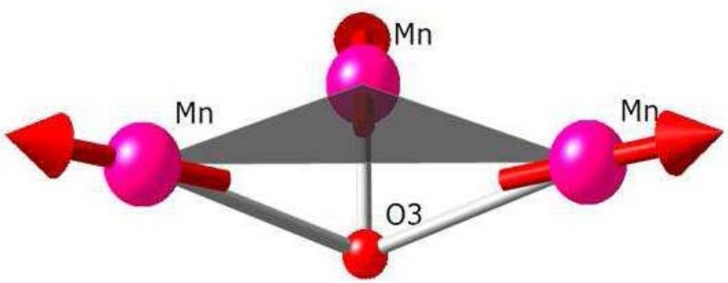


1 Displacement of oxygen is responsible to the polarization



2 Origin of the antiferromagnetism?
superexchange by oxygen

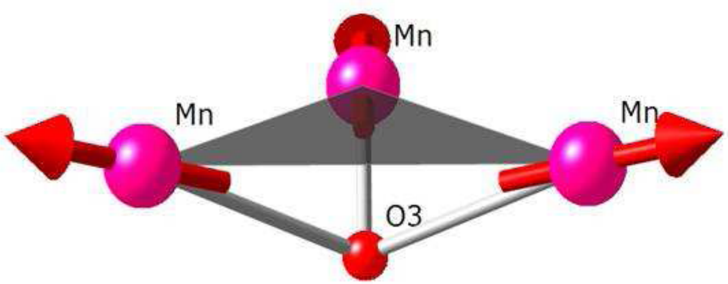
3 antiferromagnetism by superexchange changes the energy and the polarization



4 It induces a ferromagnetic component.

Superexchange explanation?

- Does superexchange enough to understand the coupling?
  - No, because of the symmetry. If you add the three contributions, they cancel by symmetry.



Cancel by symmetry

$$\delta H_{ex} = \sum_n (-1)^{n+1}[J'_{\parallel} x_0 \delta x_n + J'_{\perp}(y_0 \delta y_n + z_0 \delta z_n)](\mathbf{S}_n \cdot \mathbf{S}_{n+1}) + H_{el}, \quad (4)$$

where the elastic energy

$$H_{el} = \frac{\kappa}{2} \sum_n (\delta x_n^2 + \delta y_n^2 + \delta z_n^2) \quad (5)$$

After I. A. Sergienko and E. Dagotto

On the contrary, the Dzyaloshinskii-Moriya interaction— i.e., anisotropic exchange interaction $\mathbf{S}_n \times \mathbf{S}_{n+1}$— changes its sign under inversion.

$$\mathbf{D}^x(\mathbf{r}_n) = \gamma(0, -z_n, y_n), \quad \mathbf{D}^y(\mathbf{r}_n) = \gamma(z_n, 0, -x_n) \qquad (7)$$

for the Mn-O-Mn bonds along the x and y axes, respectively. The form of Eqs. (7) can also be obtained[23] by perturbative calculations within the Anderson-Moriya theory of superexchange.[22] For the Mn chain in the x direction, the portion of the Hamiltonian depending on $\delta\mathbf{r}_n$,

$$\delta H_{\mathrm{DM}} = \sum_n \mathbf{D}^x(\delta\mathbf{r}_n) \cdot [\mathbf{S}_n \times \mathbf{S}_{n+1}] + H_{\mathrm{el}}, \qquad (8)$$

Dzyaloshinskii-Moriya interaction

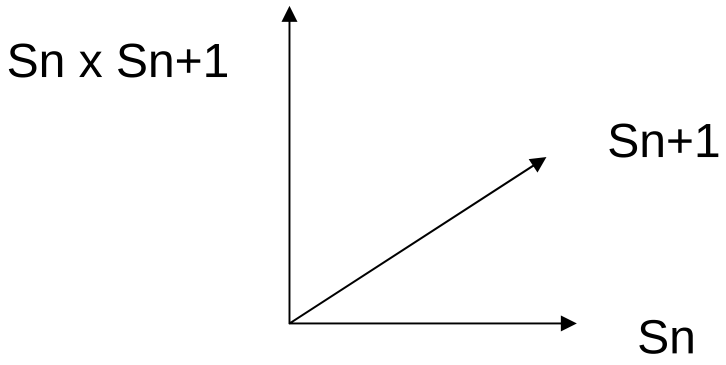
- Of course, this expansion in term of LS coupling does not mean that this term in the dominant one, but an least, this is the first one you can think about.

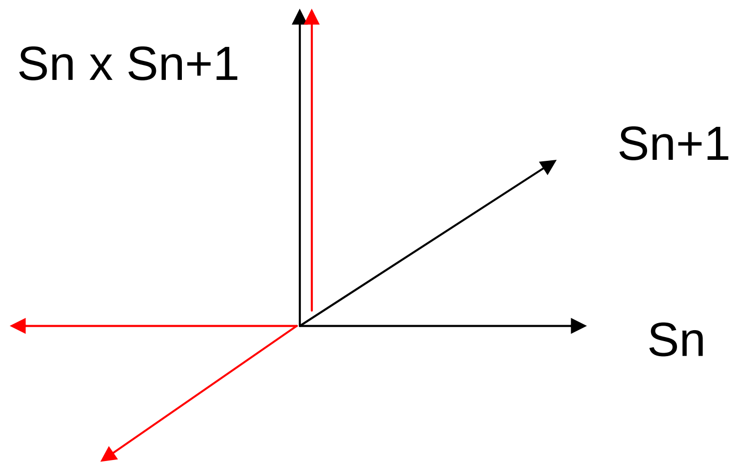
$$\hat{H}_{so} = \frac{\mu_B}{\hbar m_e e c^2} \frac{1}{r} \frac{\partial U(\vec{r})}{\partial r} \hat{\vec{L}} \cdot \hat{\vec{S}}$$

$$U(\vec{r}) = -\frac{e^2 Z_n}{r}$$

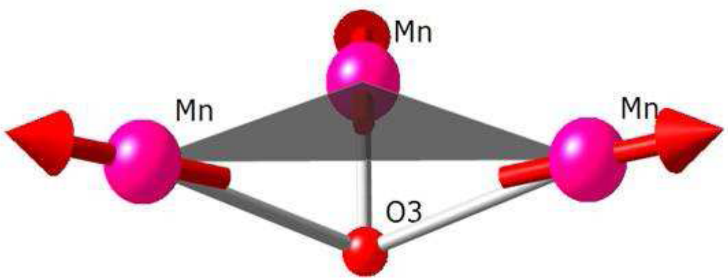
et donc

$$\hat{H}_{so} = \frac{\mu_B}{\hbar m_e e c^2}\frac{e^2 Z_n}{r^3}\,\hat{\vec{L}} \cdot \hat{\vec{S}}$$





Effect of inversion



- The problem is the symmetry
- The solution is the symmetry
- The method in Landau theory

$YMnO_3$ symmetry

- Non ferroelectric *P63/mmc* (194)

D_{3h} $(-6m2)$	Num	1	m	3	-6	2_h	m_v	Orbitales
A'_1	Γ_1	1	1	1	1	1	1	x^2+y^2, z^2
A'_2	Γ_2	1	1	1	1	-1	-1	J_z
$A"_1$	Γ_3	1	-1	1	-1	1	-1	
$A"_2$	Γ_4	1	-1	1	-1	-1	1	z
E'	Γ_6	2	2	-1	-1	0	0	(x,y), (x^2-y^2, xy)
$E"$	Γ_5	2	-2	-1	1	0	0	(xz, yz), (J_x, J_y)

M=0

- ferroelectric *P63cm* (185).

C_s (m)	Num	1	m	Orbitales
A'	γ_1	1	1	x, y, x^2, y^2, z^2, xy, J_z
$A"$	γ_2	1	-1	z, xz, yz, J_x, J_y

Mc can be non zero

1 identity

2 symmetry by a plane

$$\left\{\begin{array}{l}\mu_a(x/a,y/b,z/c)\\ \mu_b(x/a,y/b,z/c)\\ \mu_c(x/a,y/b,z/c)\end{array}\right. \longrightarrow \left\{\begin{array}{l}-\mu_a(-x/a,-y/b,z/c+c/2)\\ -\mu_b(-x/a,-y/b,z/c+c/2)\\ \mu_c(-x/a,-y/b,z/c+c/2)\end{array}\right.$$

No in plane components

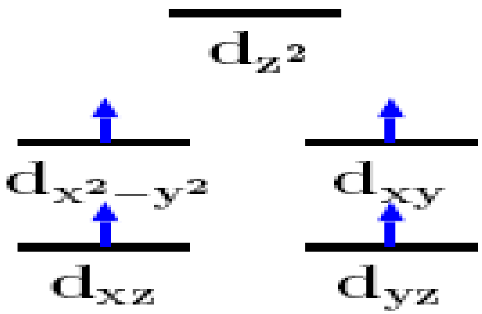
3 rotation axis 2 with translation

$$\left\{\begin{array}{l}\mu_a(x/a,y/b,z/c)\\ \mu_b(x/a,y/b,z/c)\\ \mu_c(x/a,y/b,z/c)\end{array}\right. \longrightarrow \left\{\begin{array}{l}-\mu_b(y/a,x/b,z/c)\\ -\mu_a(y/a,x/b,z/c)\\ \mu_c(y/a,x/b,z/c)\end{array}\right.$$

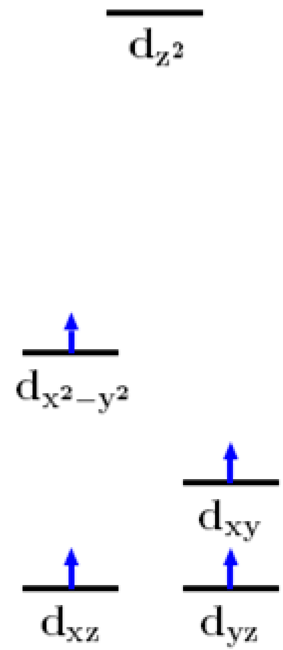
C axis component possible

4 combinations of two

YMnO3 symmetry



Non ferro



ferro

- Symmetry analysis shows that the experimental observation was the only possible one.

effect

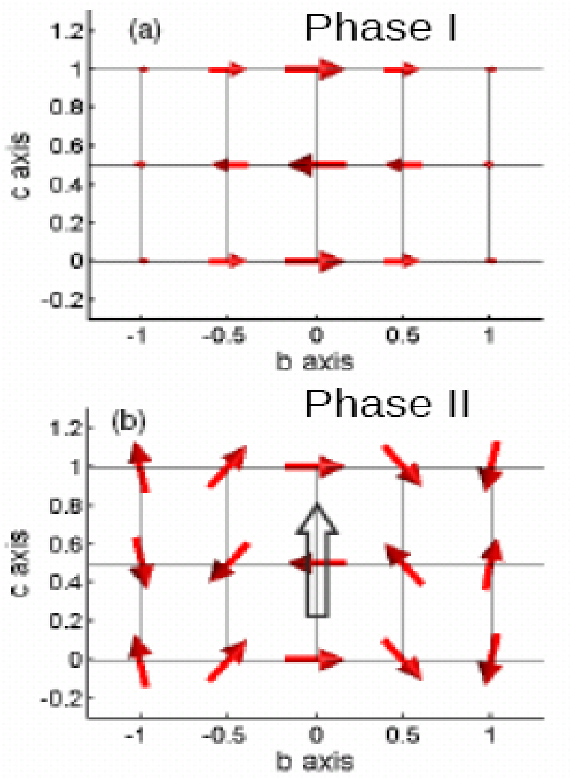
Magnetic crystal class		Matrix representation of the property tensor α_{ij}
Schoenflies	Hermann–Mauguin	
C_1 $C_i(C_1)$	1 $\bar{1}'$	$\begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{bmatrix}$
C_2 $C_s(C_1)$ $C_{2h}(C_2)$	$2\,(=121)$ $m'\,(=1m'1)$ $2/m'\,(=1\,2/m'\,1)$ (unique axis y)	$\begin{bmatrix} \alpha_{11} & 0 & \alpha_{13} \\ 0 & \alpha_{22} & 0 \\ \alpha_{31} & 0 & \alpha_{33} \end{bmatrix}$
C_s $C_2(C_1)$ $C_{2h}(C_s)$	$m\,(=1m1)$ $2'\,(=12'1)$ $2'/m\,(=1\,2'/m\,1)$ (unique axis y)	$\begin{bmatrix} 0 & \alpha_{12} & 0 \\ \alpha_{21} & 0 & \alpha_{23} \\ 0 & \alpha_{32} & 0 \end{bmatrix}$
D_2 $C_{2v}(C_2)$ $D_{2h}(D_2)$	222 $m'm'2\,[2m'm',\ m'2m']$ $m'm'm'$	$\begin{bmatrix} \alpha_{11} & 0 & 0 \\ 0 & \alpha_{22} & 0 \\ 0 & 0 & \alpha_{33} \end{bmatrix}$
C_{2v} $D_2(C_2)$ $C_{2v}(C_s)$ $D_{2h}(C_{2v})$	$mm2$ $2'2'2$ $2'mm'\,[m2'm']$ mmm'	$\begin{bmatrix} 0 & \alpha_{12} & 0 \\ \alpha_{21} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$
$C_4,\ S_4(C_2),\ C_{4h}(C_4)$ $C_3,\ S_6(C_3)$ $C_6,\ C_{3h}(C_3),\ C_{6h}(C_6)$	$4,\ \bar{4}',\ 4/m'$ $3,\ \bar{3}'$ $6,\ \bar{6}',\ 6/m'$	$\begin{bmatrix} \alpha_{11} & \alpha_{12} & 0 \\ -\alpha_{12} & \alpha_{11} & 0 \\ 0 & 0 & \alpha_{33} \end{bmatrix}$
S_4 $C_4(C_2)$ $C_{4h}(S_4)$	$\bar{4}$ $4'$ $4'/m'$	$\begin{bmatrix} \alpha_{11} & \alpha_{12} & 0 \\ \alpha_{12} & -\alpha_{11} & 0 \\ 0 & 0 & 0 \end{bmatrix}$
$D_4,\ C_{4v}(C_4)$ $D_{2d}(D_2),\ D_{4h}(D_4)$ $D_3,\ C_{3v}(C_3),\ D_{3d}(D_3)$ $D_6,\ C_{6v}(C_6)$ $D_{3h}(D_3),\ D_{6h}(D_6)$	$422,\ 4m'm'$ $\bar{4}'2m'\,[\bar{4}'m'2],\ 4/m'm'm'$ $32,\ 3m',\ \bar{3}'m'$ $622,\ 6m'm'$ $\bar{6}'m'2\,[\bar{6}'2m'],\ 6/m'm'm'$	$\begin{bmatrix} \alpha_{11} & 0 & 0 \\ 0 & \alpha_{11} & 0 \\ 0 & 0 & \alpha_{33} \end{bmatrix}$

Symmetry restrictions

“There are 31 point groups that allow a spontaneous electric polarization, **P**, and 31 that allow a spontaneous magnetic polarization, **M**.
Thirteen point groups **(1, 2, 2', *m*, *m* ', 3, 3*m*', 4, 4*m*'*m*', *m*'*m*2', *m*'*m*'2', 6, and 6*m*'*m*')**
are found in both sets, allowing both properties to exist in the same phase.”

- This is very limited
- Solution: incommensurability
  - An incommensurate modulation of the magnetism with a ferromagnetic component suppresses the corresponding symmetry elements

$TbMnO_3$



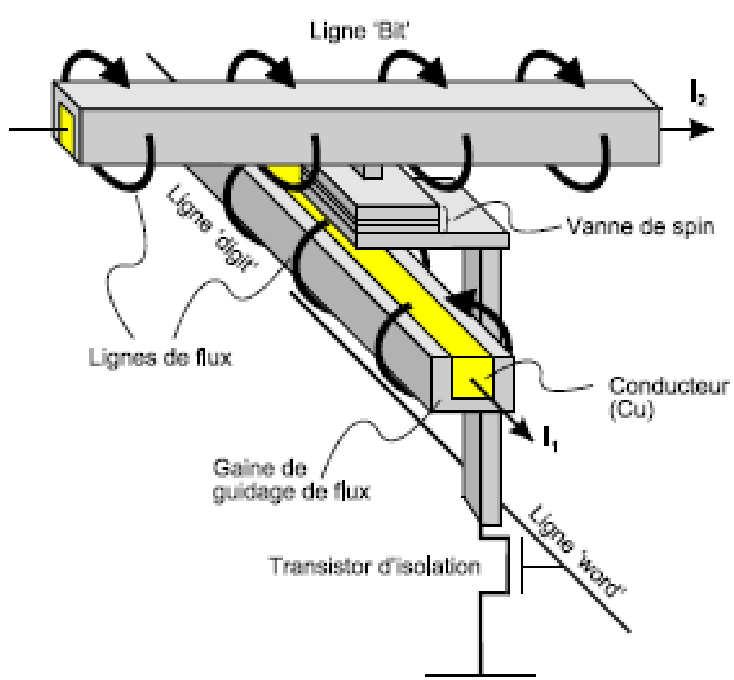
Kenzelmann, PRL 95, 087206 (2005)

Pseudo-proper ferroelectric
Electric polarisation along y in phase II
Space group Pnma
Propagation vector k=(μ,0,0)
Mn in (1/2,0,0)

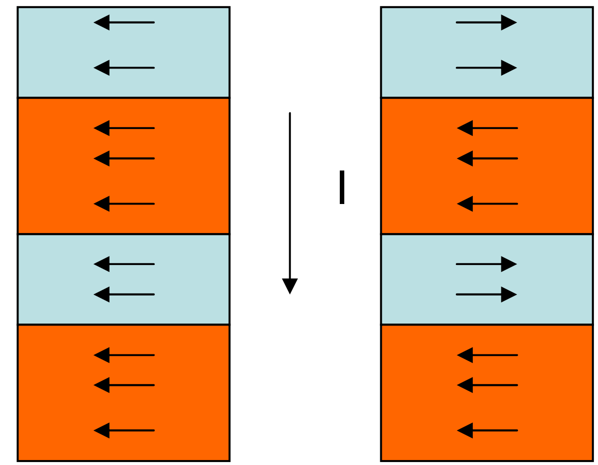
Applications

- Magnetic memories that you can write with electric field
- RAM (random acces memory) FRAM (ferroélectric, no battery), MRAM (magnétic, no battery, difficult to write).
- Multiferro: write with electric field, read with magnetic sensor.

