Joint French-Swedish school on X-rays and Neutrons techniques for the study of functional materials for energy

13-17 May 2019 Lund (Sweden)

Multiferroïcs, Magnetoelectrics

…. with a symmetry zest and a neutron scattering slice

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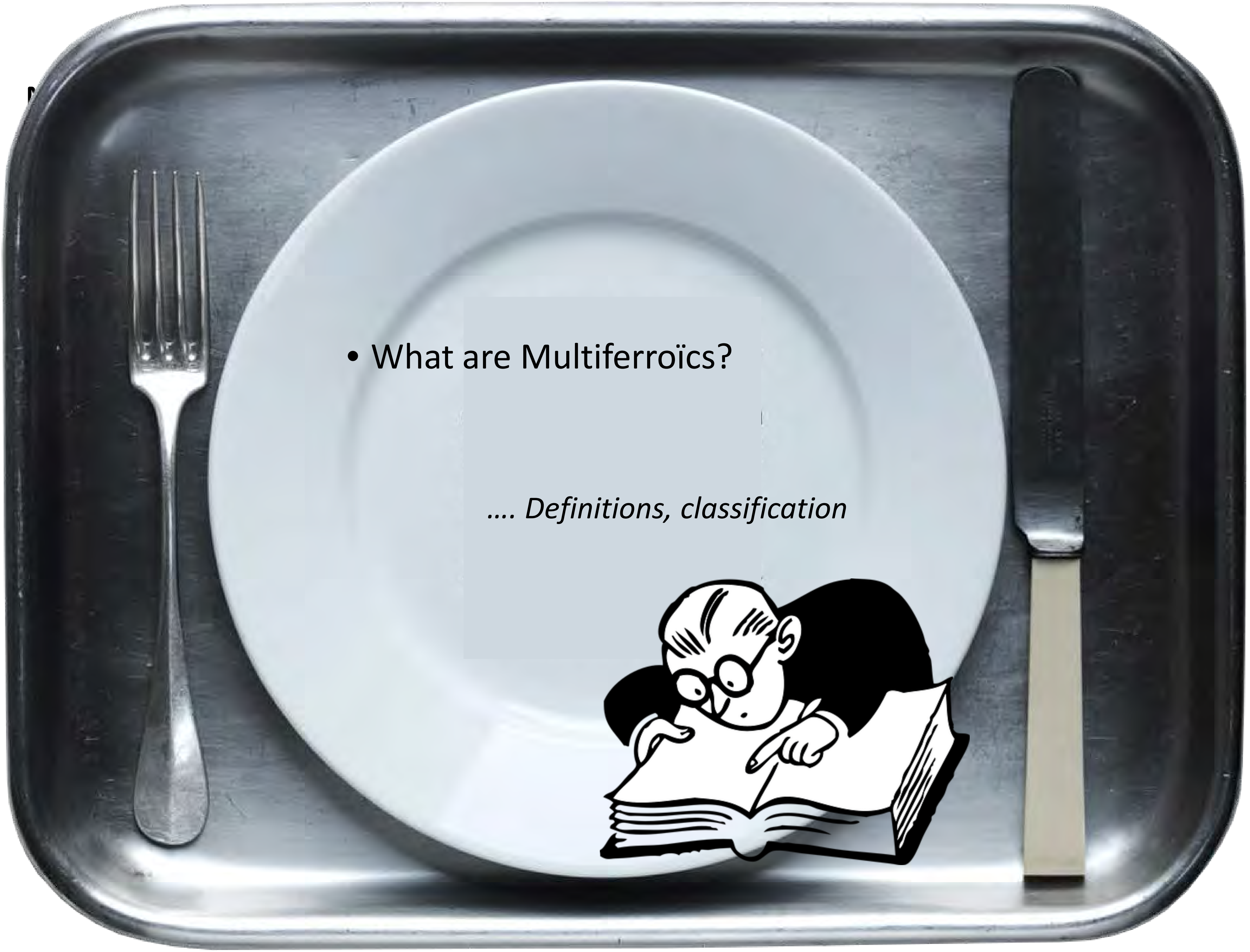
- What are Multiferroïcs?
- Motivations
- How to design multiferroïcs?
- Role of symmetry
- Examples



- What are Multiferroïcs?

…. Definitions, classification

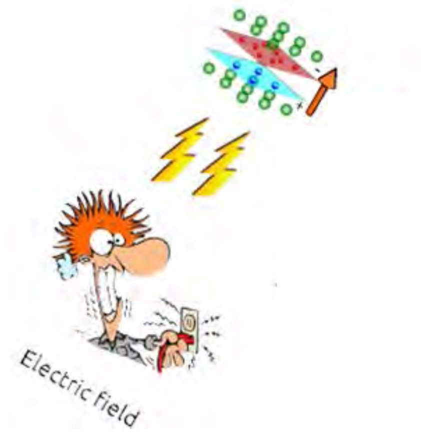
Ferroïcs

Picture from http://www.lpem.espci.fr/ocg/

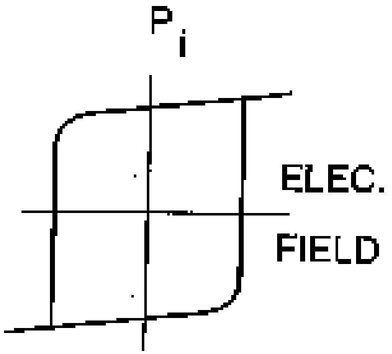
“Materials that show switchable properties under an external stimulus”

Aizu, K. (1970). Phys. Rev. B, ***2****, 754–772*

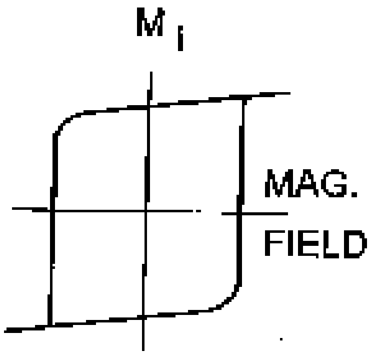
polarization



magnetization



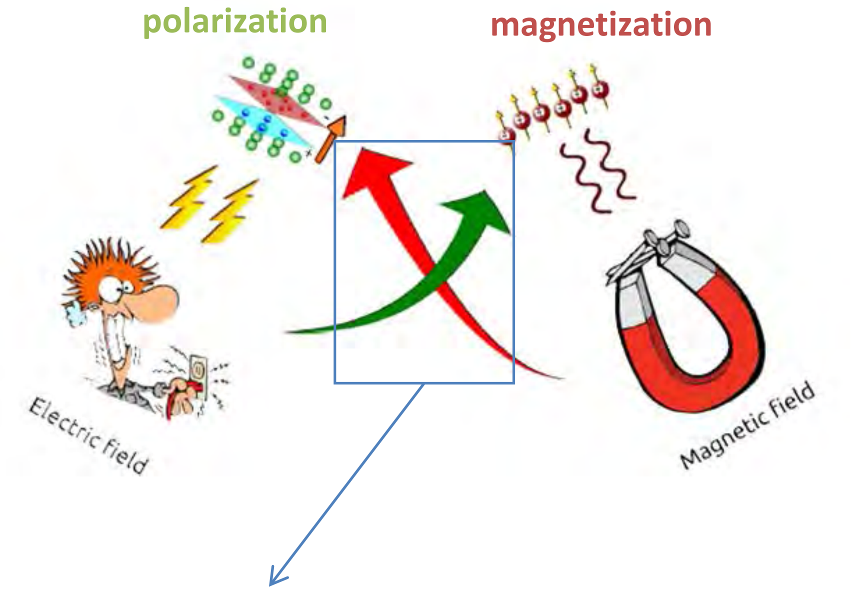
FERROELECTRIC



FERROMAGNETIC

Magnetoelectrics

Picture from http://www.lpem.espci.fr/ocg/



C'est la dissymétrie qui crée le phénomène (P. Curie, 1894)

Linear Magneto-Electric (ME) effect

Control of the Polarization by a Magnetic Field

$$P_i = \alpha_{ij} H_j$$

Control of Magnetization by an Electric Field

$$M_i = \alpha_{ij} E_j$$

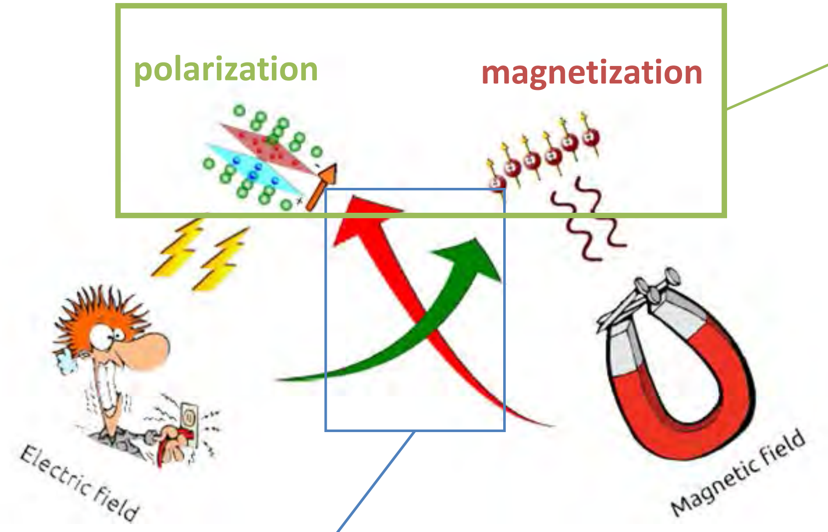
where α_{ij} is the ME tensor

Landau et Lifshitz (1957), Rado (1961)

Symmetry restriction: break of space inversion and time reversal

Magnetoelectrics vs Multiferroïcs

Picture from http://www.lpem.espci.fr/ocg/



Multiferroïcs

Magnetic and electric orders combined in the same phase.