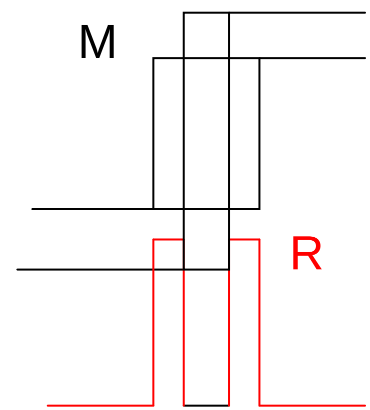
GMR



Ligne 'Bit'
I2
Vanne de spin
Ligne 'digit'
Lignes de flux
Conducteur
(Cu)
I1
Gaine de
guidage de flux
Transistor d'isolation
Ligne 'word'

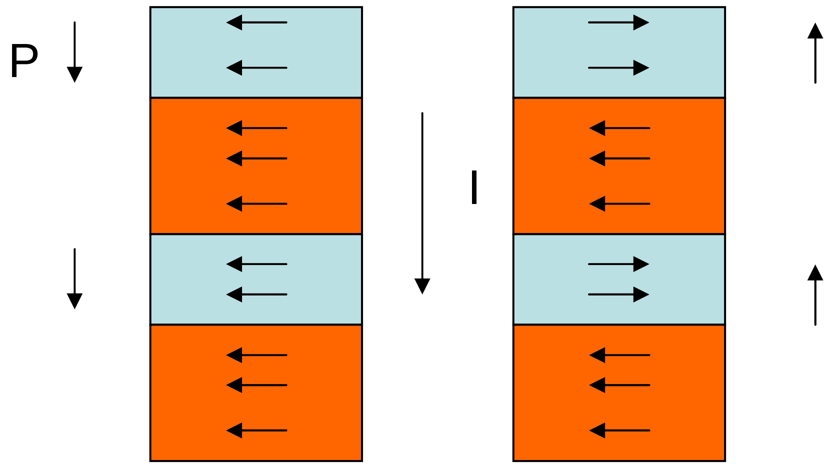


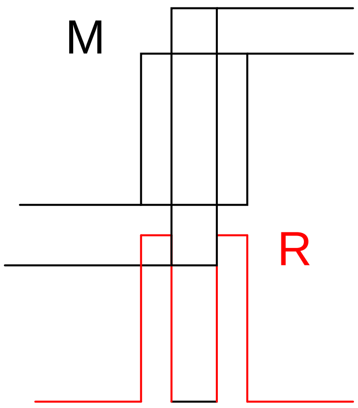
I



M
R

Write multiferro





One historical example: Boracites

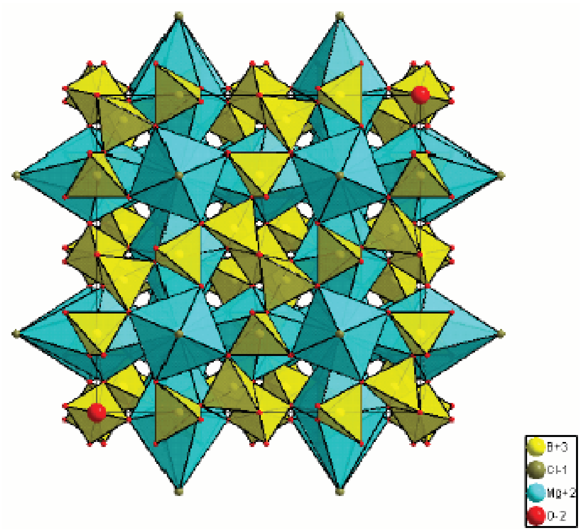
$M_3B_7O_{13}X$

M^{2+}=Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd

X^{-}=F, Cl, Br, I, OH, NO_3

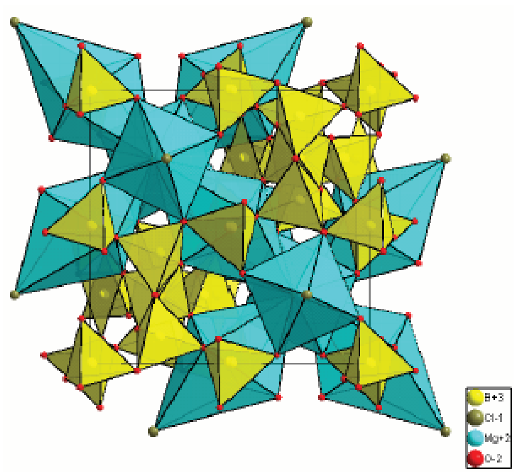
HT cubic **PE** $F\bar{4}3c$

a≈12Å, Z=8, n.a.=192



≈RT orthorhombic **FE** $Pca2_1$

a≈8.5Å, c≈12Å, Z=4, n.a.=96



$Ni_3B_7O_{13}I$

$F\bar{4}3c1' \Leftrightarrow m'$ => 12 domaines FE et 24 domaines FM

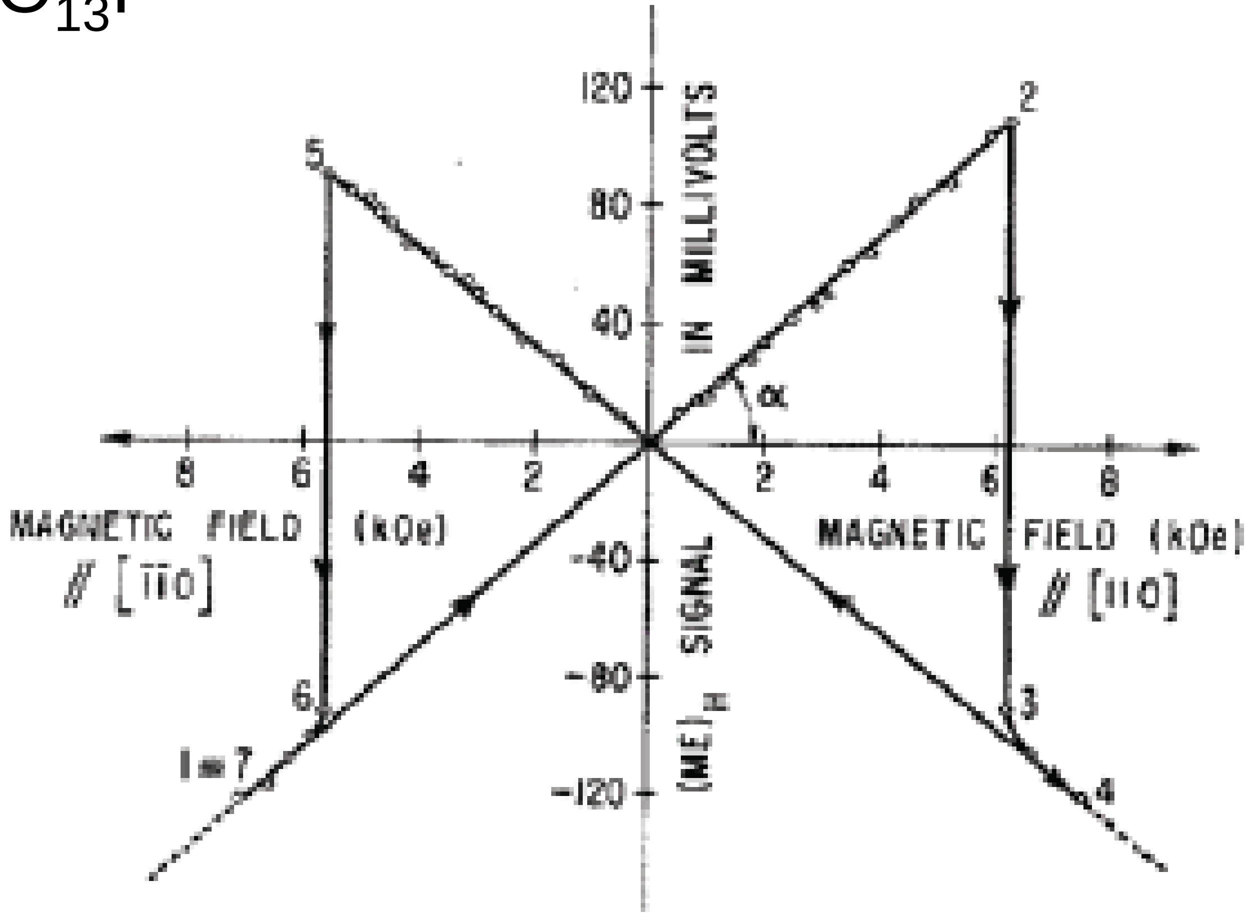
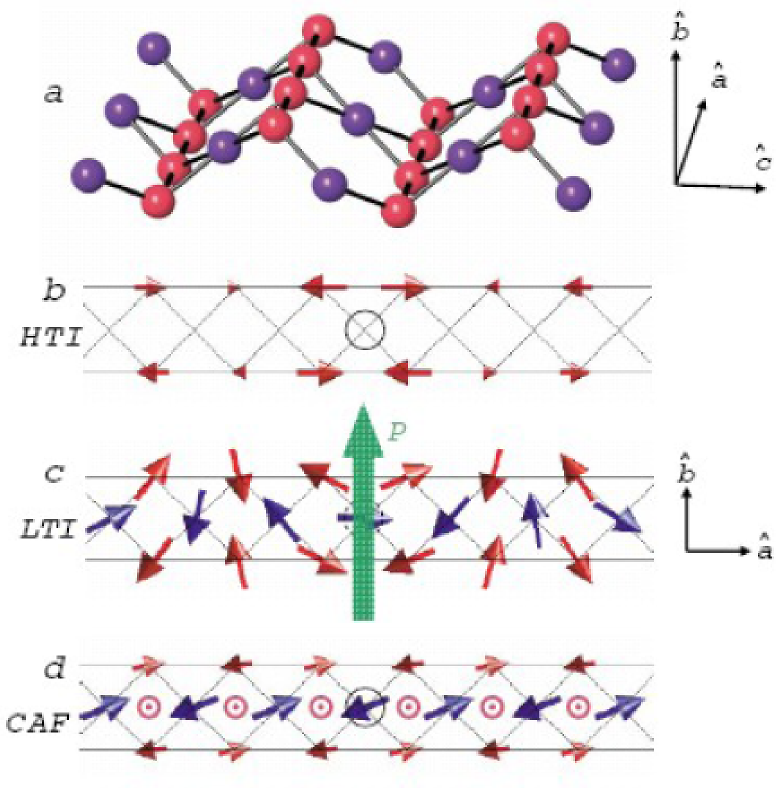


FIG. 4. Example of a quadratic magnetoelectric hysteresis loop with H along ±[110] and P along [001] at 46°K. After annealing as in Fig. 3.

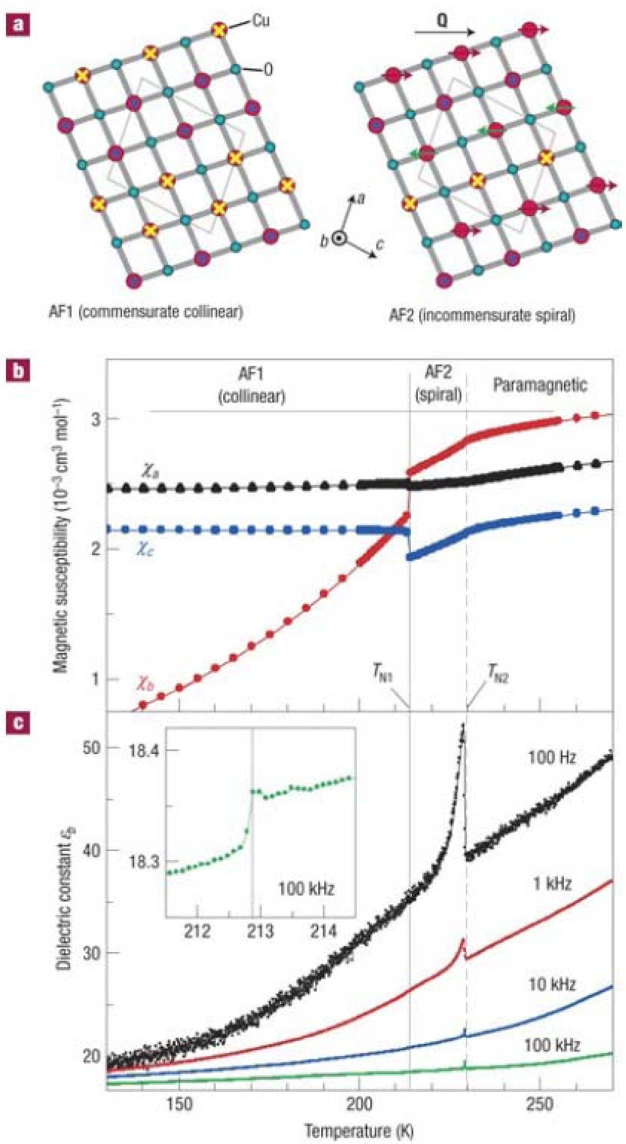
Other materials

- Structure: perovskite: $BiFeO_3$ $PrMnO_3$
- Structure: hexagonal: $MMnO_3$ M=Y, Ho, etc…
- Boracites
- Spiral magnetic order: $TbMnO_3$ $MnWO_4$
- Fe Langasites.

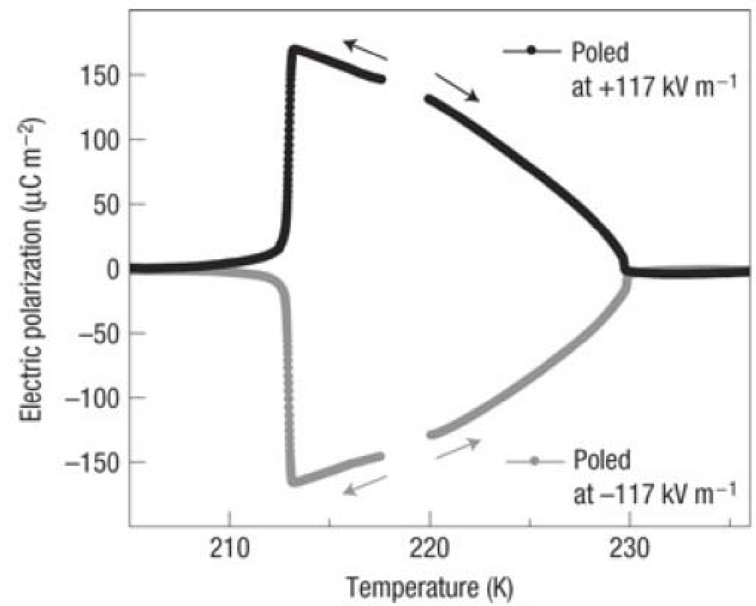
$Ni_3V_2O_8$



Lawes, PRL 95, 087205 (2005)



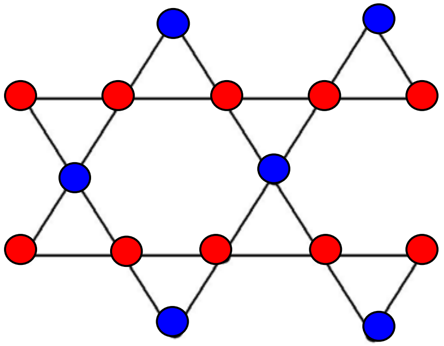
Tenurite CuO

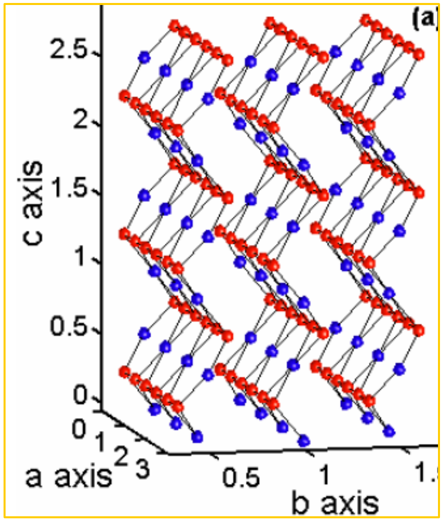


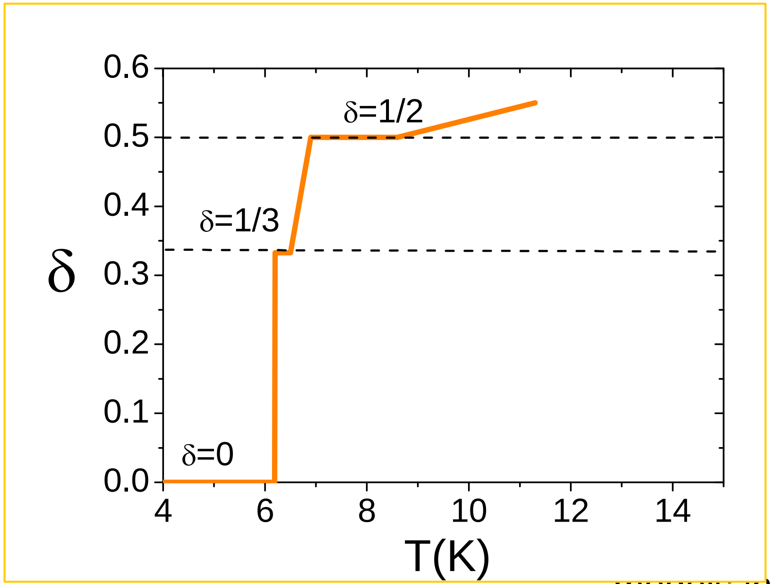
Kimura, Nature Materials 7, 291 - 294 (2008)

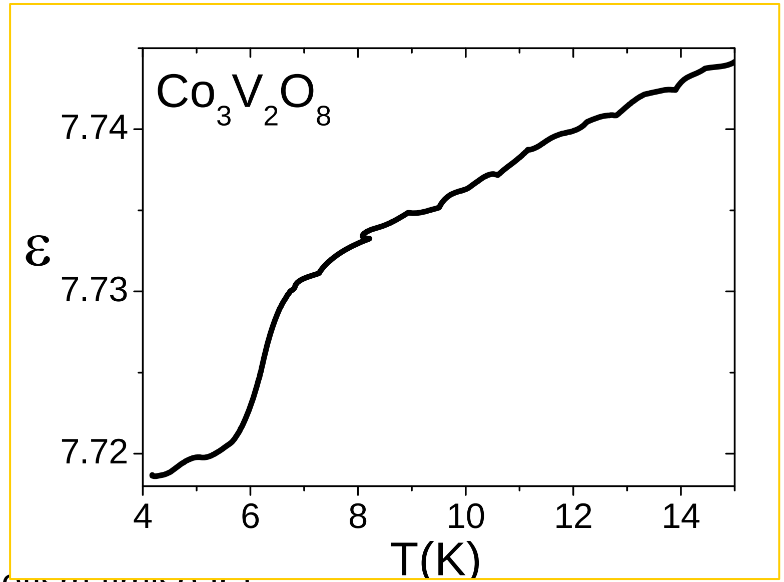
Kagome staircase - $Co_3V_2O_8$

$Ni_3V_2O_8$ [1]: S=1
$Co_3V_2O_8$ [1]: S=3/2
β-$Cu_3V_2O_8$ [2]: S=1/2

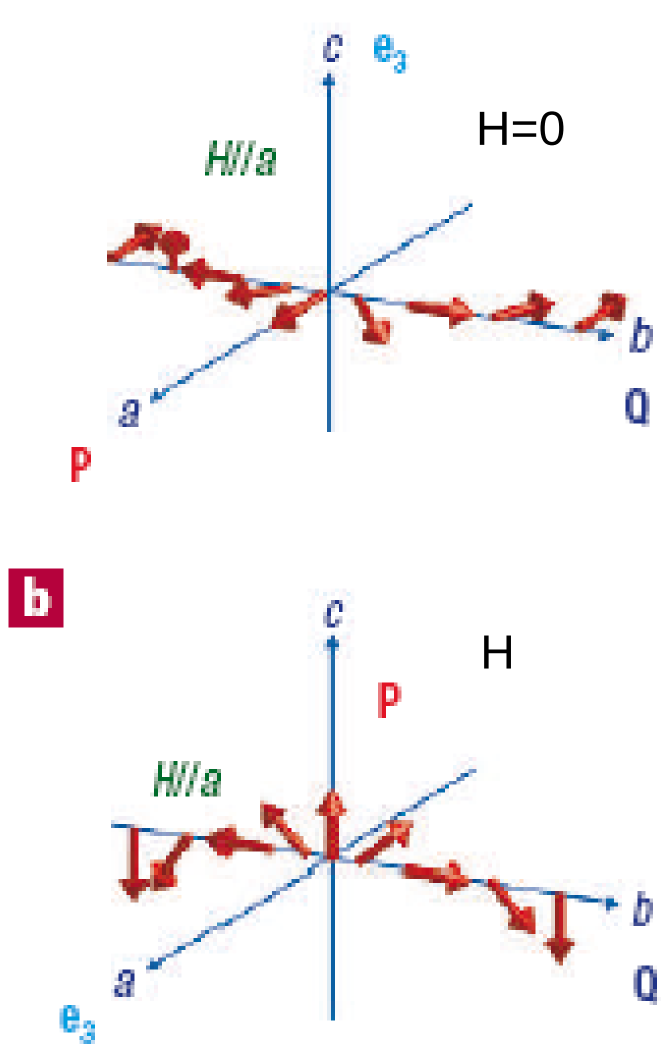




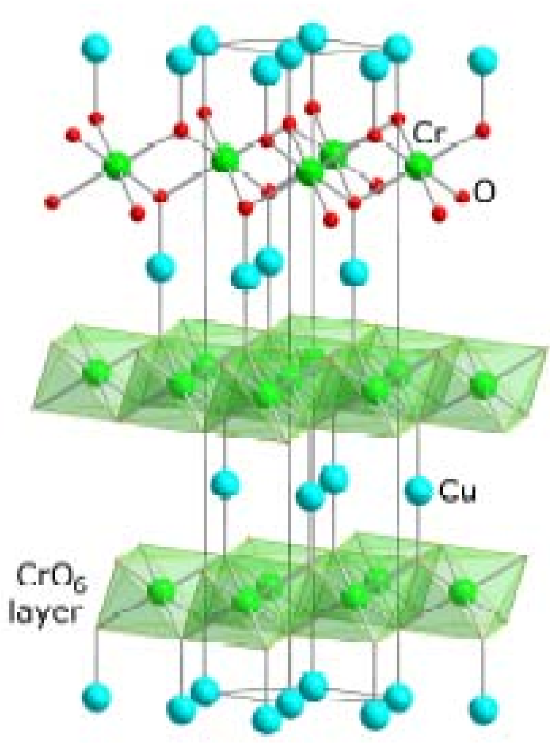




$Eu_{0.75}Y_{0.25}MnO_3$

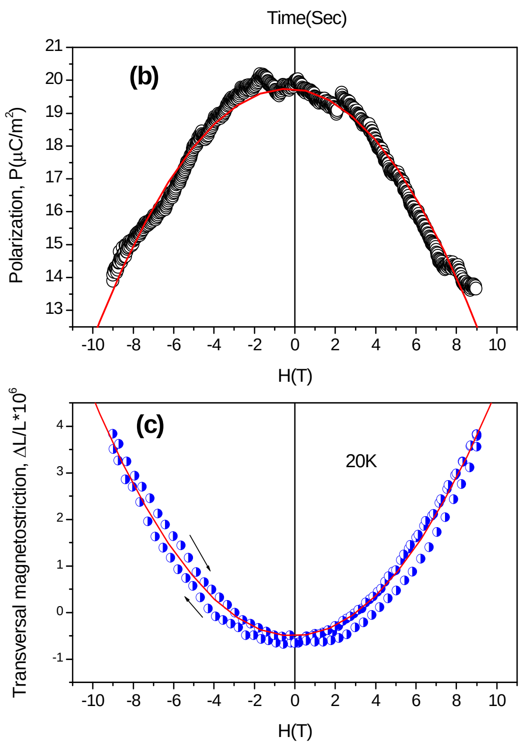


$CuCrO_2$



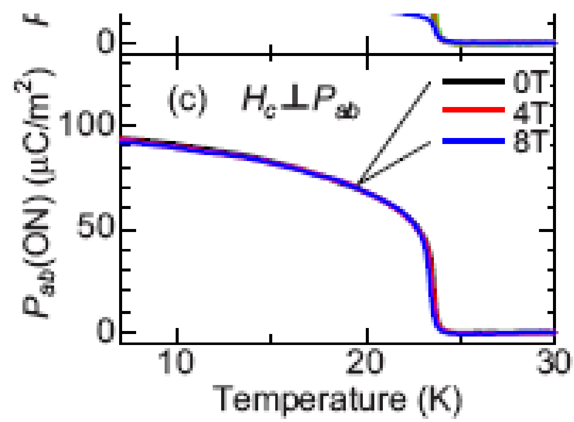
Complex incommensurate structure

$CuCrO_2$



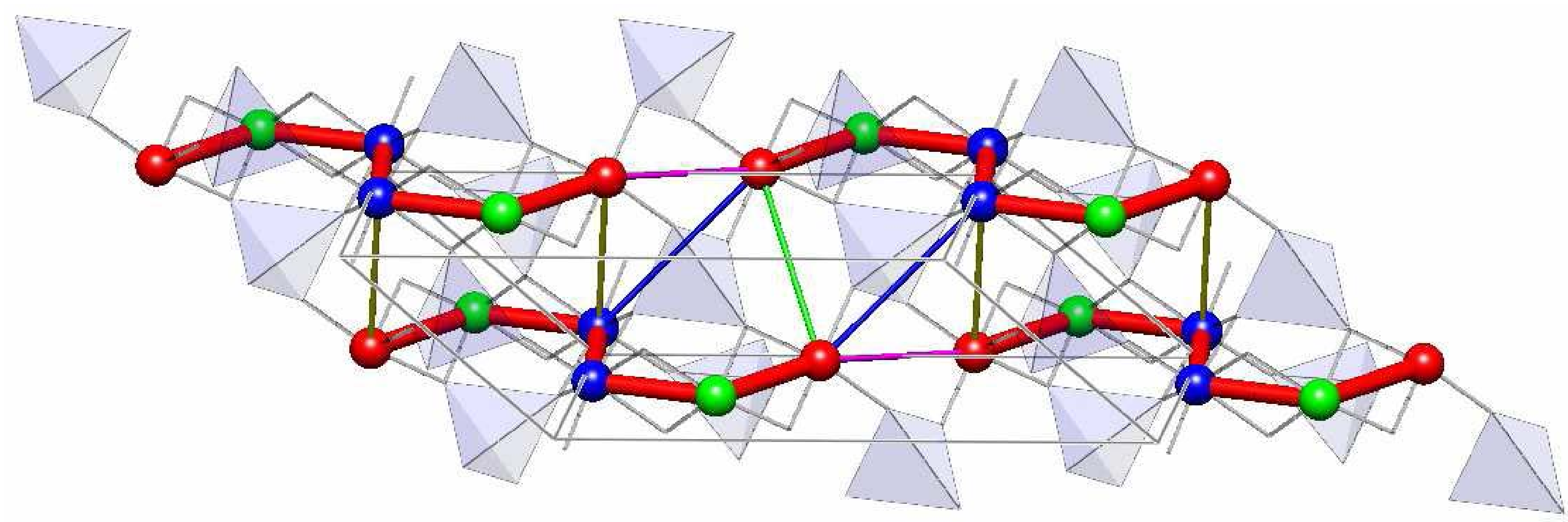
$$F = F_{AFM}(L) + \alpha P^2 - EP + gLP$$

$$L^2 = (-a(T - T_N) + dH^2)/2b$$



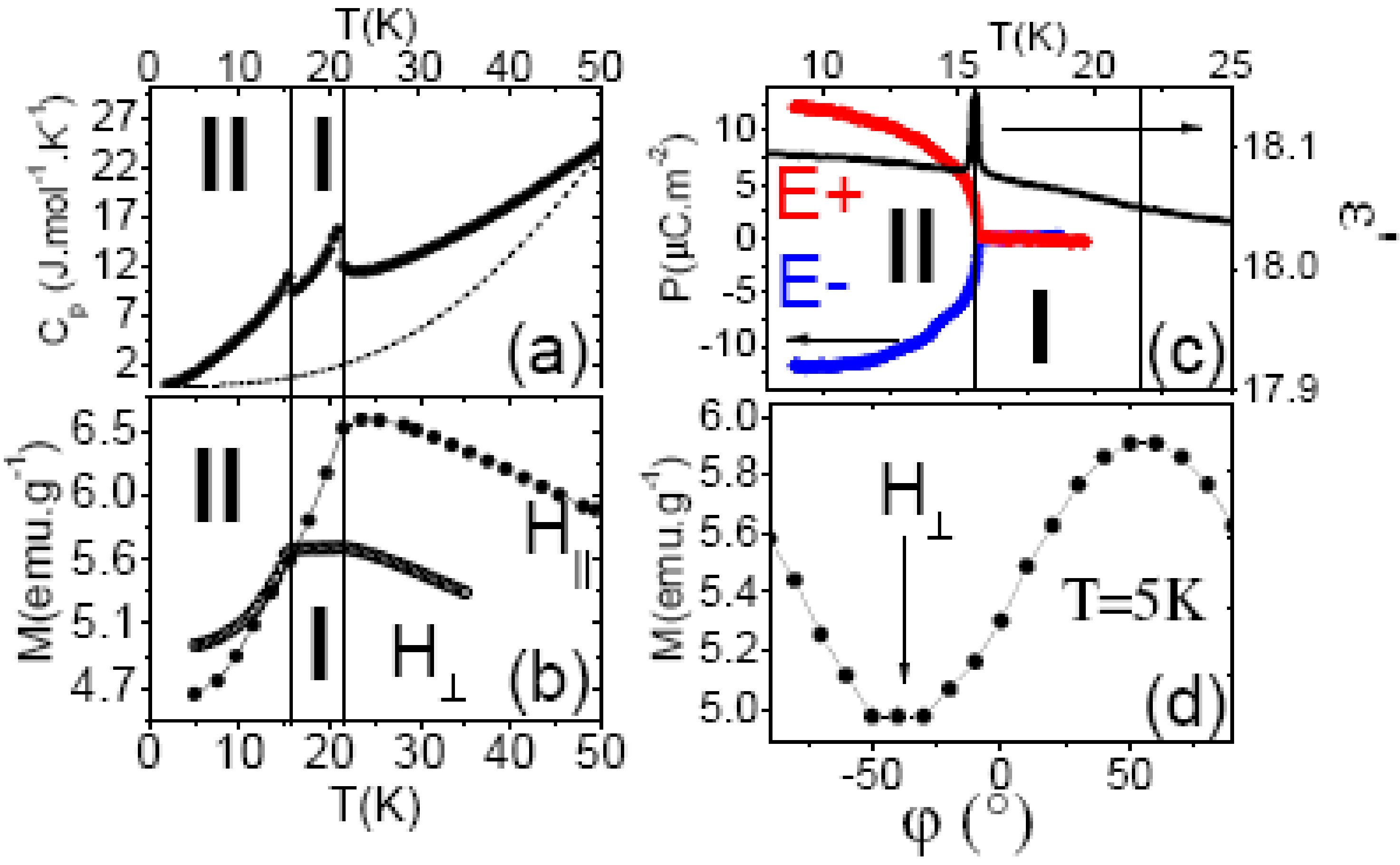
Bohdan Kundys, Maria Poienar, Antoine Maignan, Christine Martin, Charles Simon

$FeVO_4$



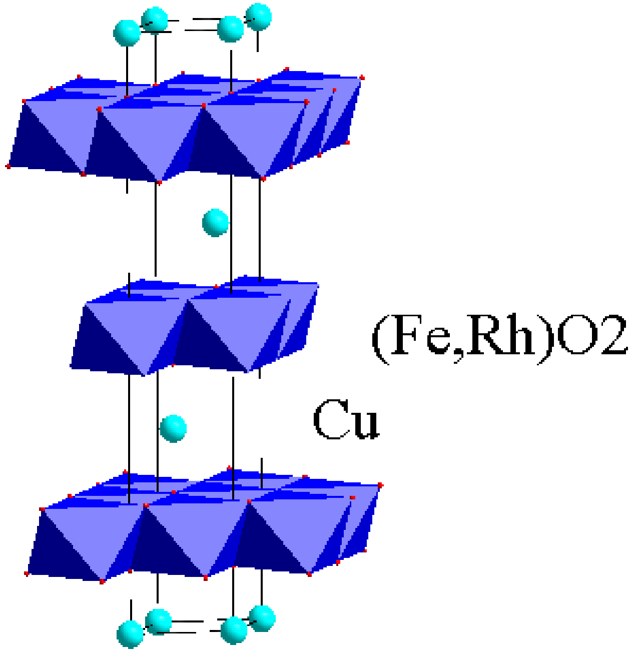
6 Fe^{3+} 5/2 in a triclinic structure 1