Type I

Magnetism and ferroelectricity have different origin

Linear Magneto-electric (ME) effect

Control of the Polarization by a Magnetic Field

$$P_i = \alpha_{ij} H_j$$

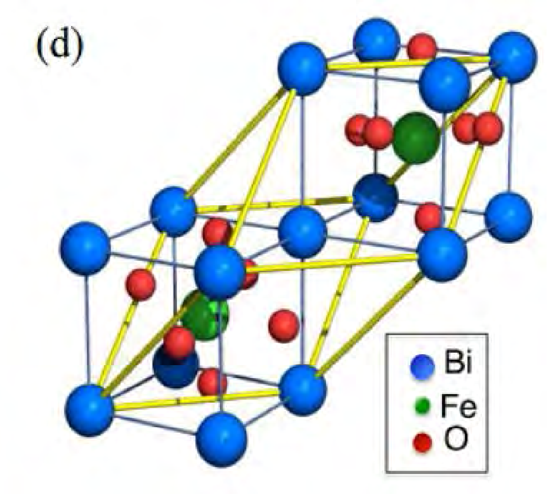
Control of Magnetization by an Electric Field

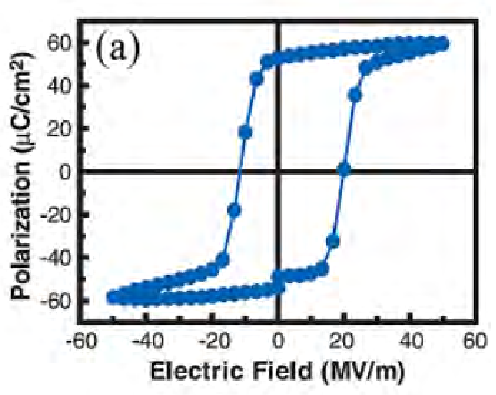
$$M_i = \alpha_{ij} E_j$$

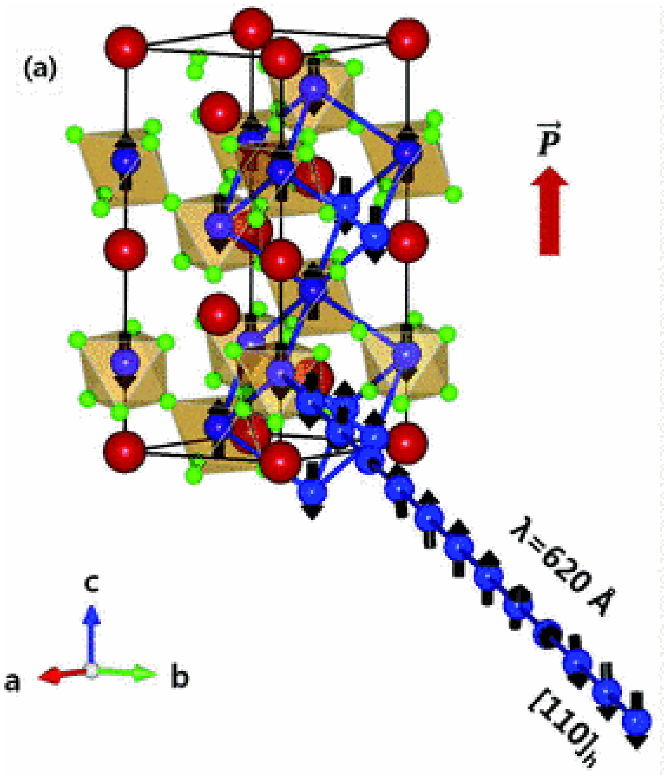
where α_{ij} is the ME tensor

Landau et Lifshitz (1957), Rado (1961)

The Type I star: $BiFeO_3$







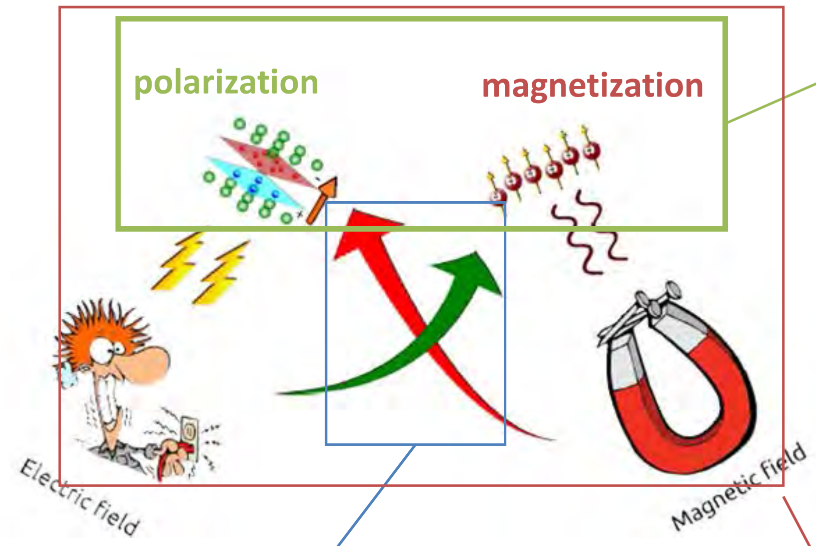
Sanghyun Lee et al Phys. Rev. B 88, 060103 (2013)

T_C ~1103 K, polar: R3c, P=*80μC.cm*$^{-2}$

T_N=653 K, G-type antiferromagnetic alignment plus the spiral spin canting

→ *Large polarization but antiferromagnetic and ME coupling weak….*

Magnetoelectrics vs Multiferroïcs



Picture from http://www.lpem.espci.fr/ocg/

Multiferroïcs

Magnetic and electric orders combined in the same phase.

Type I

Magnetism and ferroelectricity have different origin
→ *Weak coupling*

Type II: Magnetoelectric Multiferroics

Magnetism induce ferroelectricity
→ *Strong coupling*

Linear Magneto-electric (ME) effect

Control of the Polarization by a Magnetic Field

$$P_i = \alpha_{ij} H_j$$

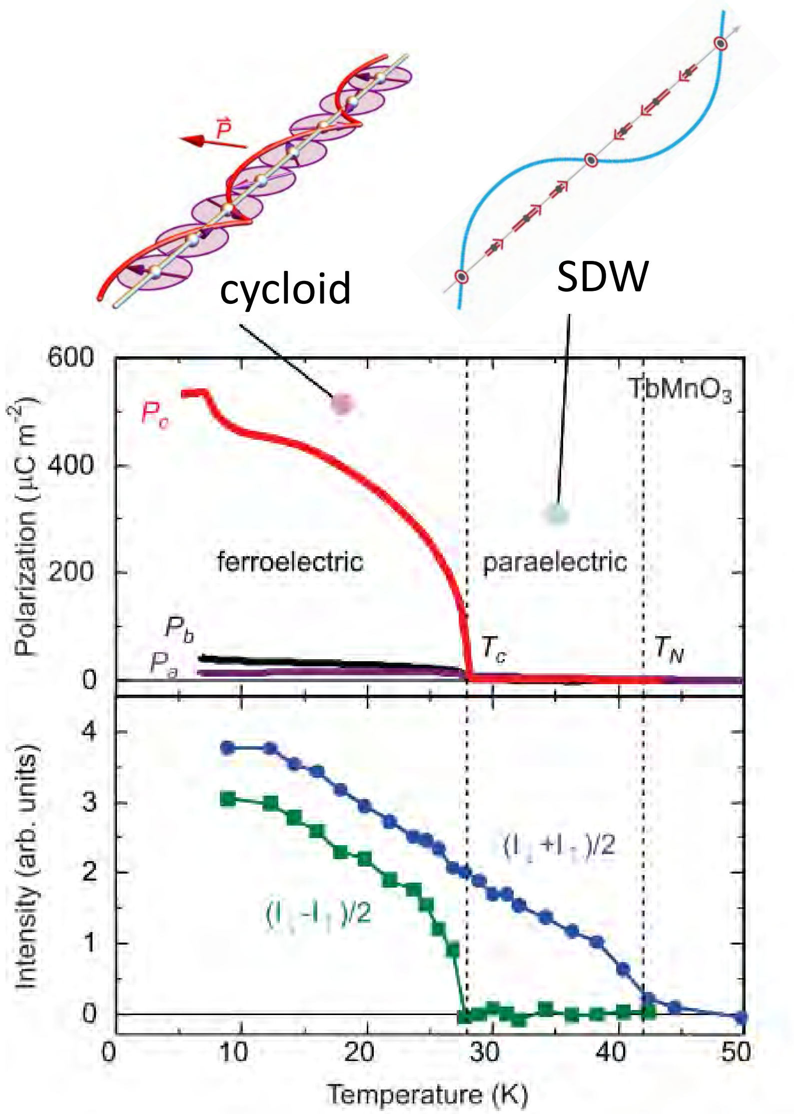
Control of Magnetization by an Electric Field