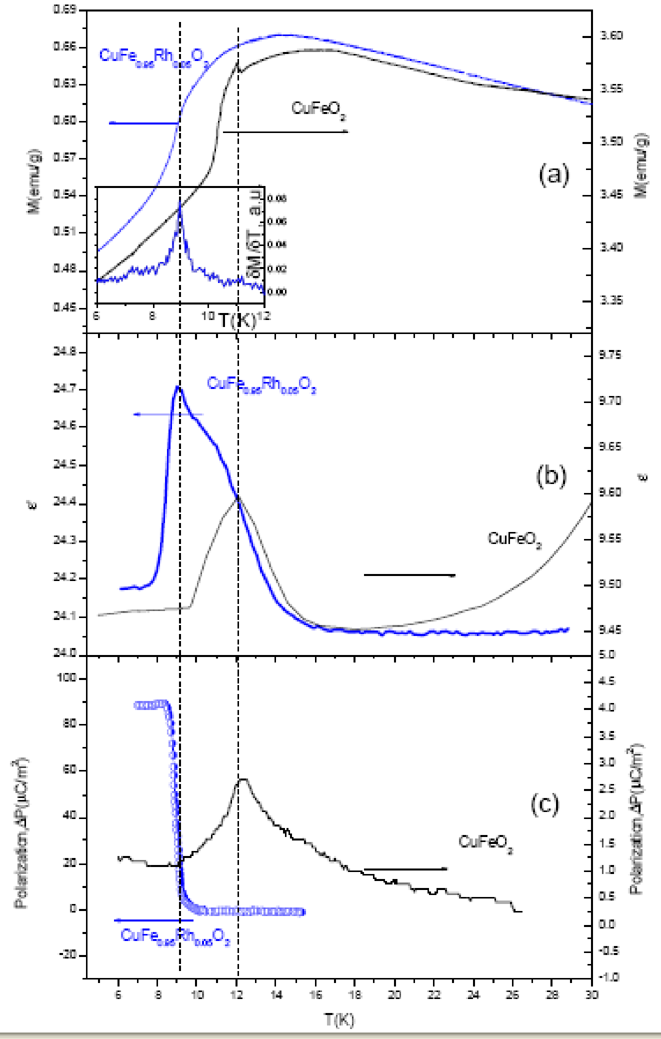
$FeVO_4$



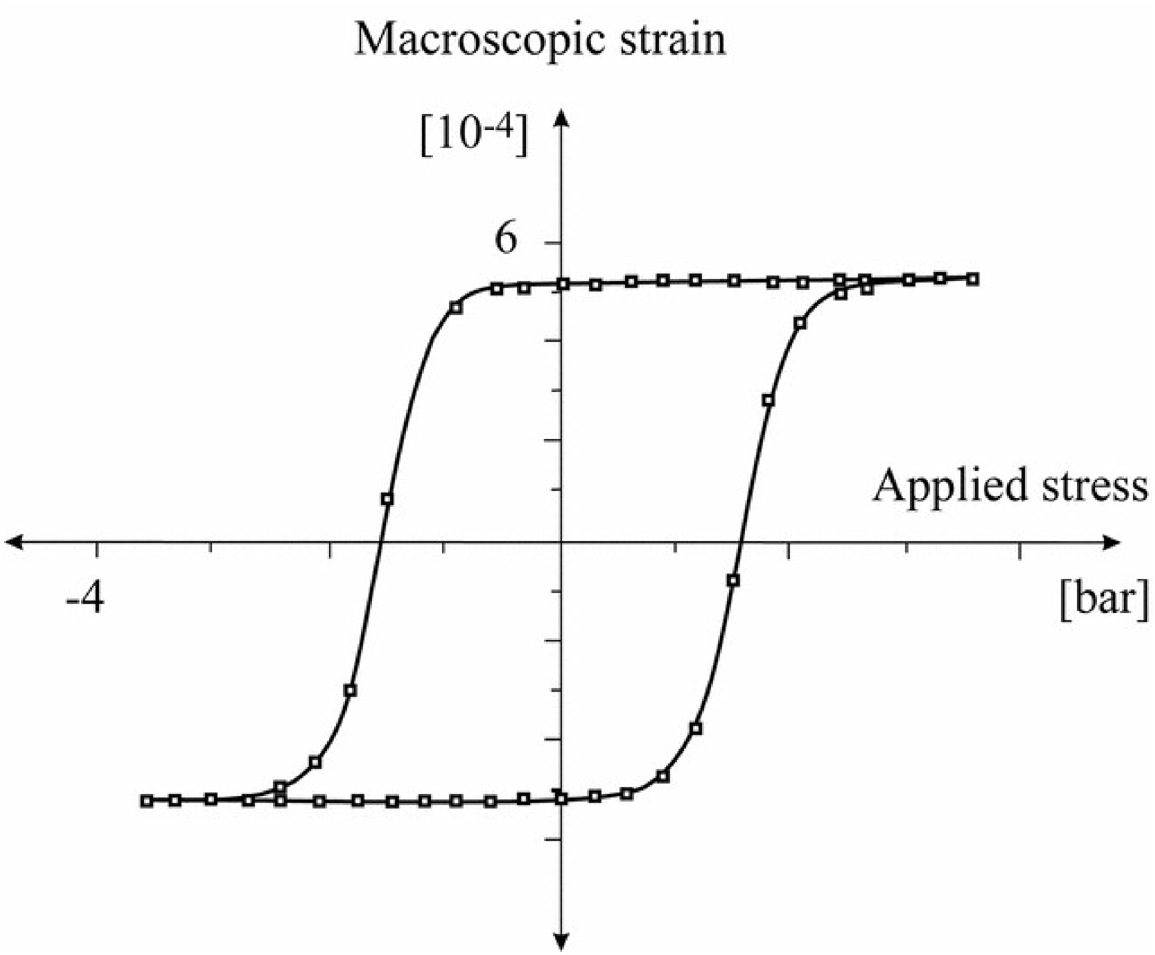
T(K)
0 10 20 30 40 50
27 22 17 12 7 2
C_p (J.mol^{-1}.K^{-1})
II
I
(a)
6.5 6.0 5.6 5.1 4.7
M(emu.g^{-1})
II
I
$H_{\parallel}$
$H_{\perp}$
(b)
0 10 20 30 40 50
T(K)
T(K)
10 15 20 25
10 5 0 -5 -10
P(μC.m^{-2})
E+
E-
II
I
(c)
18.1 18.0 17.9
ε
6.0 5.8 5.6 5.4 5.2 5.0
M(emu.g^{-1})
$H_{\perp}$
T=5K
(d)
-50 0 50
φ (°)

$FeCuO_2$



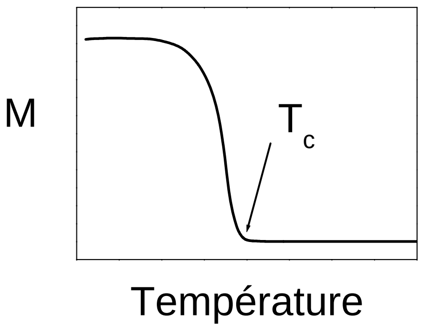


A ferroic material

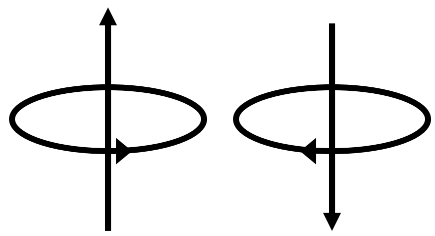


Free energy from "Landau"

Ferromagnet

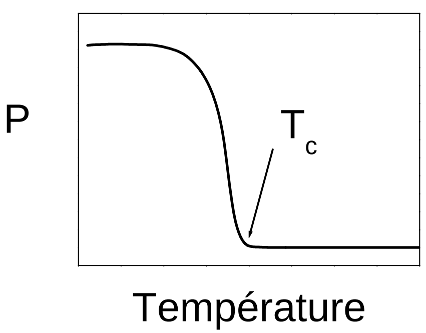


$$F = F_0 + c_1 M + c_2 M^2 + c_3 M^3 + c_4 M^4 + \dots - MH$$

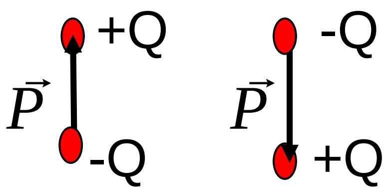


$$F_{FM} = F_{FM_0} + \frac{a}{2} M^2 + \frac{b}{4} M^4 - MH$$

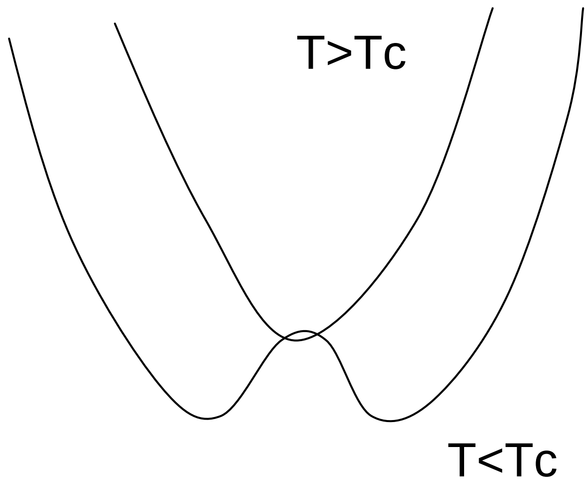
Ferroelectric



$$F = F_0 + c_1 P + c_2 P^2 + c_3 P^3 + c_4 P^4 + \dots - PE$$



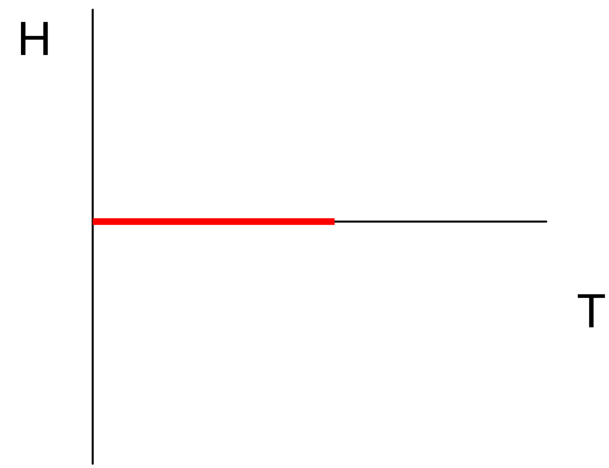
$$F_{FE} = F_{FE_0} + \frac{\alpha}{2} P^2 + \frac{\beta}{4} P^4 - PE$$



$$F_{FM} = F_{FM_0} + \frac{a}{2}M^2 + \frac{b}{4}M^4 - MH$$

a is linear in T-Tc

M^2 = -a/b



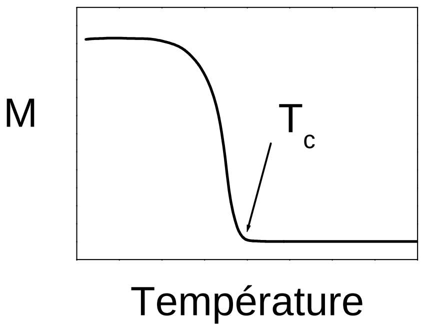
Interactions and symmetries

- This example is too simple: the symmetry is hidden and the role of the interactions is not clear

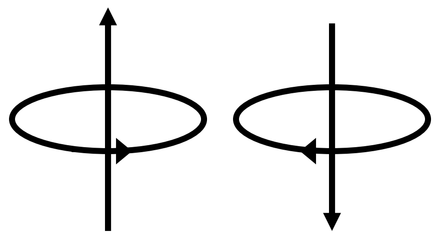
- We have already discussed in this school the possible origins of ferromagnetism
- Let us discuss briefly the possible origin of ferroelectricity:
  - A shift of one of the atoms from the symmetrical position due electron electron repulsion

Free energy from "Landau"

Ferromagnet

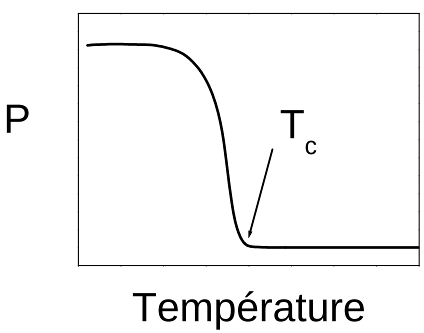


$$F = F_0 + c_1 M + c_2 M^2 + c_3 M^3 + c_4 M^4 + \ldots. - MH$$

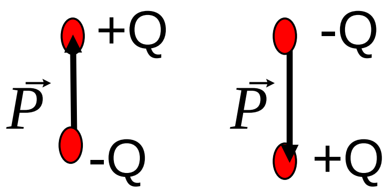


$$F_{FM} = F_{FM_0} + \frac{a}{2} M^2 + \frac{b}{4} M^4 - MH$$

Ferroelectric



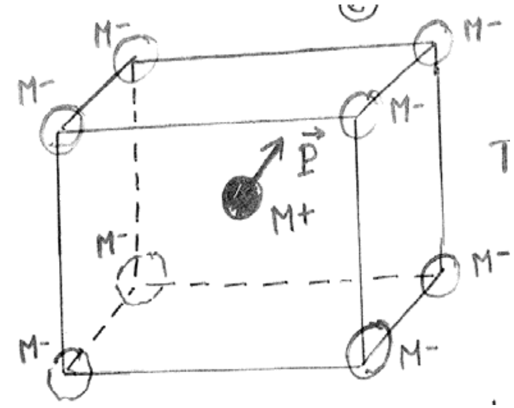
$$F = F_0 + c_1 P + c_2 P^2 + c_3 P^3 + c_4 P^4 + \ldots. - PE$$



$$F_{FE} = F_{FE_0} + \frac{\alpha}{2} P^2 + \frac{\beta}{4} P^4 - PE$$

A little more about Landau

- Paraelectric I 4/mmm to ferroelectric II at Tc.
- F is formed by successive invariants



4/mmm	C_1	C_4	C_2	C_4^3	σ_x	σ_y	σ_{xy}	$\sigma_{\bar{x}y}$	I	S_4^3	σ_z	S_4	U_x	U_y	U_{xy}	[illegible]
P_x	P_x	P_y	$-P_x$	$-P_y$	$-P_x$	P_x	P_y	$-P_y$	$-P_x$	$-P_y$	P_x	P_y	P_x	$-P_x$	P_y	[illegible]
P_y	P_y	$-P_x$	$-P_y$	P_x	P_y	$-P_y$	$-P_x$	P_x	$-P_y$	P_x	P_y	$-P_x$	$-P_y$	P_y	P_x	[illegible]
P_z	P_z	P_z	P_z	P_z	P_z	P_z	P_z	P_z	$-P_z$	$-P_z$	$-P_z$	$-P_z$	$-P_z$	$-P_z$	$-P_z$	[illegible]

From P. Toledano

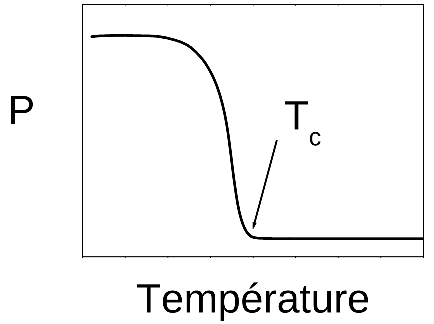
- Quadratic invariants Px^2+Py^2, Pz^2
- Quartic invariants $(Px^2+Py^2)^2$, Pz^4, Px^4+Py^4, $(PxPy)^2$

- $F=F_0+a/2(Px^2+Py^2)+a'/2\ Pz^2+\ldots$

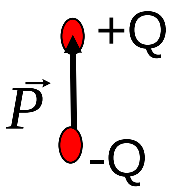
- Minimization of F with respect to Px,Py,Pz
- a or a' changes sign first (assume a, a'>0)

- Then, $Pz^2 = -a/b$
- Pz is the order parameter.

Ferroelectric



$$F = F_0 + c_1 P + c_2 P^2 + c_3 P^3 + c_4 P^4 + ... - PE$$



- Two possibilities:

Pz   4mm dimension 1
Pxy   2mm dimension 2

Subgroups of 4/mmm

Secondary order parameter

Let us call e the strain tensor

$$F(T,P,P_z,e_{zz}) = F(T,P,P_z) + \delta P_z^2 e_{zz} + \frac{1}{2} C_{33} e_{zz}^2$$

Minimization with respect to e_{zz} yields the equilibrium value:

$$e_{zz}^e = -\frac{\delta}{C_{33}} P_z^2$$

Magnetic energy

$$\vec{M} = \vec{\mu}_1 + \vec{\mu}_2 + \vec{\mu}_3 + \vec{\mu}_4$$
$$\vec{L}_1 = \vec{\mu}_1 + \vec{\mu}_2 - \vec{\mu}_3 - \vec{\mu}_4$$
$$\vec{L}_2 = \vec{\mu}_1 - \vec{\mu}_2 + \vec{\mu}_3 - \vec{\mu}_4$$
$$\vec{L}_3 = \vec{\mu}_1 - \vec{\mu}_2 - \vec{\mu}_3 + \vec{\mu}_4$$

Example 4 atoms in $Pca2_1$

Taking into account the transformation properties of the atoms by the symmetry operations of $Pca2_1$ 1' one can verify that the $\vec{M}$ and $\vec{L}_i$ vectors form a basis for the Γ_n corepresentations. Table IV shows the distribution of these vectors and of their components $M_u, L_{iu}, (u = x, y, z)$ among the Γ_n. The Table allows building the Landau free-energy, separating the exchange energy from the magnetic anisotropy energy:

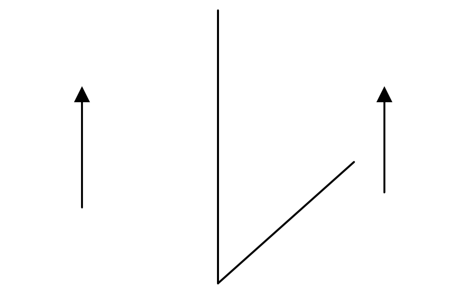
$$F(T, P, \vec{M}, \vec{L}_i, M_u, L_{iu}) = F_o(T, P) + \sum_i a_i L_i^2 + \sum_i b_i L_i^4 + cM^2 + dM^4$$

$$+ \sum_{i,u} \alpha_{iu} L_{iu}^2 + \sum_u \beta_u M_u^2 + \gamma_1 L_{1z} L_{2x} + \gamma_2 L_{1z} L_{3y} + \gamma_3 L_{2x} L_{3y} + \gamma_4 L_{2y} L_{3x} + \gamma_5 L_{1y} L_{3z}$$
$$+ \gamma_6 L_{1x} L_{2z} + \delta_1 M_z L_{2y} + \delta_2 M_z L_{3x} + \delta_3 M_x L_{1y} + \delta_4 M_x L_{3z} + \delta_5 M_y L_{1x} + \delta_6 M_y L_{2z}$$

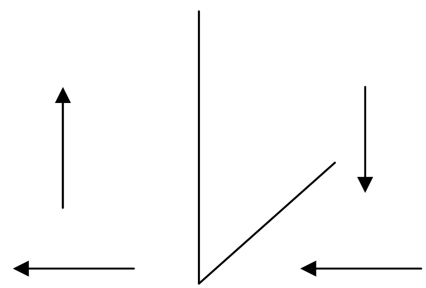
The first line represents the exchange energy truncated at the fourth degree and formed from the scalar products $\vec{L}_i.\vec{L}_i$ and $\vec{M}.\vec{M}$. The two following lines correspond to the magnetic anisotropy energy restricted to the second degree.

- This is rather complex, because spins don’t transform with the same symmetry operations than the “real” vectors,
- S x S is also different.

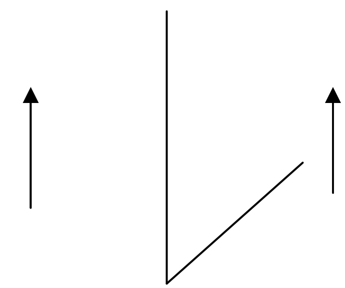
- One example: in a mirror



Real vector



Axial vector



S x S vector

In addition

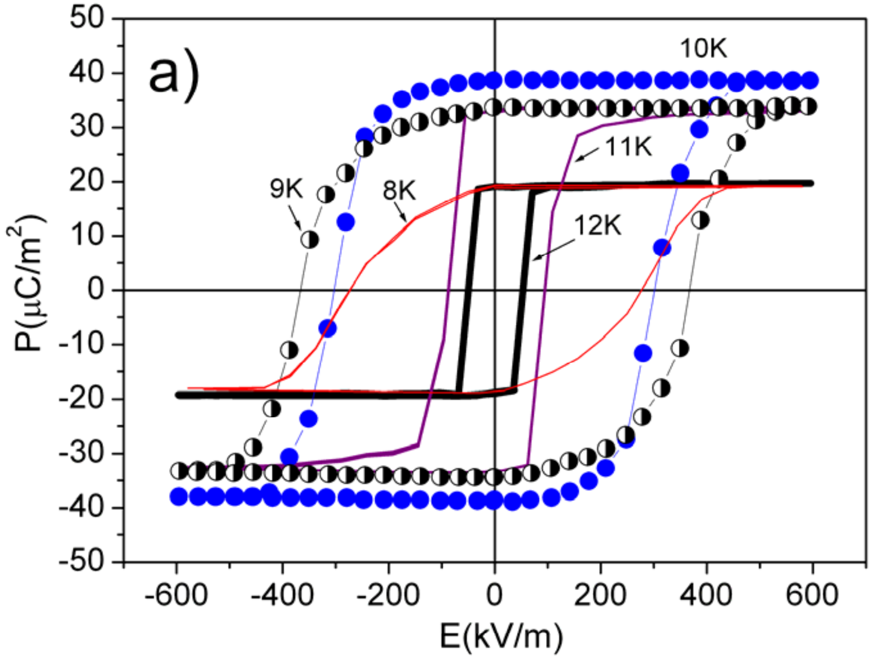
- Incommensurate modulations suppresses

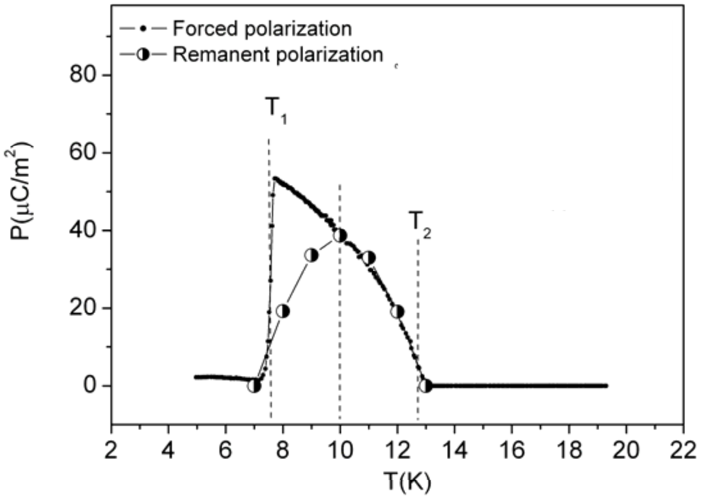
Symmetry elements.

I have no time to explain details

$MnWO_4$

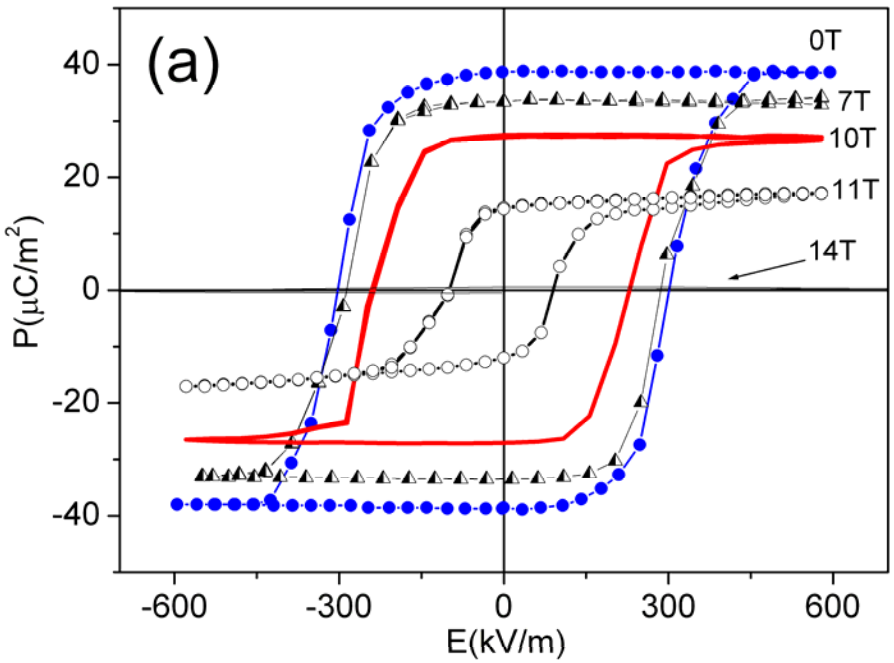
ferroelectric

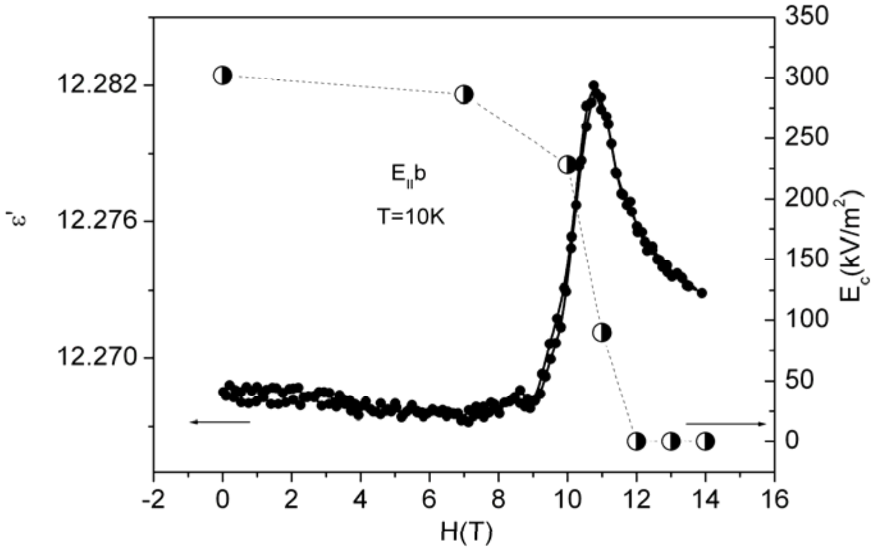




$MnWO_4$

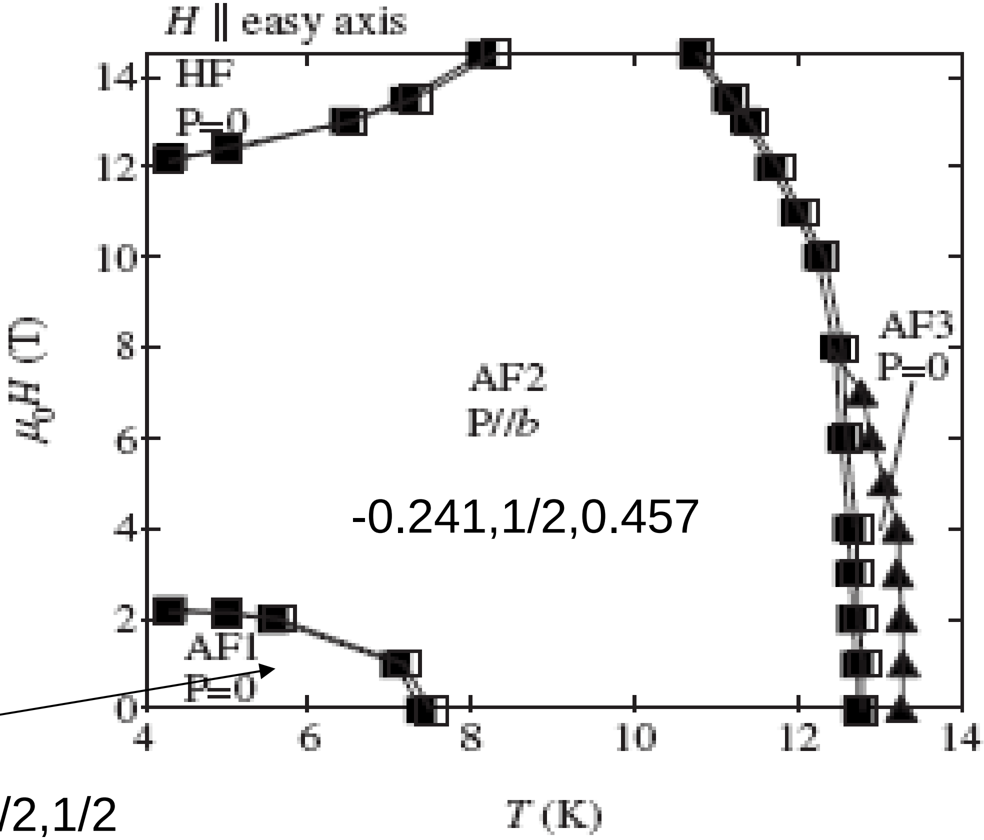
sensitive to magnetic field





AF1, AF2, AF3

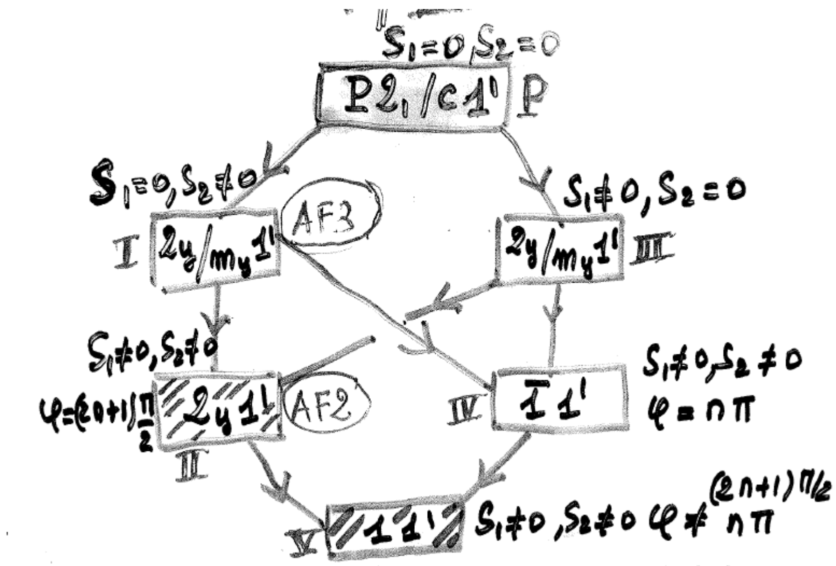
P along a

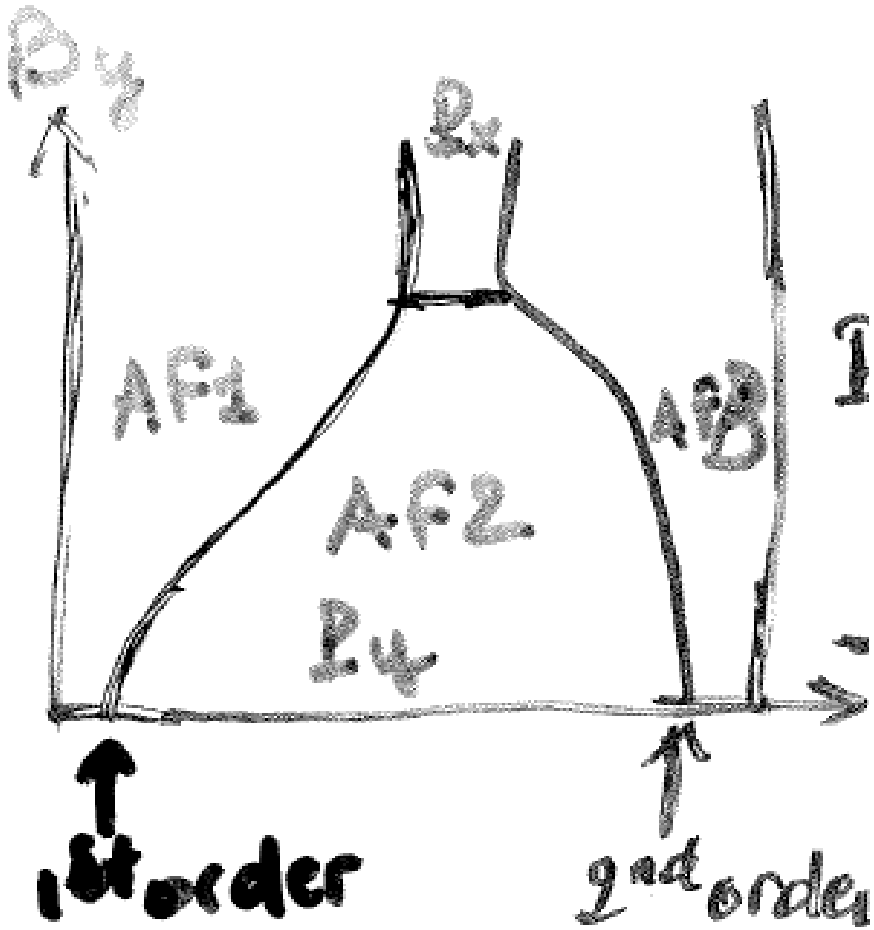


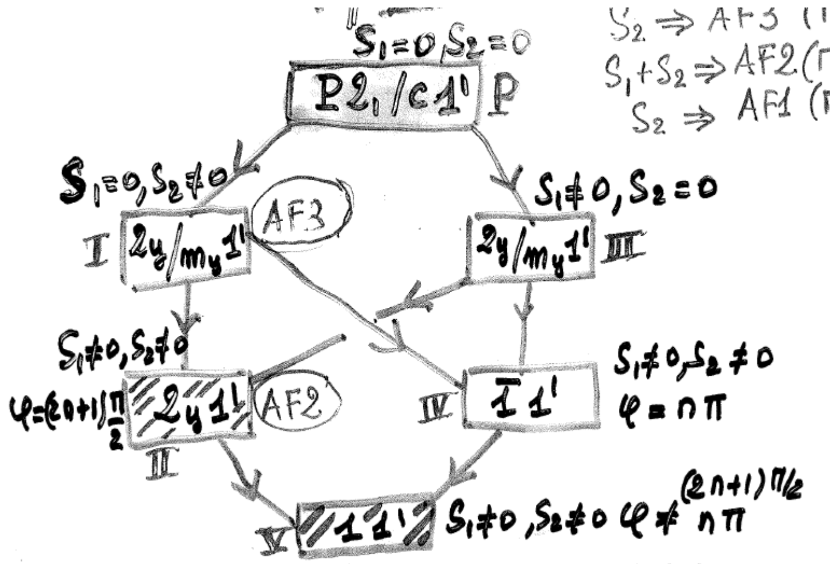
-0.241,1/2,0.457

Collinear 1/4,,1/2,1/2

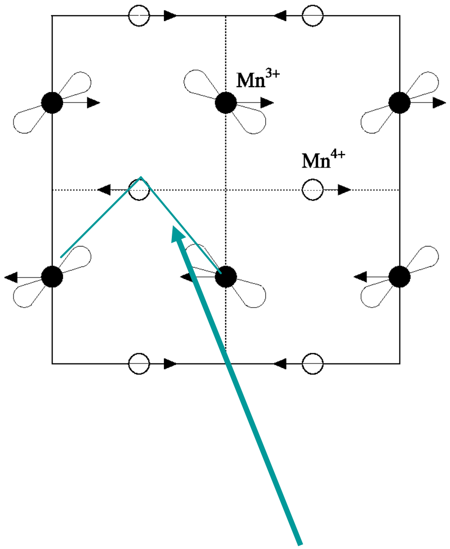
- The symmetry analysis was made by P. Toledano, and we find all the observed phases as possible sub groups



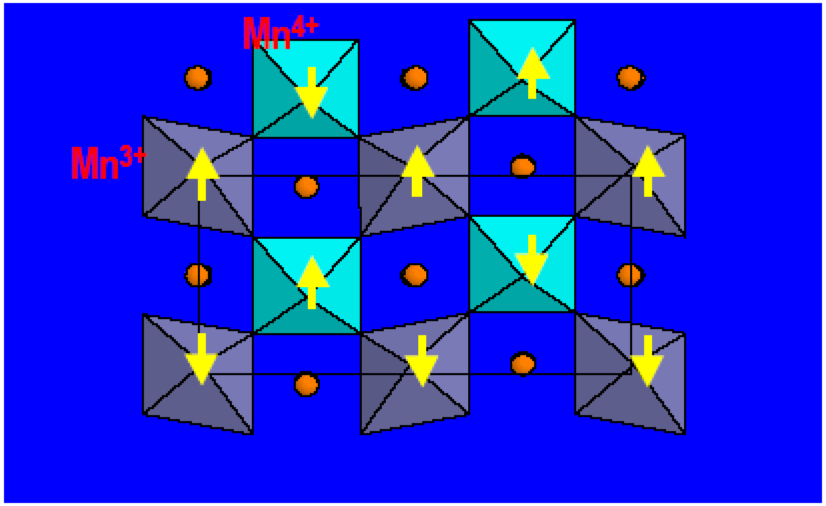

AF1
AF2
1st order
2nd order

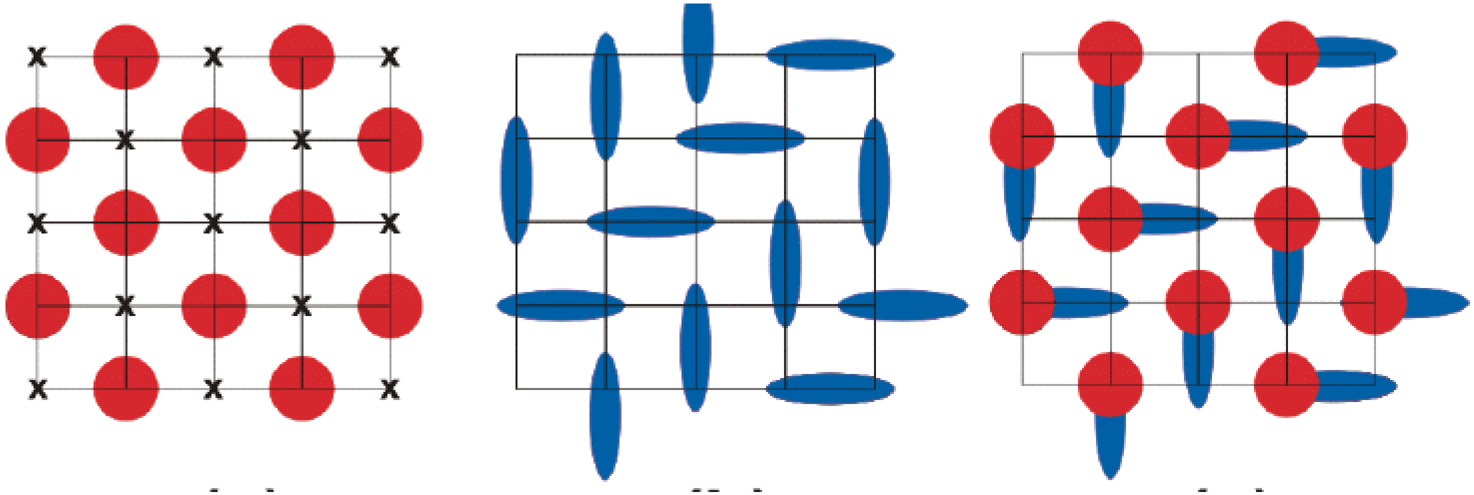

S1=0,S2=0
P21/c1'
S1=0,S2≠0
S1≠0,S2=0
2y/my1'
AF3
AF2
I1'
1 1'