$$M_i = \alpha_{ij} E_j$$

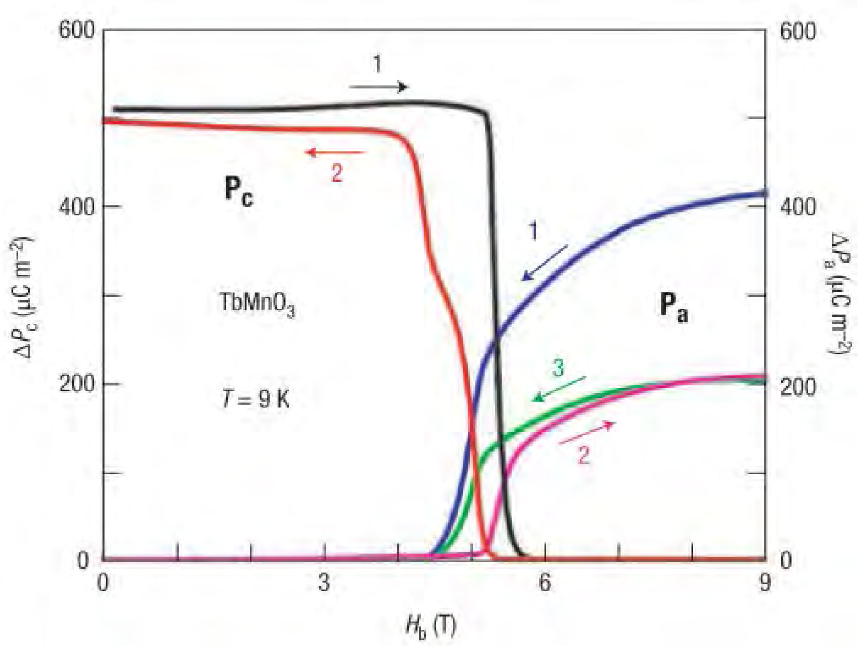
where α_{ij} is the ME tensor

Landau et Lifshitz (1957), Rado (1961)

Archetypal multiferroïc of spin origin: $TbMnO_3$



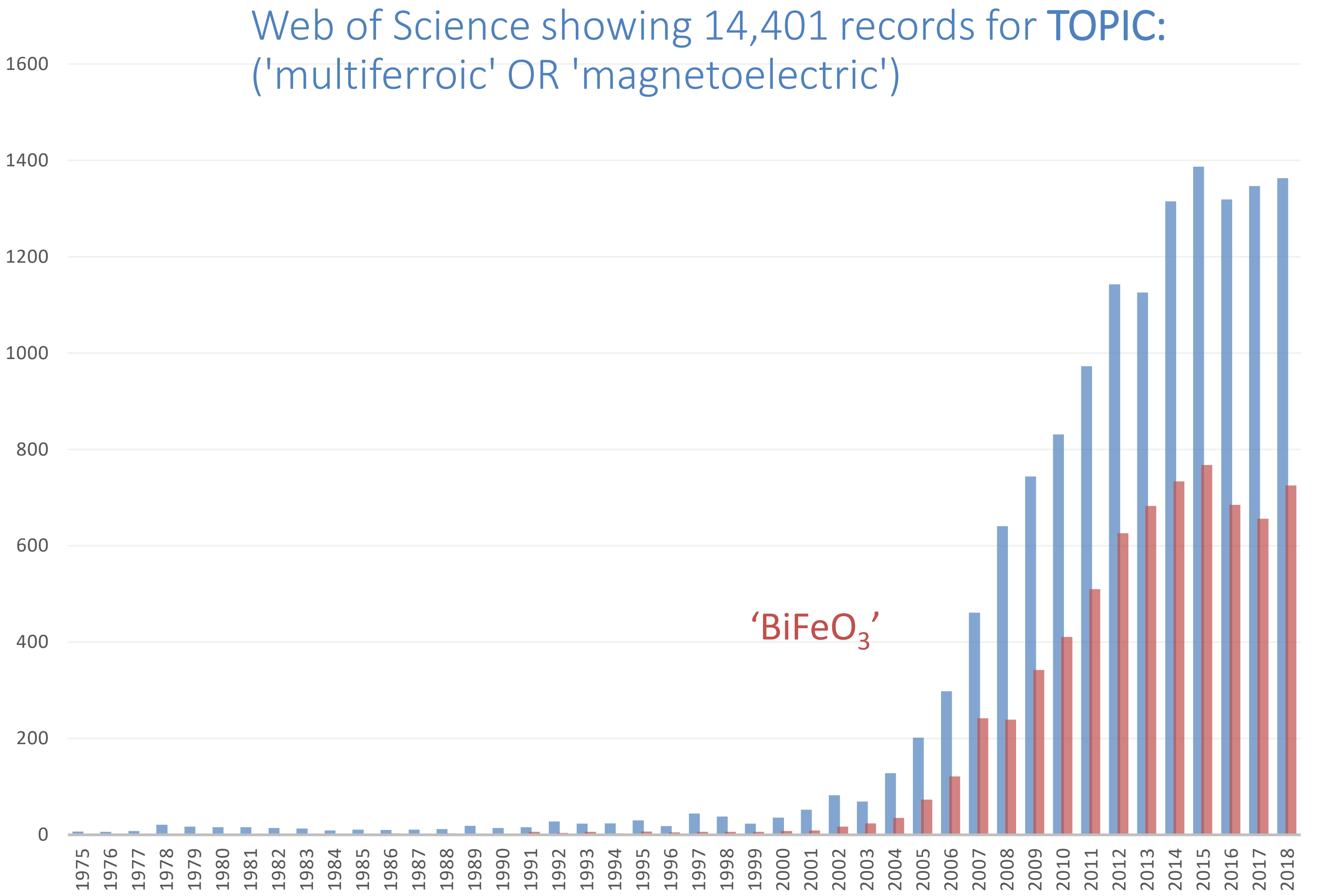
Weak ferroelectricity appears at the magnetic ordering transition (cycloid) $T_N=T_C=27K$



Strong coupling

- Motivations

Strong scientific interest



Two fold interest

Technological:

Application: density, speed, energy cost in devices

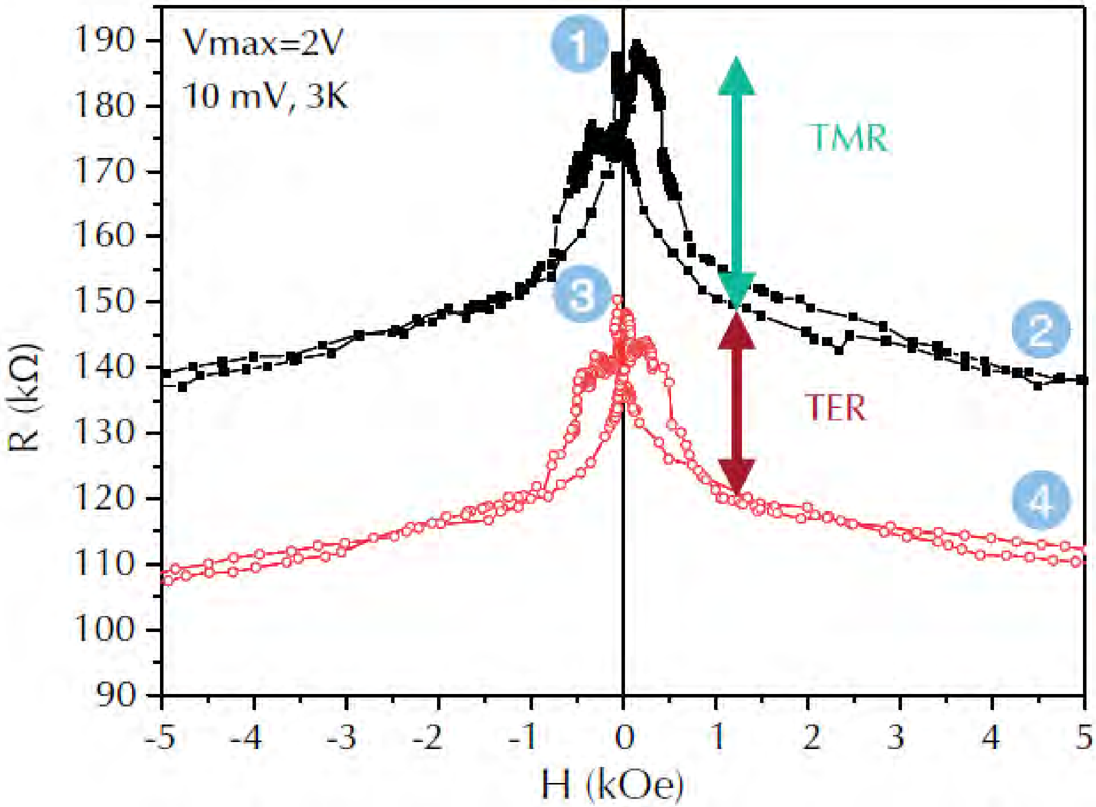
Two types of devices:

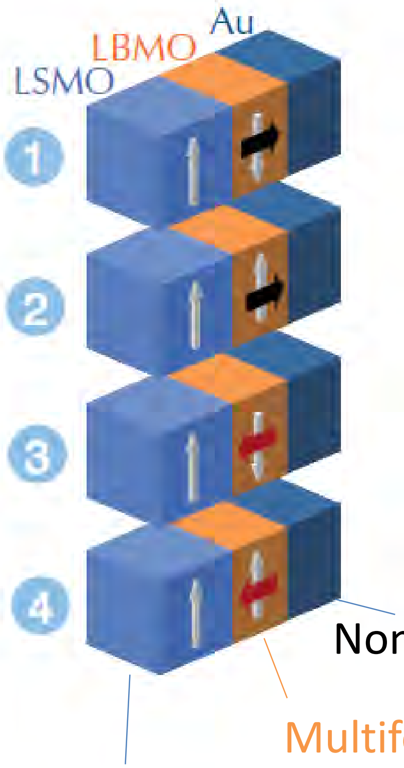
- Magnetic and ferroelectric ordering without coupling (Type I) :
  →4 states devices

- Magnetoelectric coupling (type II) : handling of a magnetization by an electric field
  → spintronic based memory devices

Four logic states devices

Tunnel junctions with multiferroïc barriers: : 4 resistive states (2-magnetic and 2-electric)





Non ferromag

Multiferroïc

FerroMagnet

TMR: Tunnel Magneto Resistance
TER: Tunnel Electroresistance Effect

→ Increase density

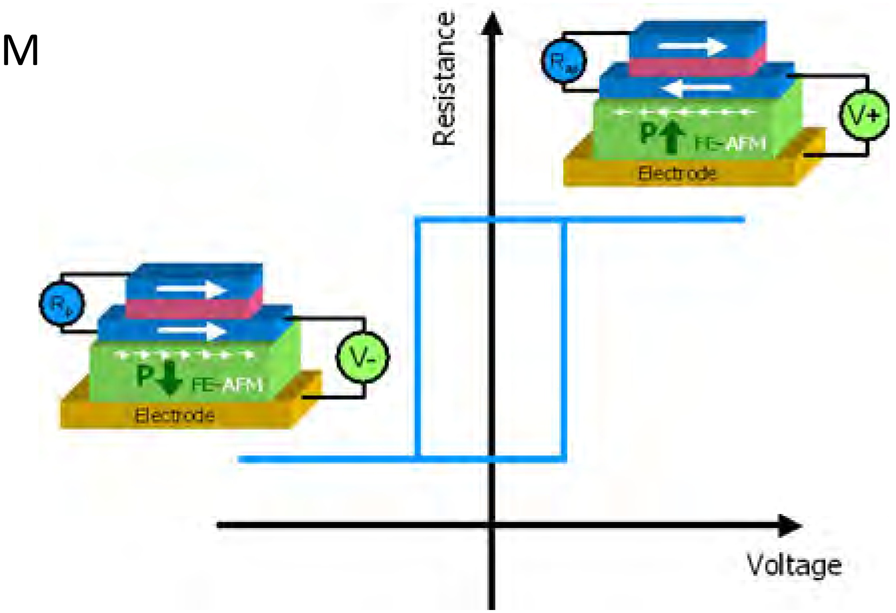
Gajek M., Nat Mater. 2007

Magnetoelectric devices: handling of a magnetization by an electric field

MagnetoElectric Random Access Memories (MERAMs): non-volatile magnetic storage bits that are switched by an electric field

MERAM

Read



write

Magnetoelectric coupling with the interfacial **exchange coupling** between a multiferroic and a ferromagnetic to switch the magnetization of the ferromagnetic layer by using a voltage.

Advantages of:
- ferroelectric memories: low energy consumption
- magnetic memories: non-volatility

https://oxitronics.wordpress.com/research/multiferroics/

Two fold interest

Technological:

Application: density, speed, energy cost in devices

Nanomaterials and nanotechnologies for the products of the future

Stimulating industrial renewal

ANR AGENCE NATIONALE DE LA RECHERCHE

Metallic and inorganic materials and related processes

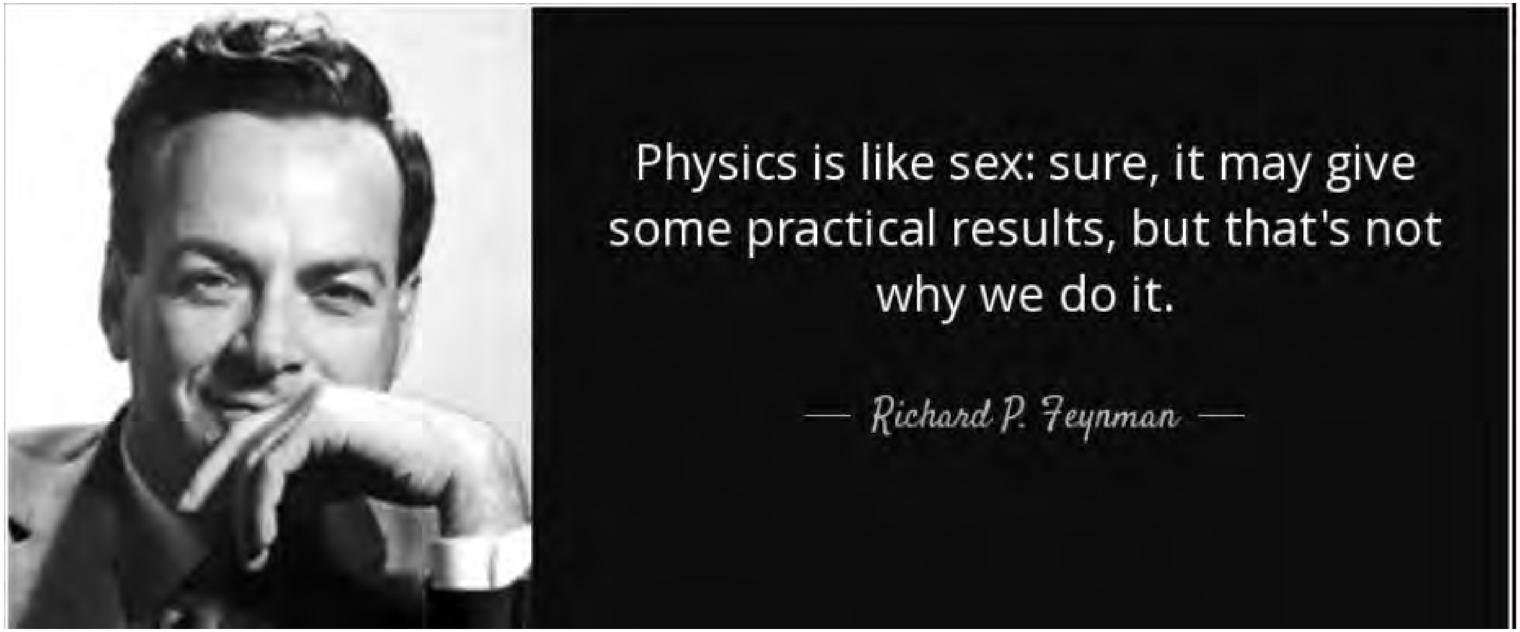
Micro and nanotechnologies for information and communication processing