$Pr_{1/2}Ca_{1/2}MnO_3$
CE type



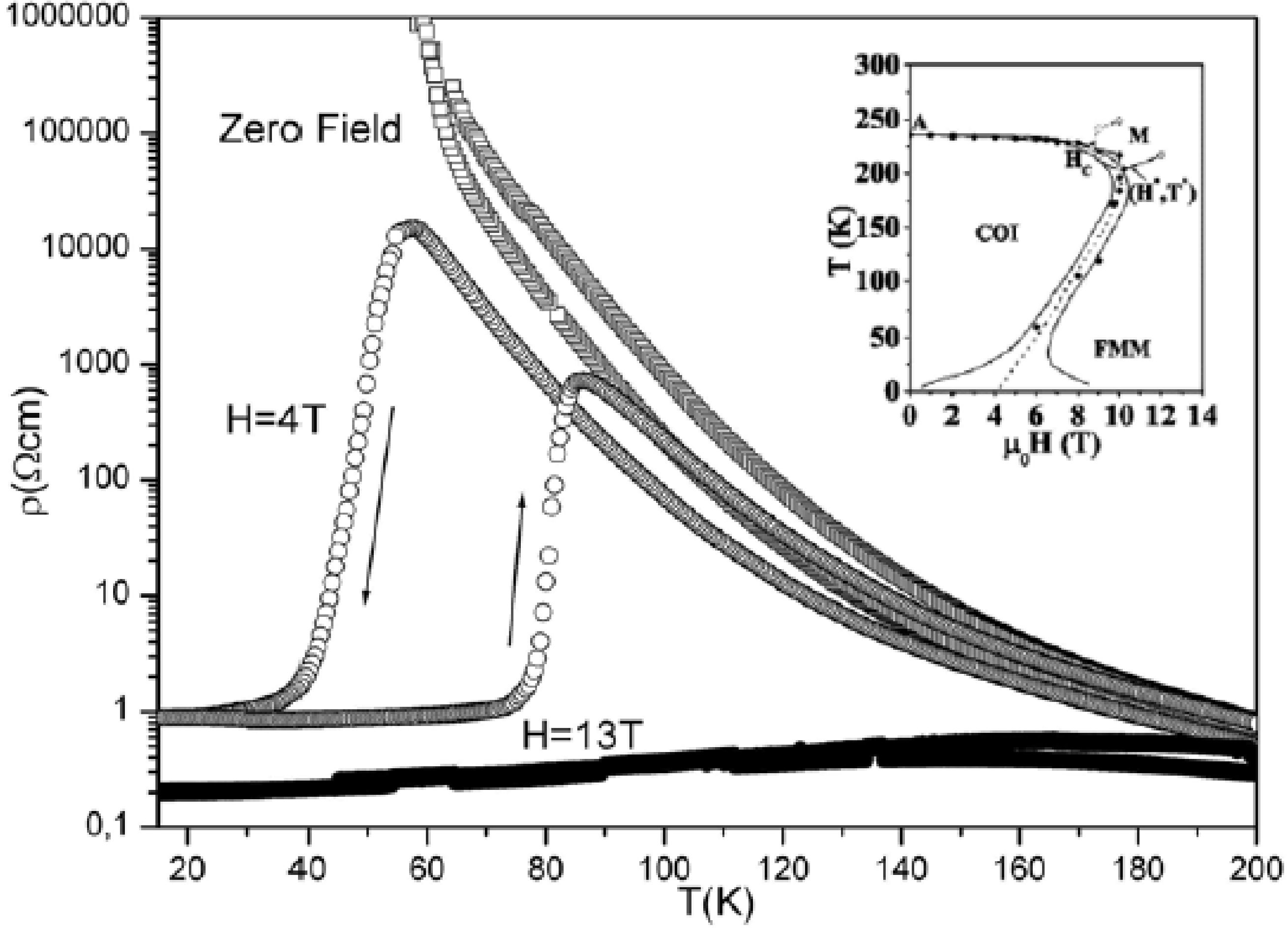
Ferromagnetic coupling

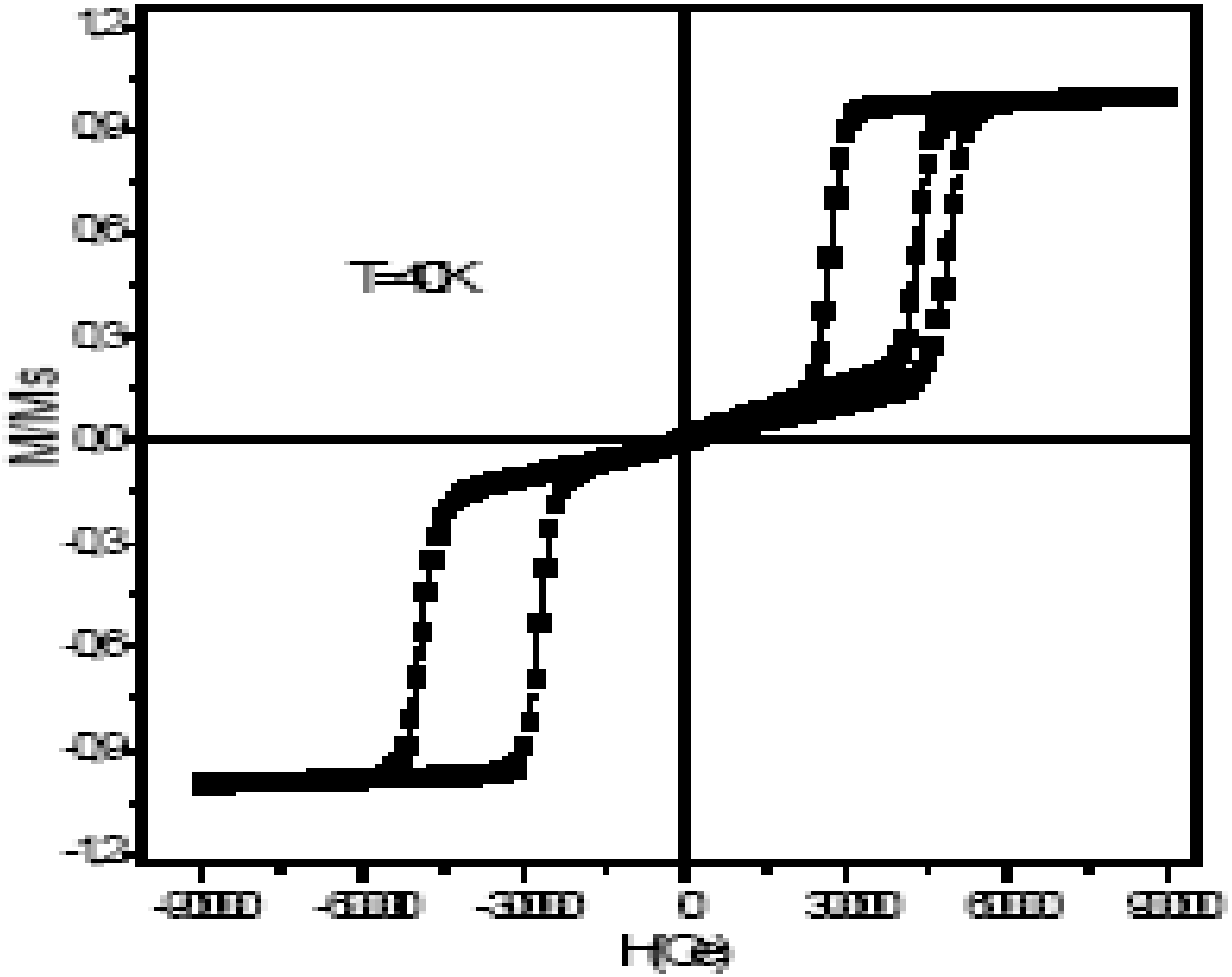




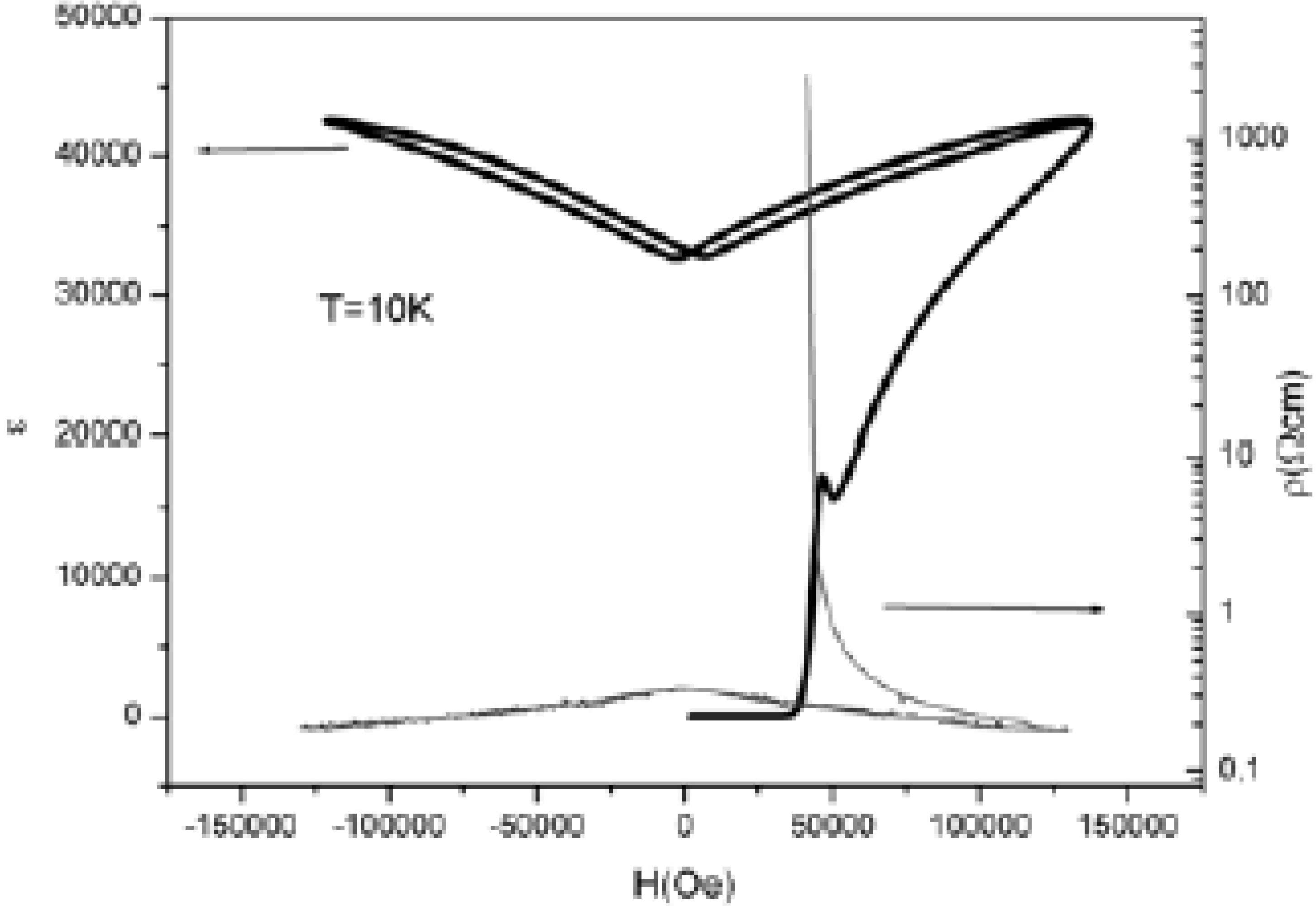
No centrosymmetry

From Khomskii et al.

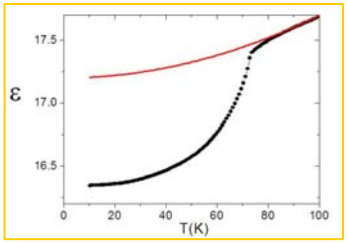

Zero Field
H=4T
H=13T
ρ(Ωcm)
T(K)
1000000
100000
10000
1000
100
10
1
0,1
20
40
60
80
100
120
140
160
180
200
T (K)
μ0H (T)
COI
FMM
A
M
Hc
(H*,T*)


1.2
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
-1.2
M/Ms
-9000
-6000
-3000
0
3000
6000
9000
H(Oe)

No ferroelectricity

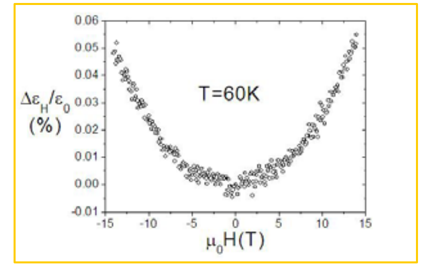


$YMnO_3$ - Landau



$$\varepsilon = \varepsilon_0 + c_1 T^2 - c_2 L^2(T) + c_3 H^2$$

~20 ~1 ~10^{-4}



Free energy :

$$F = F_0 + F_{AFM} + F_{FE} + F_{coupl} =$$

$$= F_0 + a\frac{L^2}{2} + b\frac{L^4}{4} + cL^2H^2 + \alpha\frac{P^2}{2} - EP + \frac{g}{2}P^2L^2 + \frac{\gamma}{2}P^2H^2$$

Minimization :

$$\frac{\partial F}{\partial P} = 0 \Rightarrow \alpha P - E + gPL^2 + \gamma PH^2 = 0$$

$$P = \frac{1}{\alpha + gL^2 + \gamma H^2} E$$

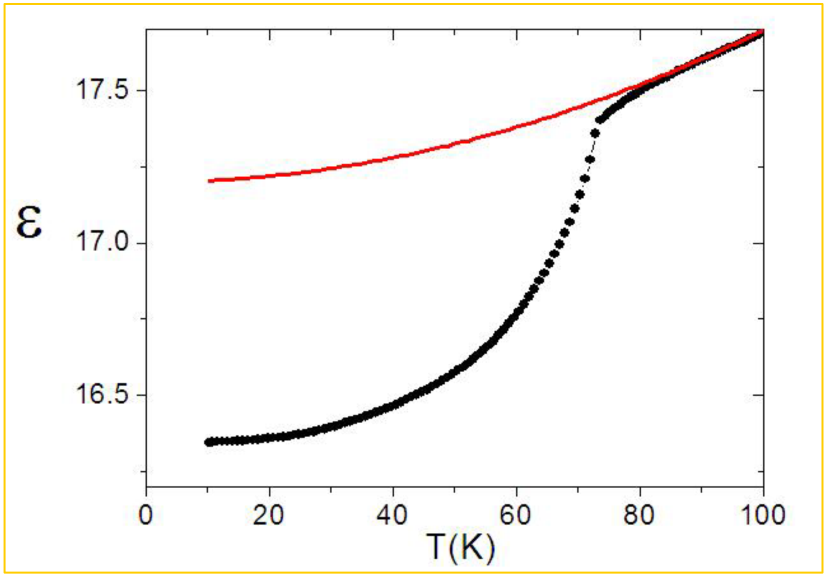
Electric susceptibility

$\chi = \varepsilon - 1$

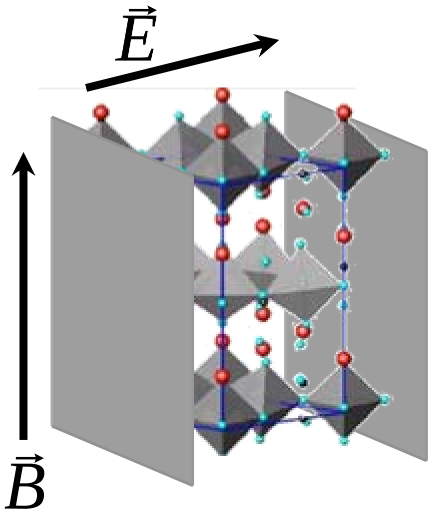
$YMnO_3$ – Anomaly in ε(T)