Physics of condensed and diluted matter

Two fold interest

Technological:

Application: density, speed, energy cost in devices



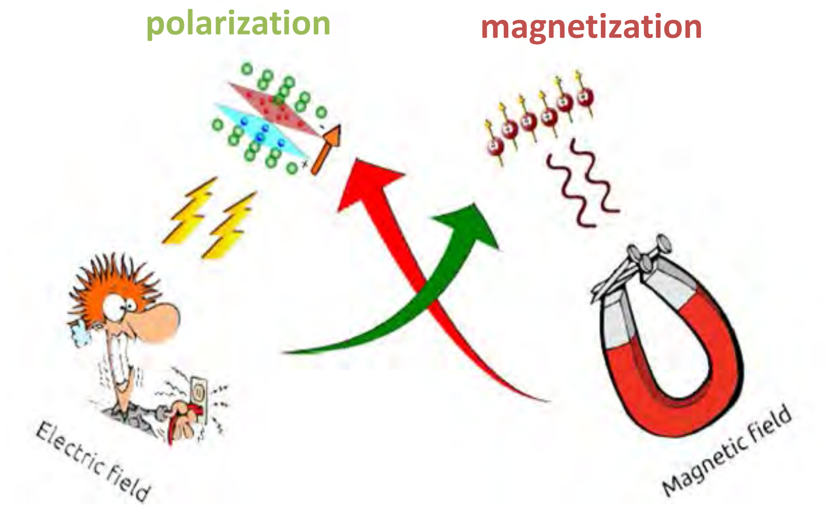
Physics is like sex: sure, it may give some practical results, but that's not why we do it.

— Richard P. Feynman —

Fundamental:

-What are the microscopic mechanism responsible for magneto-electric coupling?
-How to design new magnetoelectrics materials?

How to combine and or couple magnetic and ferroelectric properties in a same phase?



✓ (Ferro-)Magnetism

Exchange interaction of localized magnetic moment: TM $3d^n$, RE $4f^n$

? Ferroelectricity

Classical recipe: Empty d shell (Ti^{4+} in $BaTiO_3$)

"d^0 vs d^n problem"

N. A. Hill, J. Phys. Chem. B 104, 6694 (2000)

Type I

- Stereochemically active lone pair ($6s^2$ in Bi^{3+}, $BiFeO_3$)
- Charge ordering ($LuFe_2O_4$)
- Geometric ferroelectricity (h-$YMnO_3$)

Type II

- Spin-driven ferroelectricity ($TbMnO_3$, YMn_2O_5)
  - spiral magnetic structure
  - collinear magnetic structure

Multiferroïc family tree

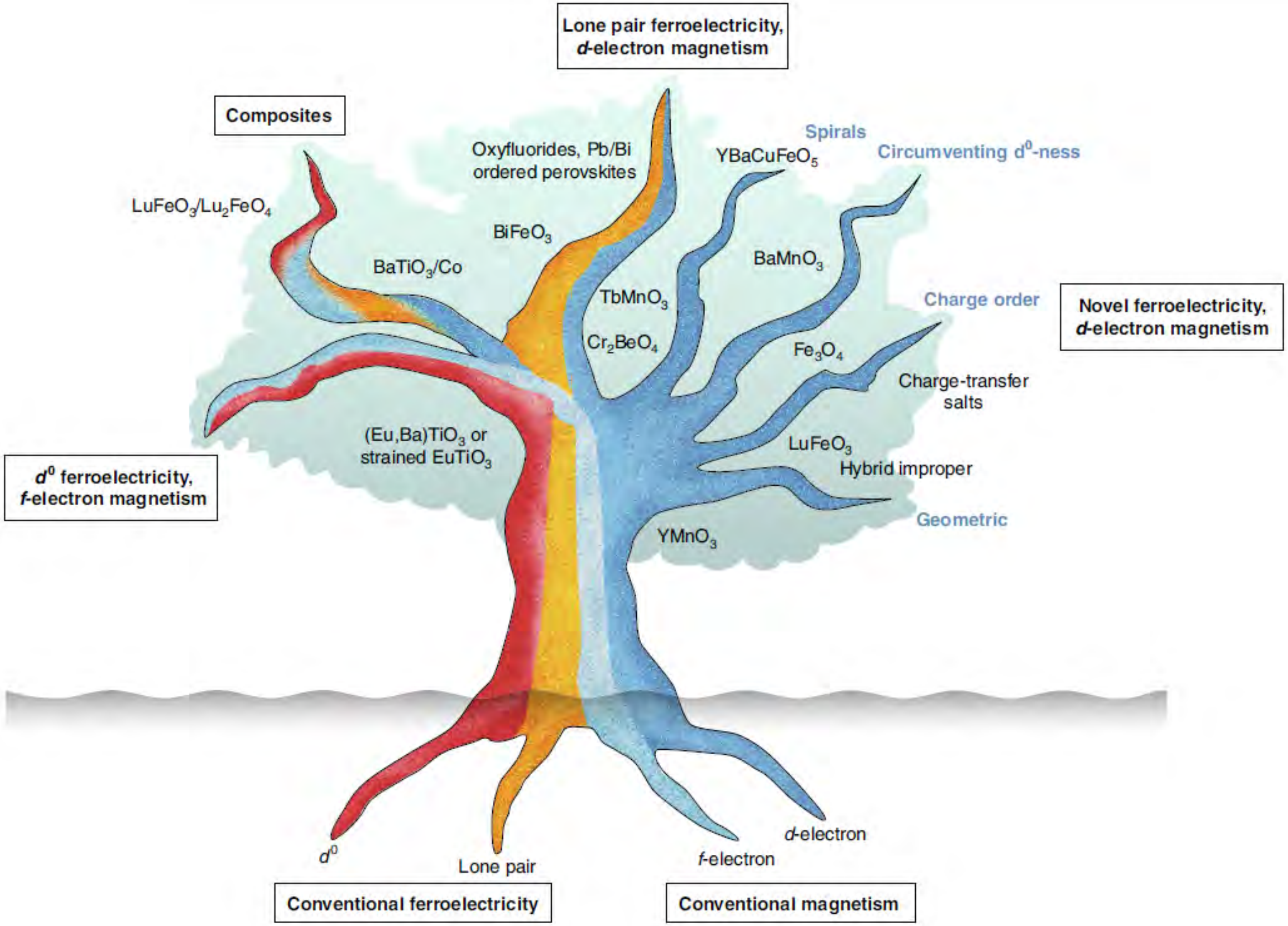
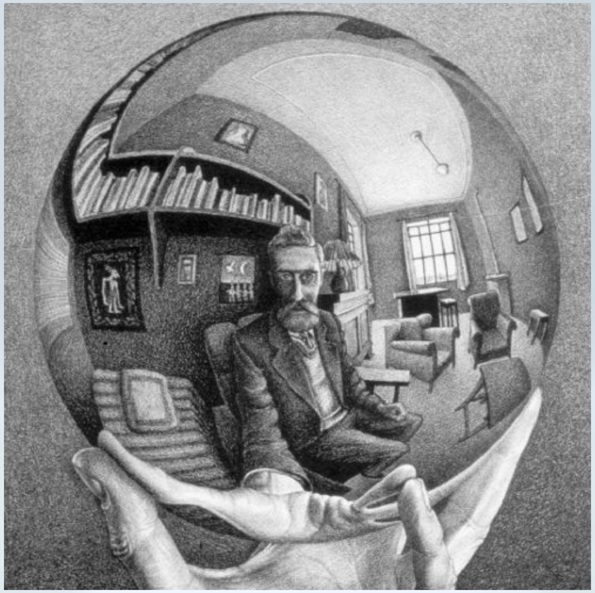


Fig. 1 | The multiferroic family tree. Multiferroicity, arising from the combined interplay of magnetic and ferroelectric mechanisms, can result from several different sources. Here, we outline different combinations of these 'root' mechanisms and how they are responsible for different types of multiferroic materials. This visualization shows the combinations of magnetic and ferroelectric mechanisms that occur in existing multiferroics, and also suggests less-explored options that may prove fruitful in the future.