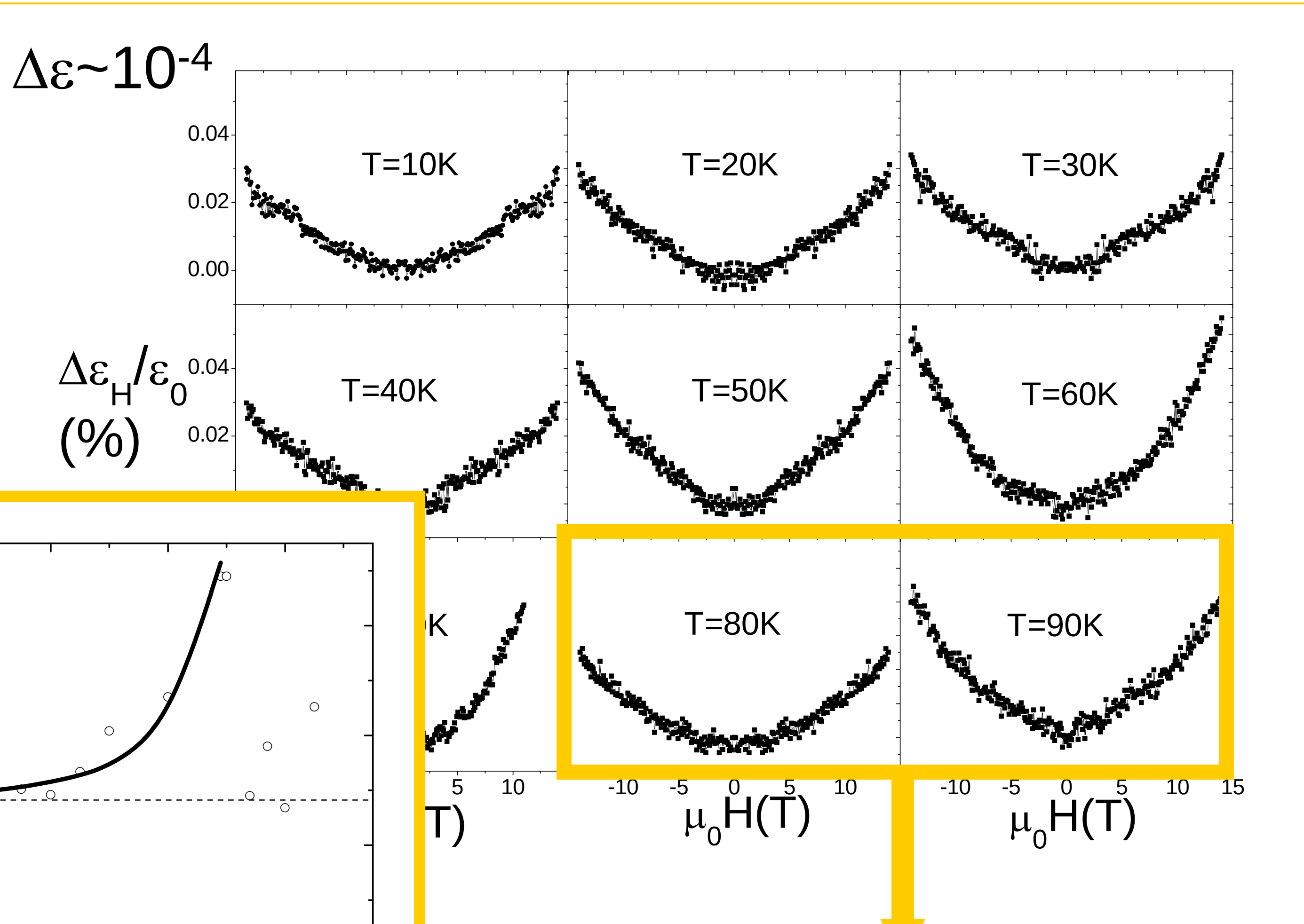
$$\chi = \frac{1}{\alpha + gL^2 + \gamma H^2}$$

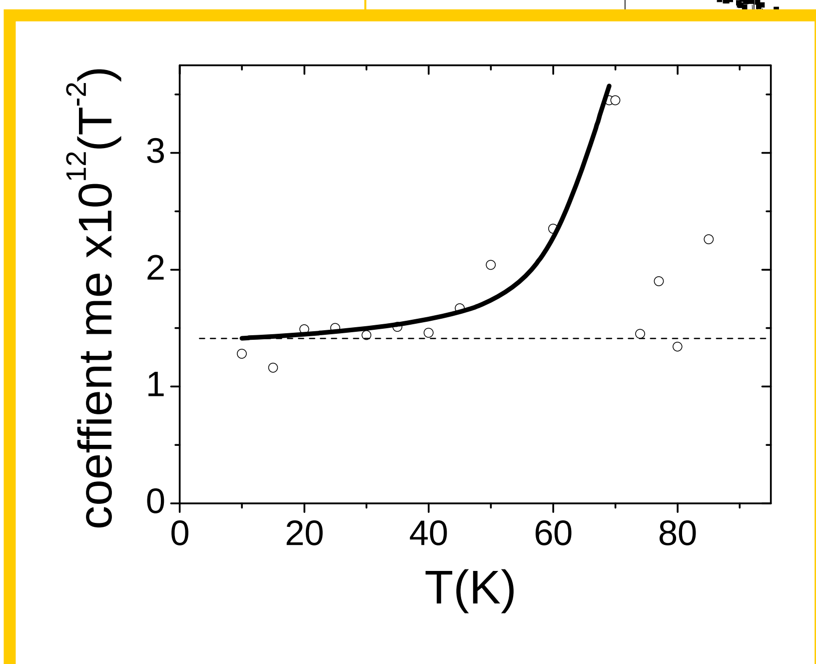
$$\Delta\varepsilon(T) = \varepsilon(H=0, L) - \varepsilon(H=0, L=0) = \frac{1}{\alpha + gL^2} - \frac{1}{\alpha} \approx -\frac{gL^2}{\alpha^2}$$



$YMnO_3$ – ε(H)



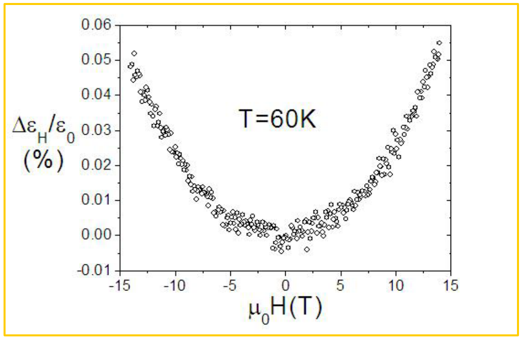




Paramagnet

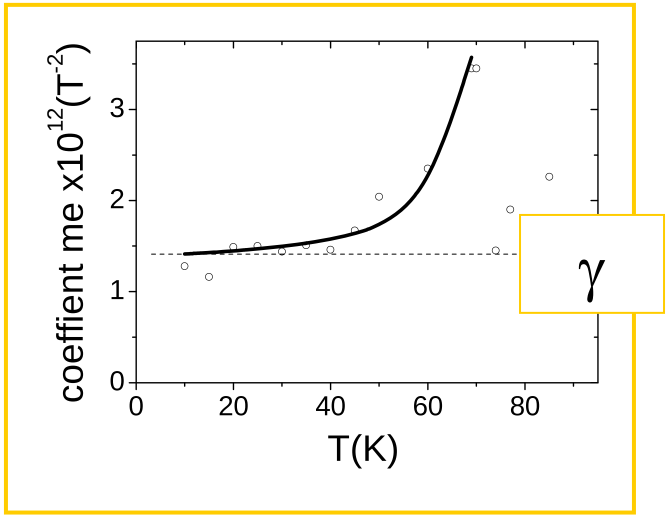
$YMnO_3$ –magnétodiélectric effect ε(H) in H^2

$$\chi = \frac{1}{\alpha + gL^2 + \gamma H^2}$$



$$\Delta\varepsilon(H) = \varepsilon(H, L) - \varepsilon(H=0, L) =$$

$$= \frac{1}{\alpha + gL^2 + \gamma H^2} - \frac{1}{\alpha + gL^2} \approx -\frac{\gamma H^2}{\alpha^2}$$



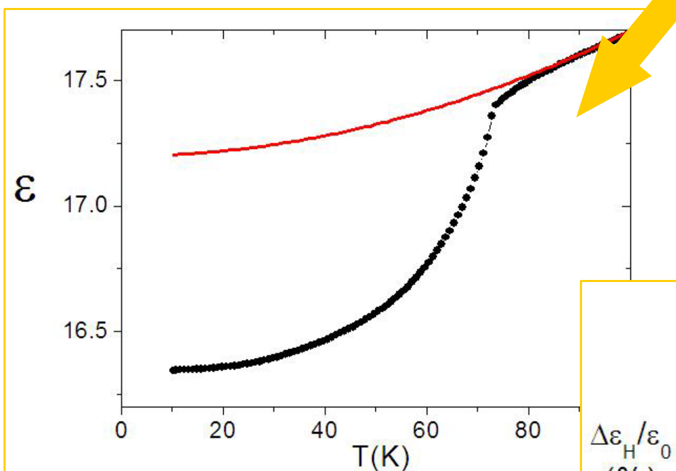
$$\Delta\varepsilon(H) \approx -\frac{\gamma H^2}{\alpha^2}\left(1 - 2\frac{gL^2}{\alpha}\right)$$

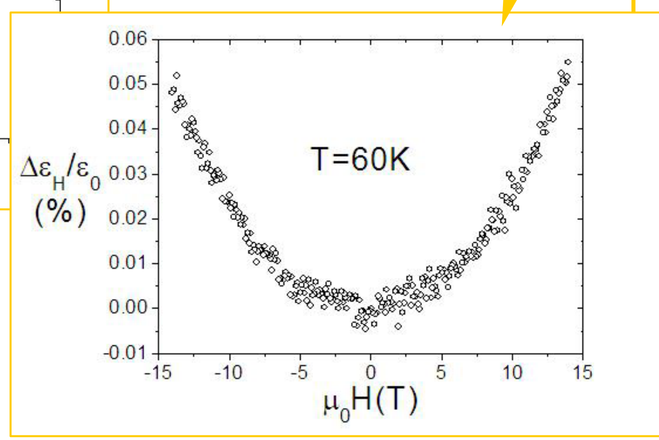
$$L^2 = \langle L \rangle^2 + \left(L^2 - \langle L^2 \rangle\right)$$

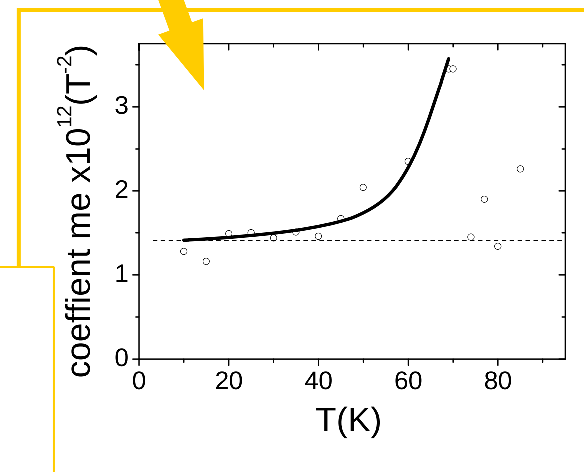
fluctuations~χ_L

$YMnO_3$ constante diélectrique

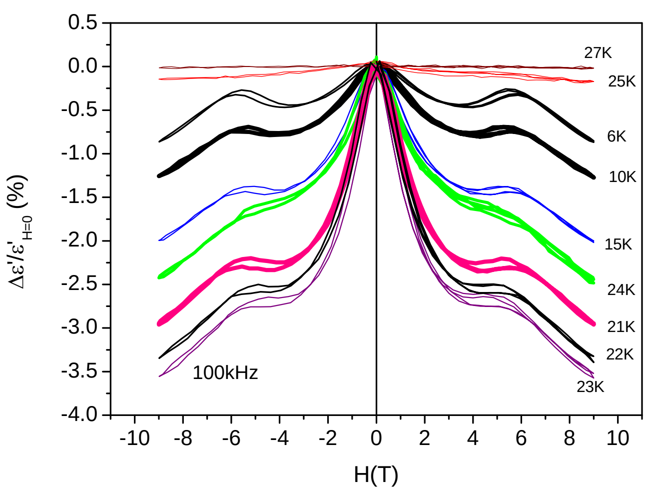
$$\varepsilon = \varepsilon_0 + c_1 T^2 - \frac{g}{\alpha^2} L^2 - \frac{\gamma}{\alpha^2} H^2 \left(1 + \frac{\lambda}{T - T_N} \right)$$



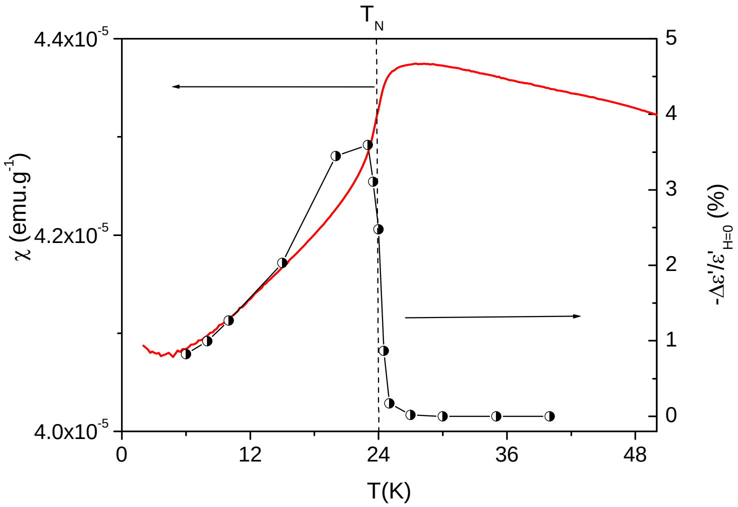




$CuCrO_2$



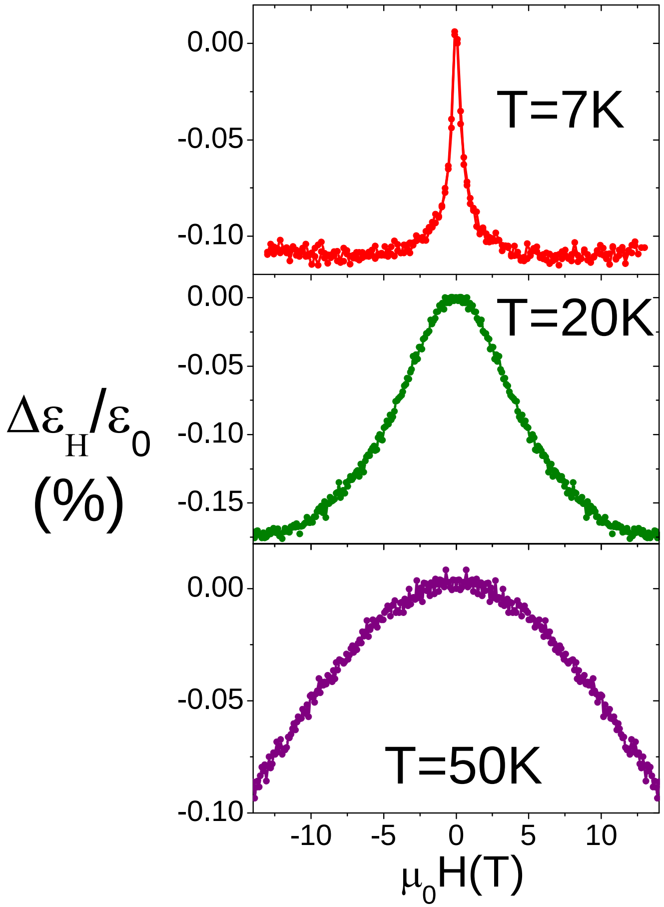
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
-4.0
Δε'/ε'H=0 (%)
-10 -8 -6 -4 -2 0 2 4 6 8 10
H(T)
27K
25K
6K
10K
15K
24K
21K
22K
23K
100kHz

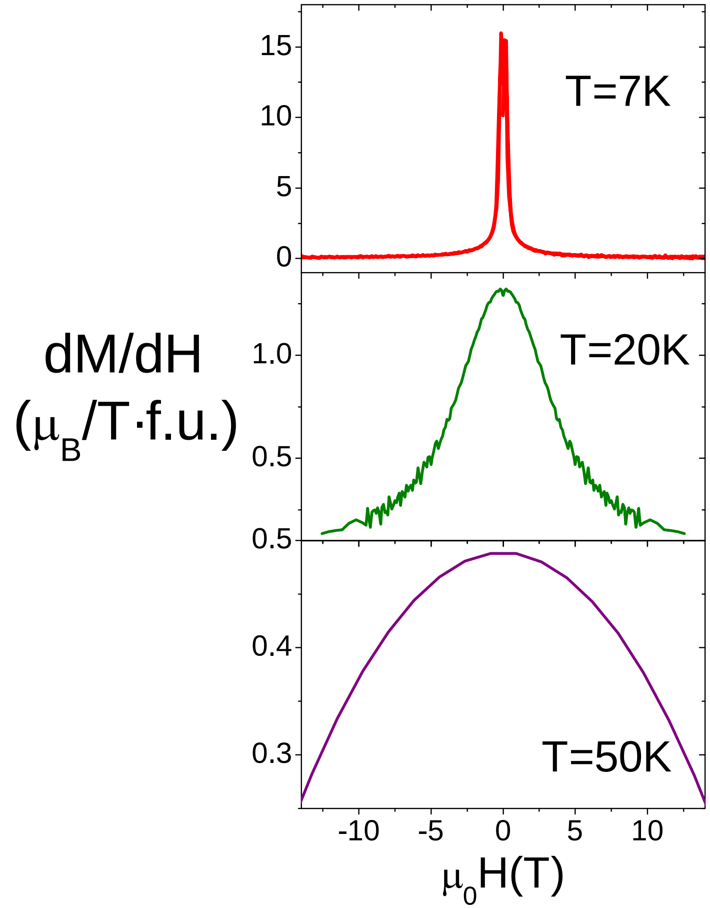


T_N
4.4x10^-5
4.2x10^-5
4.0x10^-5
χ (emu.g^-1)
0 12 24 36 48
T(K)
5
4
3
2
1
0
-Δε'/ε'H=0 (%)

$Co_3V_2O_8$

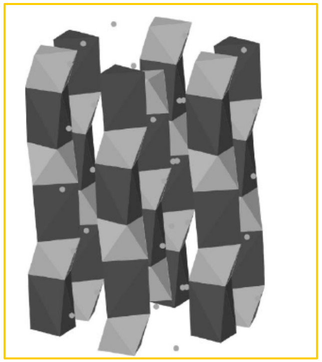
$\Delta\varepsilon \sim \chi$





$Ca_3Co_2O_6$ – magnetization plateaux

R-3cm

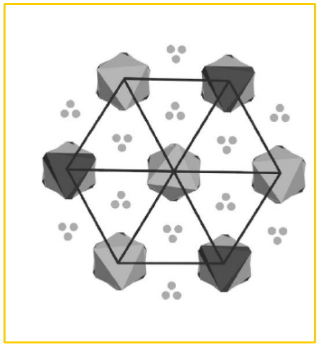


Polyhèdra CoO_6 :

triangular prism *S=2*

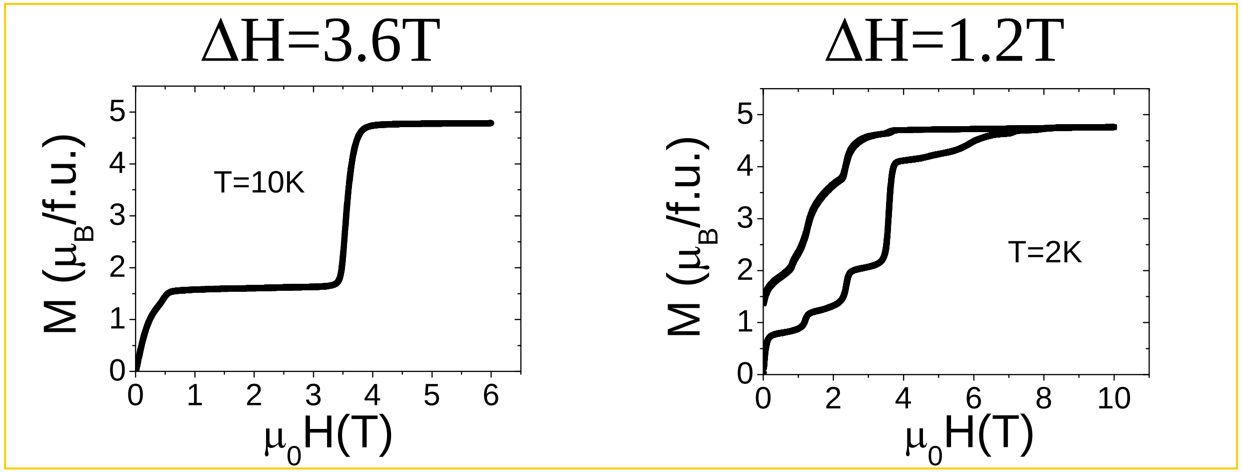
octahedra *S= 0*

Ferromagnet intrachain interac.