N. A. Spaldin and R. Ramesh, Nature materials , 2019

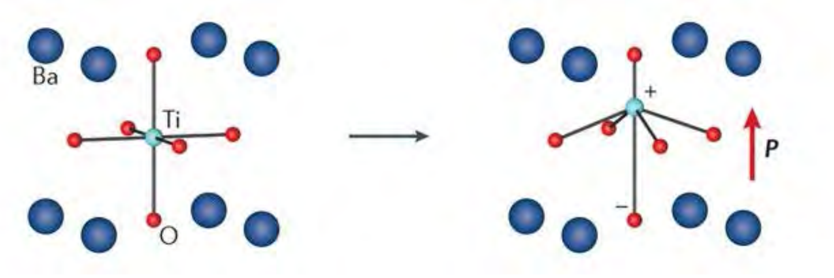
- Role of symmetry



Role of symmetry

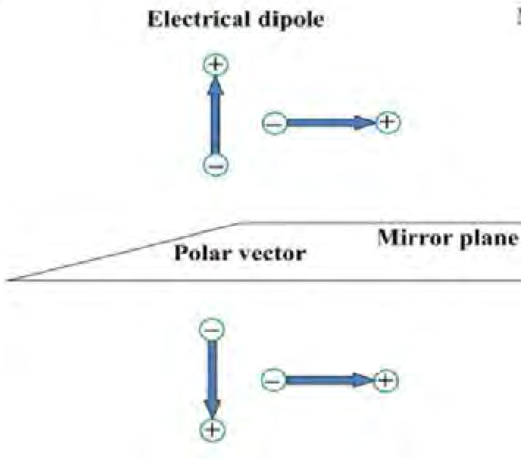
- Control existence of polarization

  breaking of spatial inversion symmetry is the requirement for ferroelectricity and polarization.



- Control the orientation of the polarization

  For a mirror, polarization only in the mirror plane



- Allow MagnetoElectric coupling

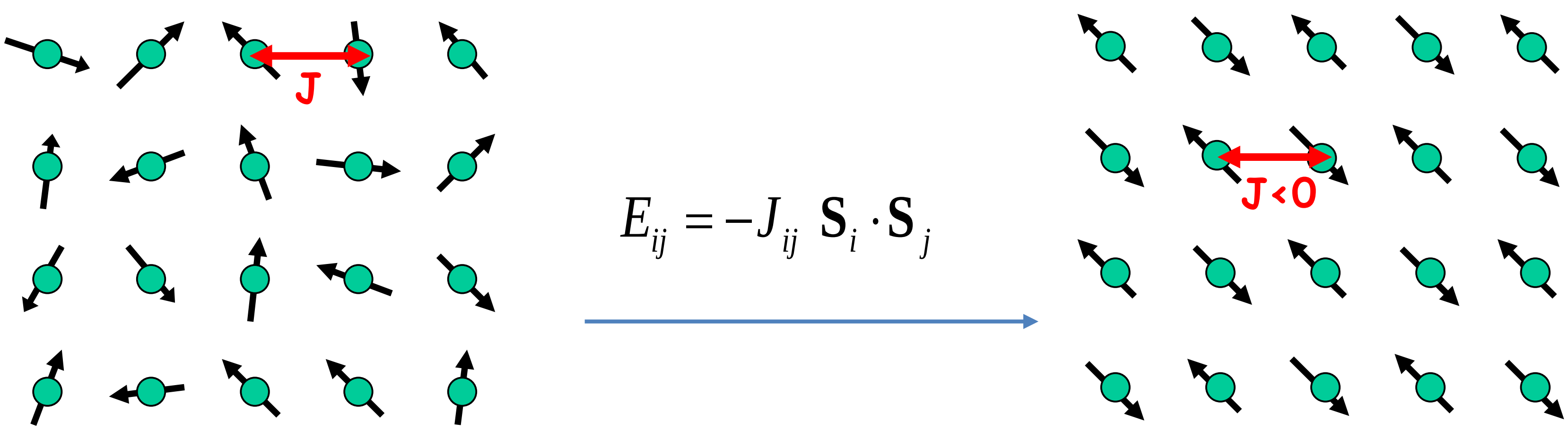
  P and M must belong to the same Irrep

(Neutron) diffraction is an essential probe to determine the correct (magnetic) symmetry

Magnetic ordering

$$\langle \mathbf{S}_i \rangle = 0$$

$$\langle \mathbf{S}_i \rangle \neq 0$$



$$E_{ij} = -J_{ij}\, \mathbf{S}_i \cdot \mathbf{S}_j$$

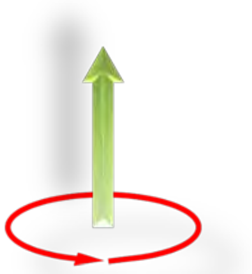
$T>T_C$
Paramagnetic

$T<T_C$
AntiFerromagnetic

Magnetic ordering is a symmetry-breaking process

A bit of magnetic symmetry

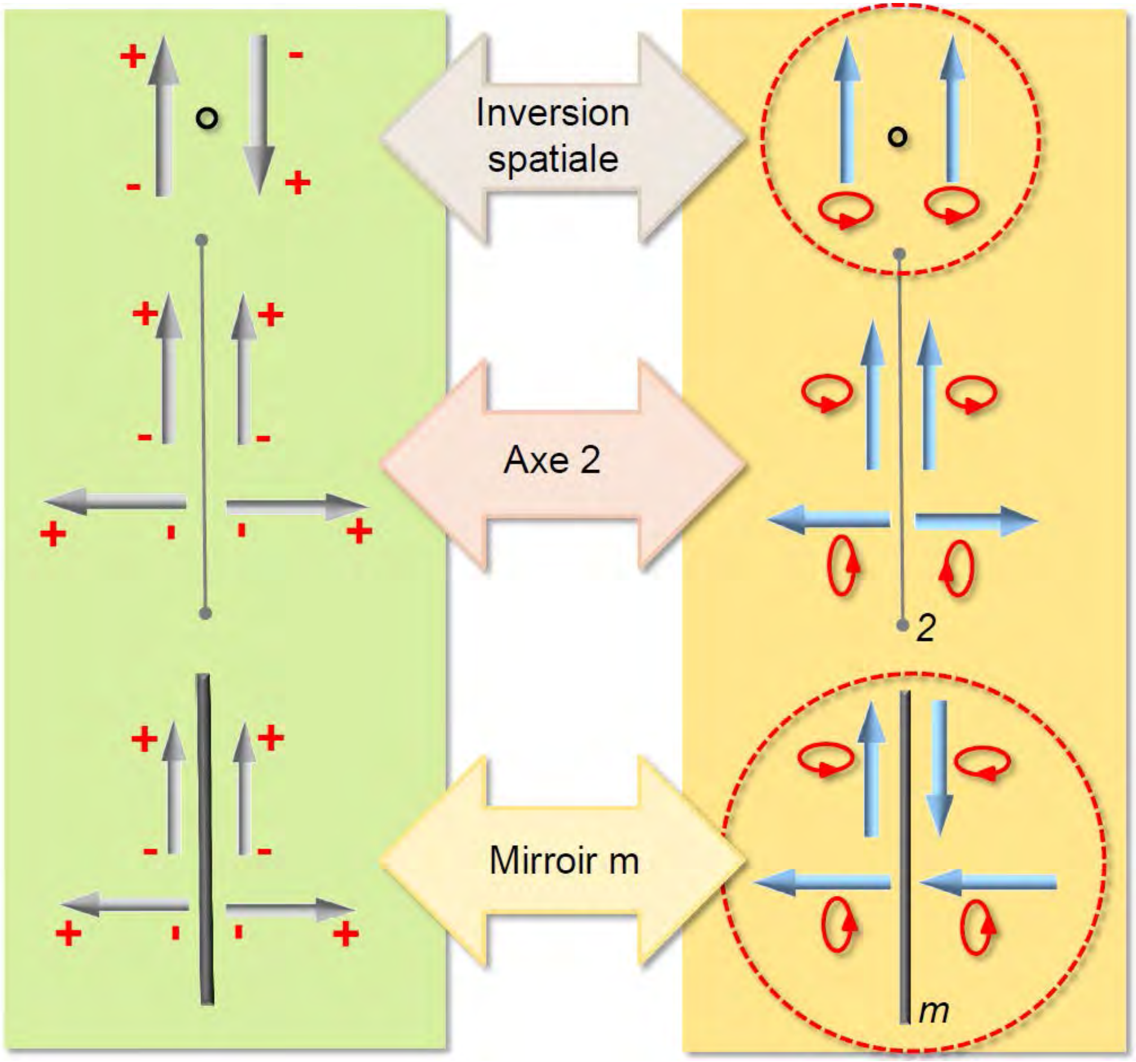
Magnetic moment is an axial vector



Current loop

Polar vector

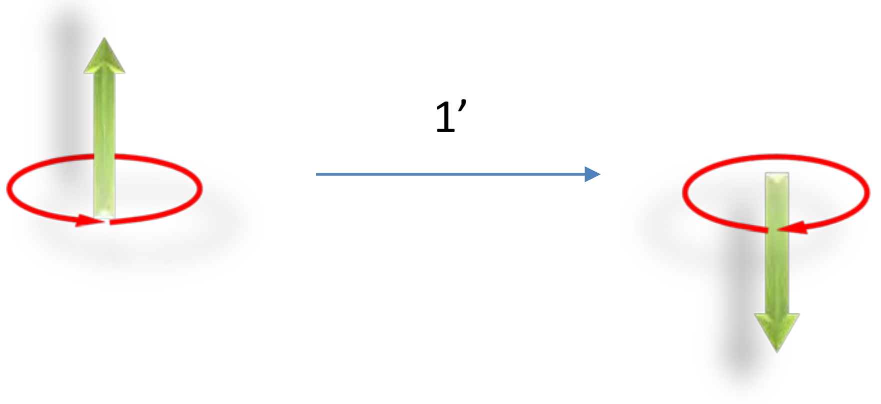
Axial vector



©F. Damay

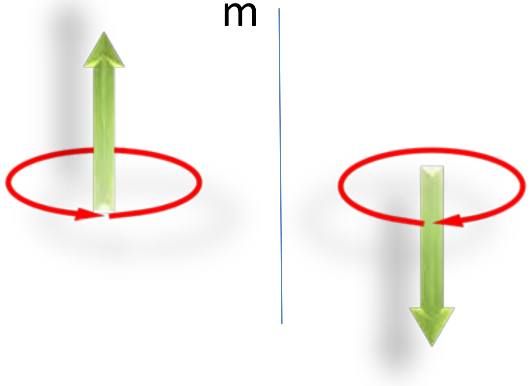
Magnetic symmetry

New symmetry operator =
1’ time reversal: flip
magnetic moment

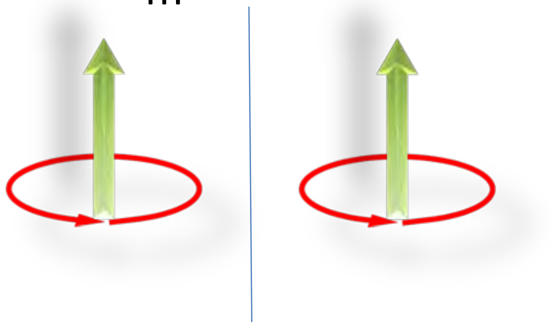


1’ can be combined with any other sym. operator

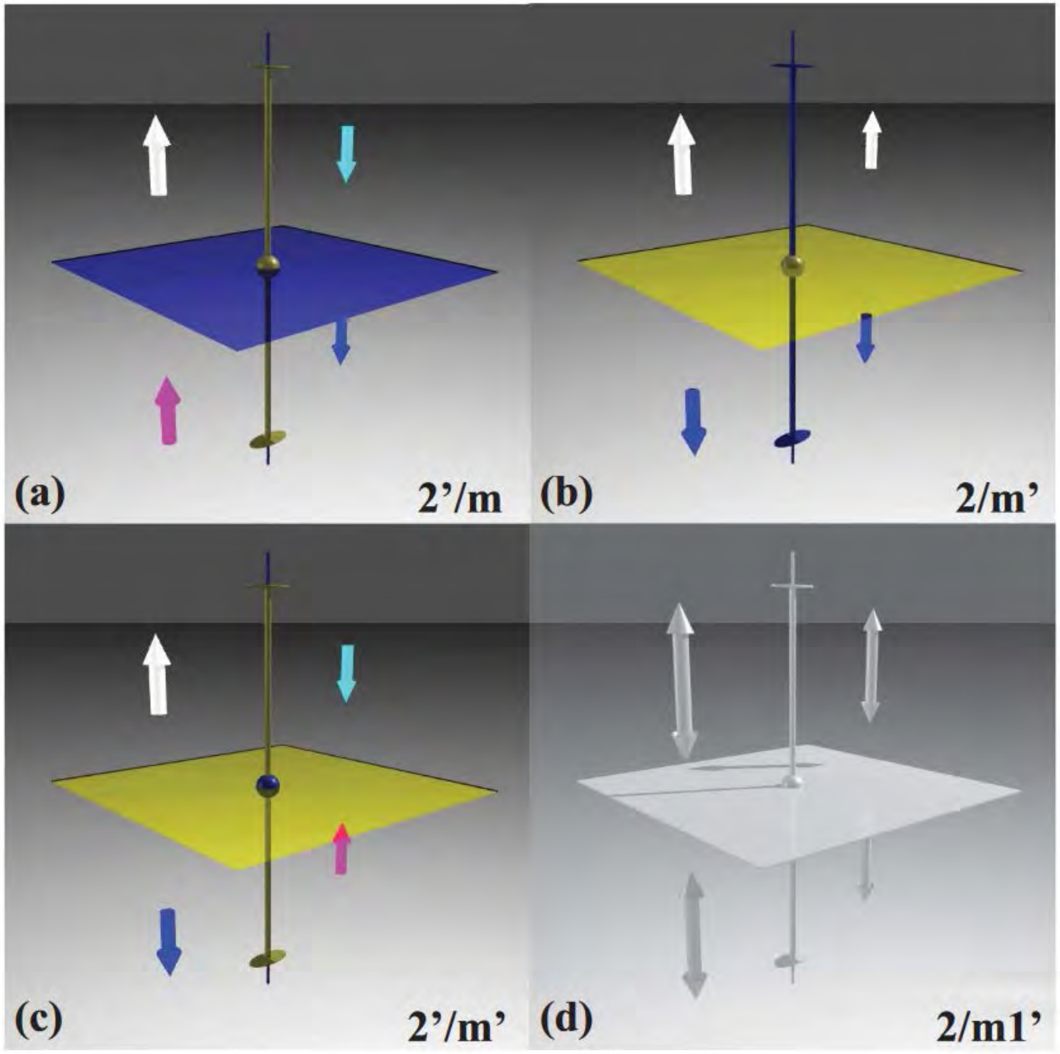
Mirror
m



Primed mirror
m’



Magnetic point group



Representation of the operations of the magnetic point groups derived from 2/m on an axial vector *(from Marc De Graef)*

32 crystallographic point groups→ 122 magnetic point groups

Symmetry analysis is crucial

- Allows the prediction of electrical properties: polarization direction
- "Recipe" to examine phase transitions (structural and magnetic) and determine possible Magnetic Space Group

MAXMAGN (BCS)

$HoMnO_3$

k= ½ 0 0

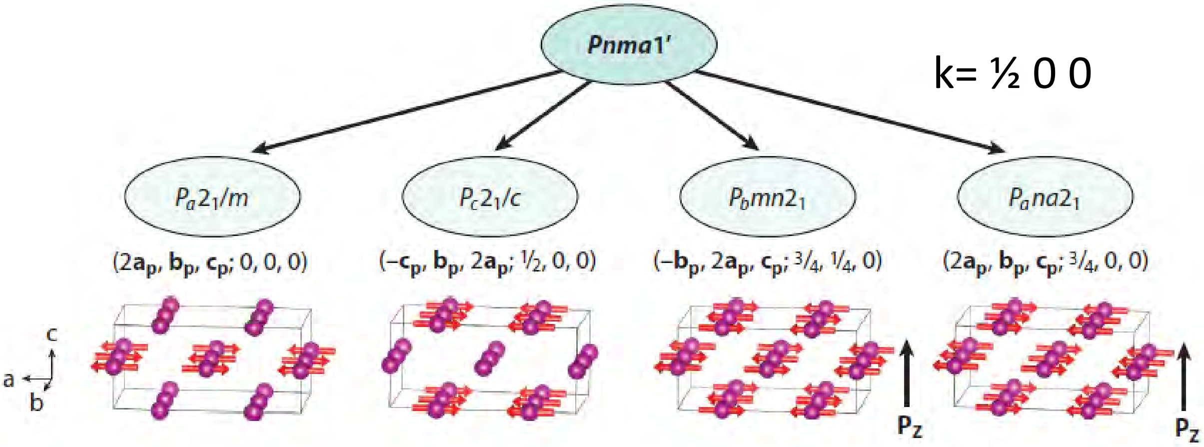


Figure 3

The four possible distinct magnetic orderings of maximal symmetry with propagation vector **k** = (1/2, 0, 0) for the Mn site in orthomanganites, as obtained with MAXMAGN, assuming that the spins are aligned along the *a* direction. The magnetic space group label associated with the magnetic symmetry of each structure is shown, together with the transformation (from the parent $Pnma1'$ basis) to its standard setting. The index of the four subgroups is four. The magnetic unit cell used in all figures is $(2\mathbf{a}_p, \mathbf{b}_p, \mathbf{c}_p; 0, 0, 0)$. The direction (with arbitrary sense) of the possible magnetically induced electric polarization P_z, when it is symmetry allowed, is indicated. The P_bmn2_1 ordering is the one observed in $HoMnO_3$ (22, 49). Abbreviation: P_z, possible magnetically induced electric polarization.