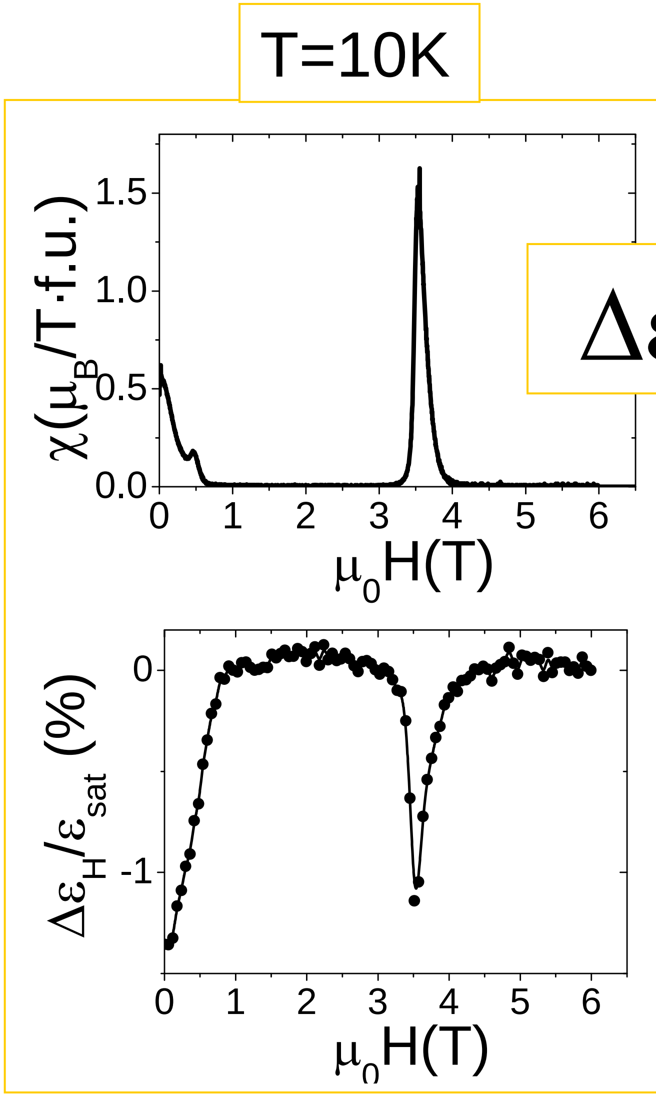


Triangular ising lattice

Antiferromagnetic interchain (T_N=24K)



$Ca_3Co_2O_6$

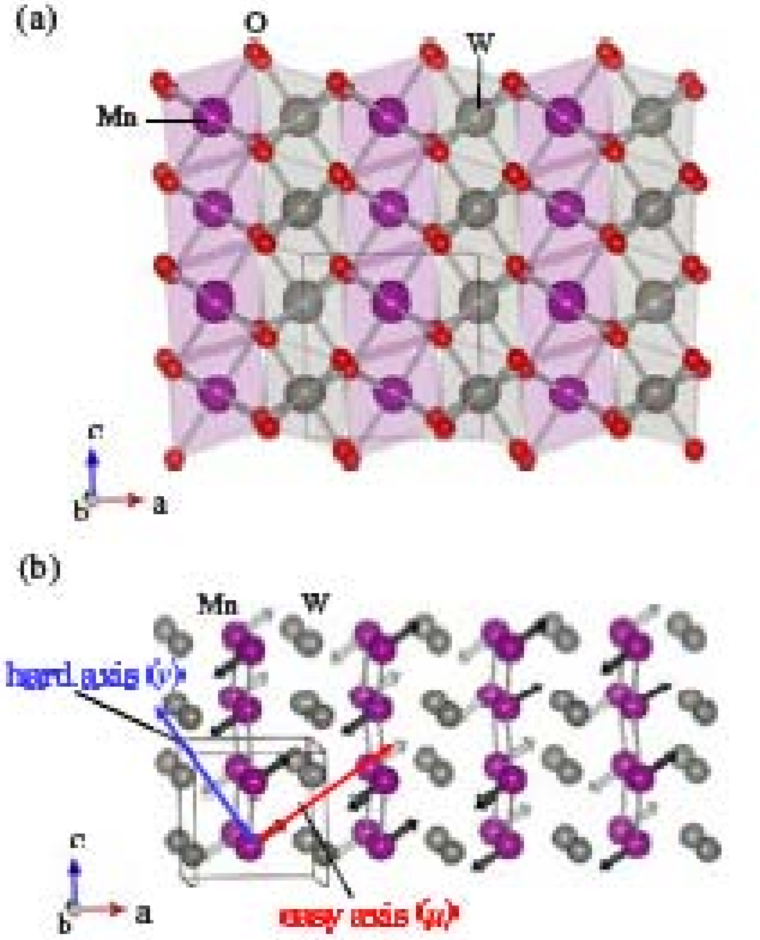


$\Delta\varepsilon \sim -\chi$

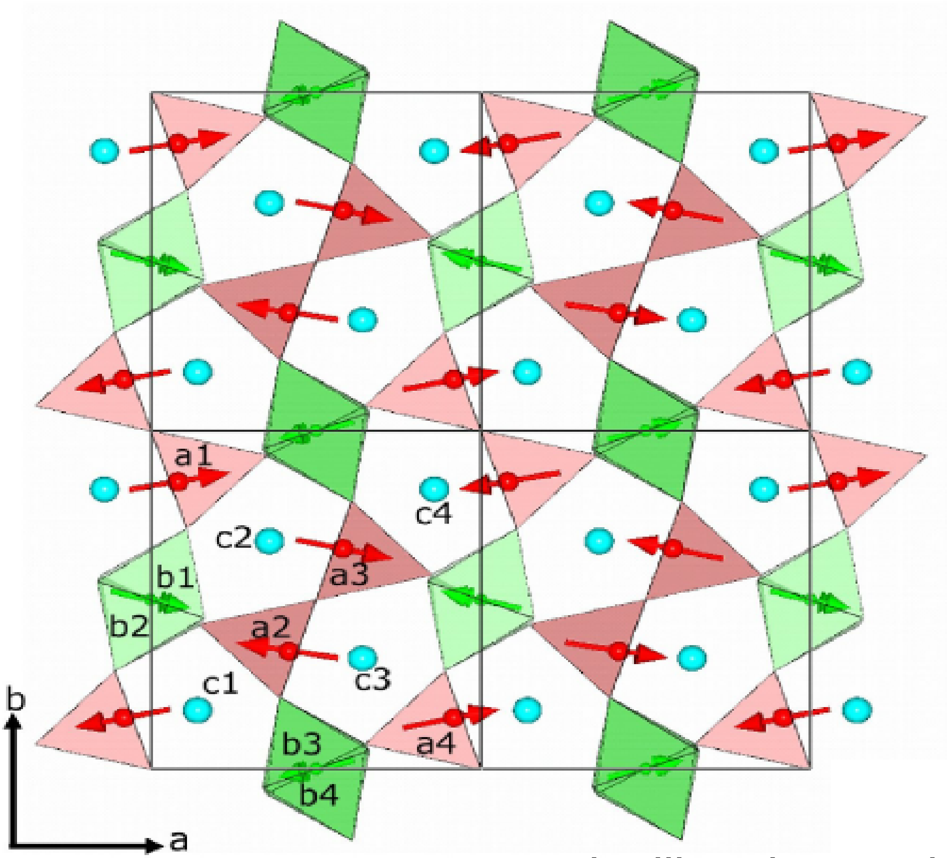
No polarization

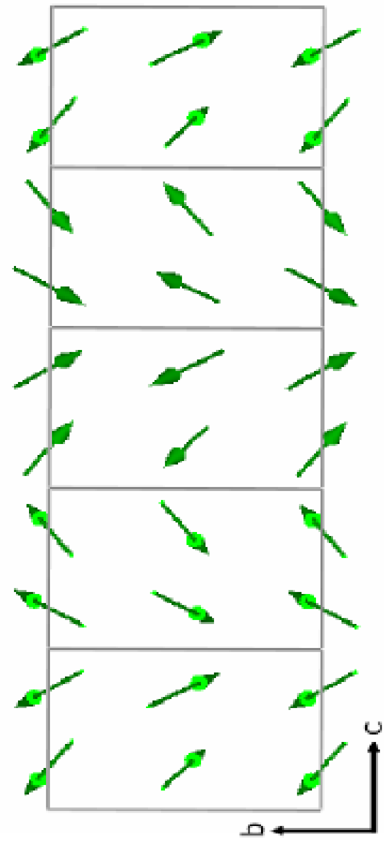
$MnWO_4$

A nice example

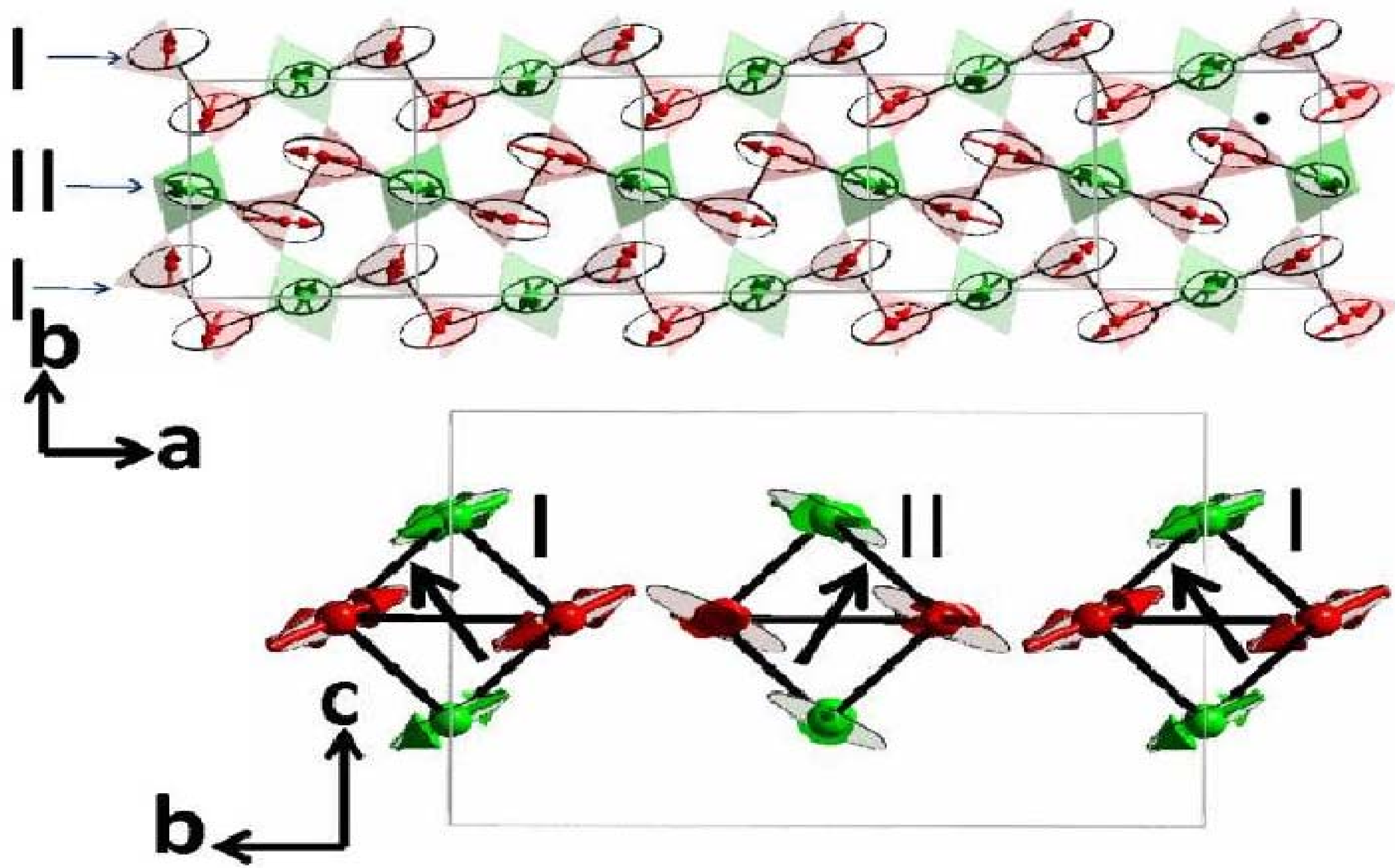


YMn_2O_5





P.G. Radaelli and L.C. Chapon, PRB, 76054428(2007)



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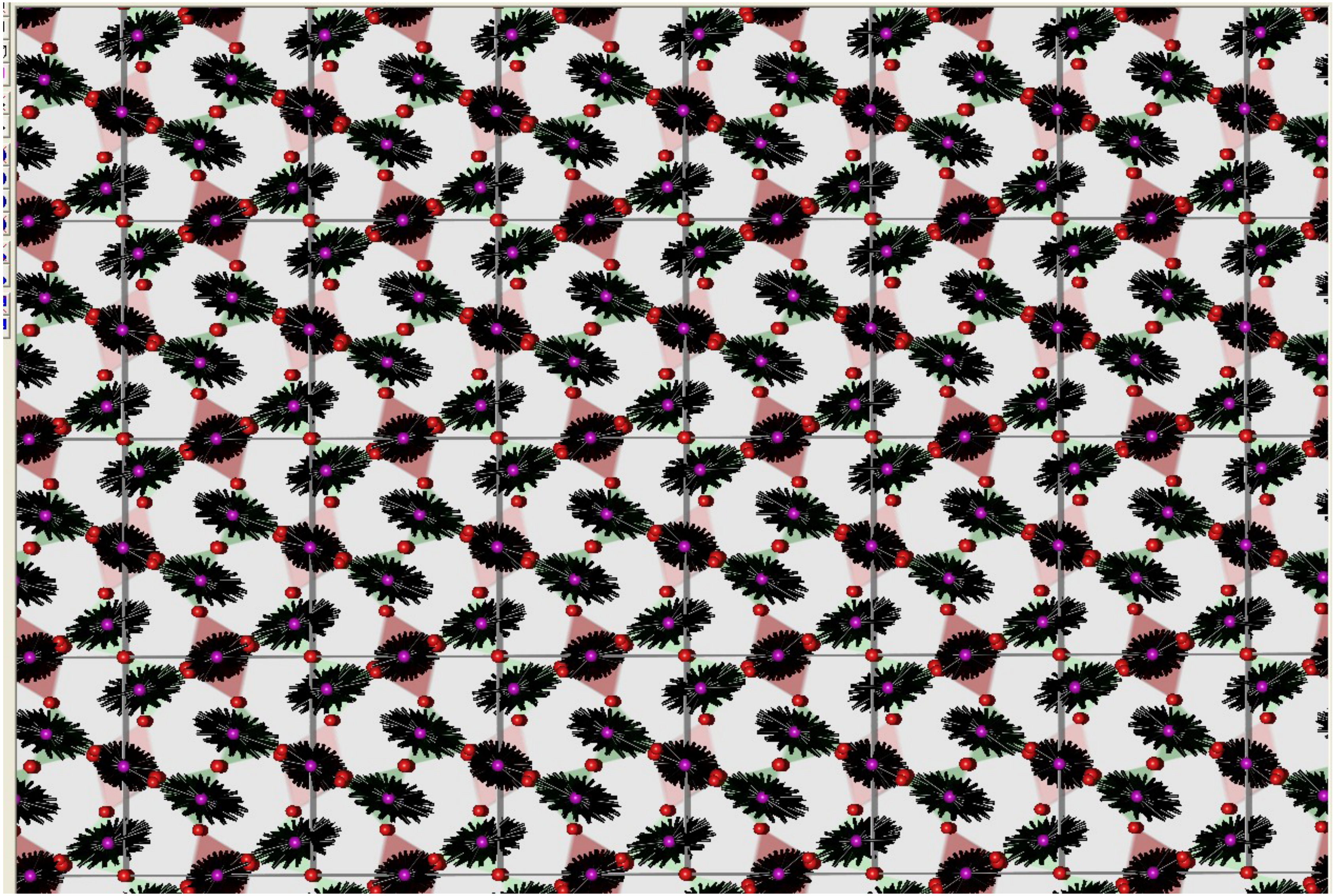

Conclusion

- Spin orbit coupling is necessary to create coupling between ferromagnetism and ferroelectricity
- Incommensurability is very useful to help with symmetry
- There is no ab initio calculation of the intensity of the coupling
- There is more to understand in the coupling terms
- Magnetic group theory is needed.