New Symmetry-Based Computational Tools for Magnetic crystallography:

→ **Bilbao Crystallographic Server: Magnetic Symmetry and Applications**

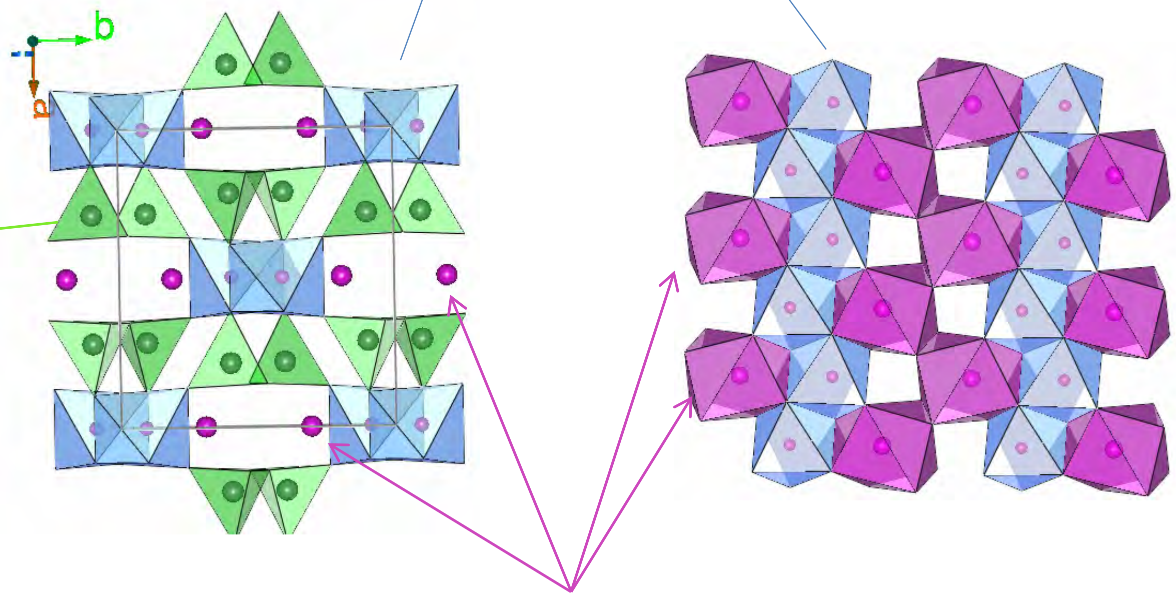
→ **Isodistort**

- Examples

©Monty Python

“Finally Monsieur, a wafer-thin mint”

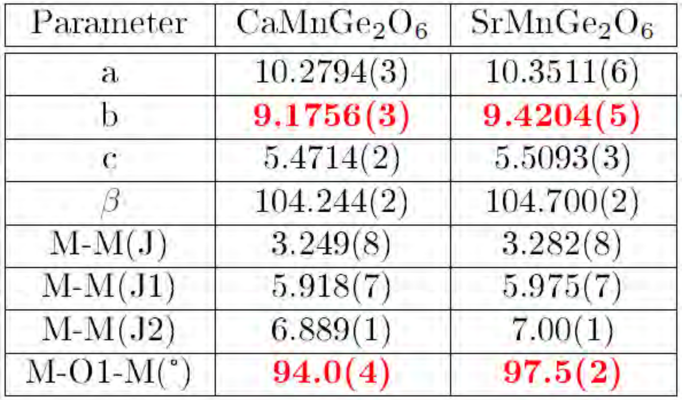
Magnetoelectric and Multiferroic pyroxene $CaMnGe_2O_6$ vs $SrMnGe_2O_6$



Edge-sharing **MnO_6** octahedra chain

Corner-sharing **GeO_4** tetrahedra

Ca/Sr



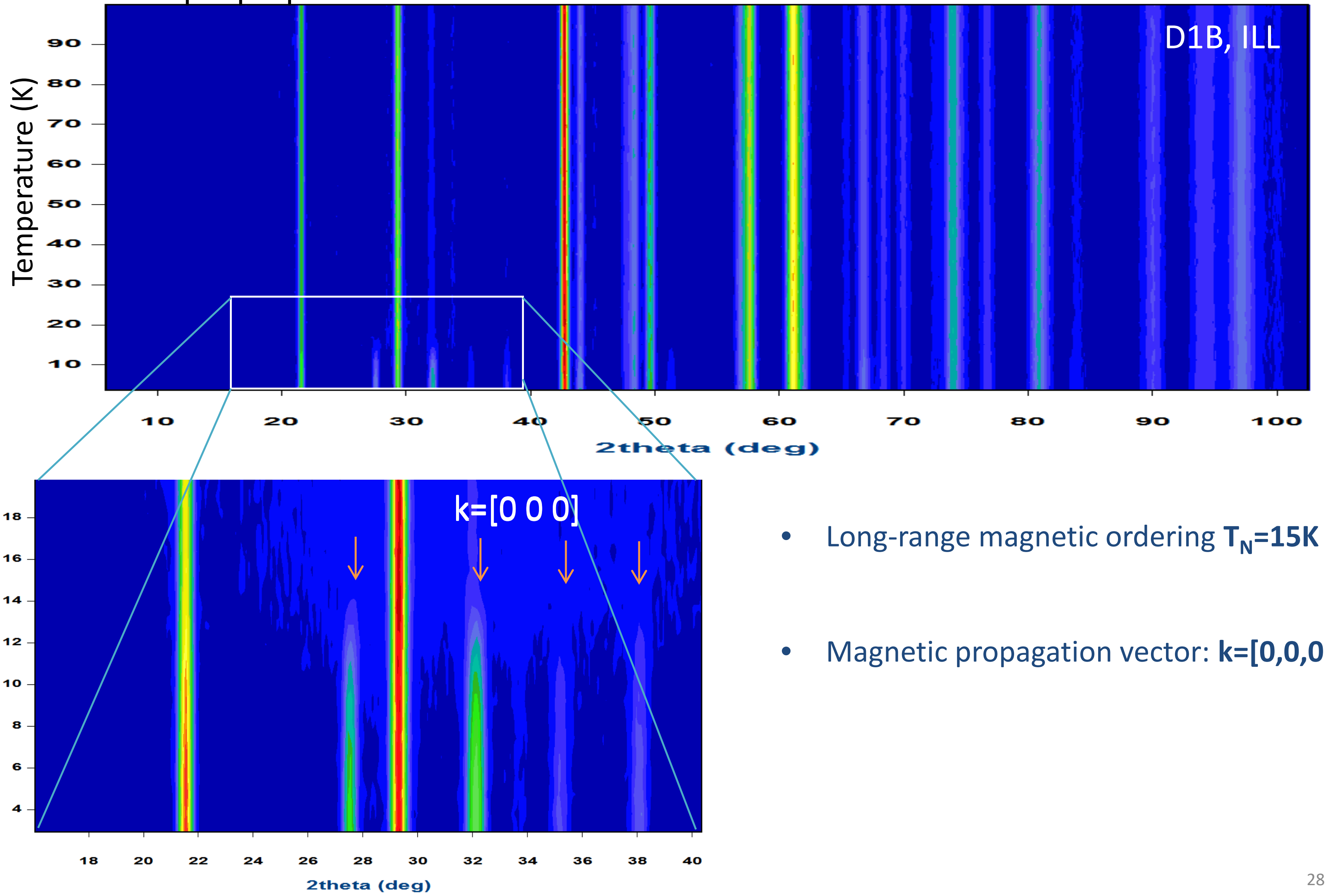
Parameter	$CaMnGe_2O_6$	$SrMnGe_2O_6$
a	10.2794(3)	10.3511(6)
b	**9.1756(3)**	**9.4204(5)**
c	5.4714(2)	5.5093(3)
β	104.244(2)	104.700(2)
M-M(J)	3.249(8)	3.282(8)
M-M(J1)	5.918(7)	5.975(7)
M-M(J2)	6.889(1)	7.00(1)
M-O1-M(°)	**94.0(4)**	**97.5(2)**

Similar crystalline structure: C2/c

Small structural changes but drastic changes on magnetic structures stabilized….

$CaMnGe_2O_6$: Neutron Diffraction

Sample preparation: solid state reaction at 1200C



- Long-range magnetic ordering **T_N=15K**
- Magnetic propagation vector: **k=[0,0,0]**

$CaMnGe_2O_6$: magnetic structure

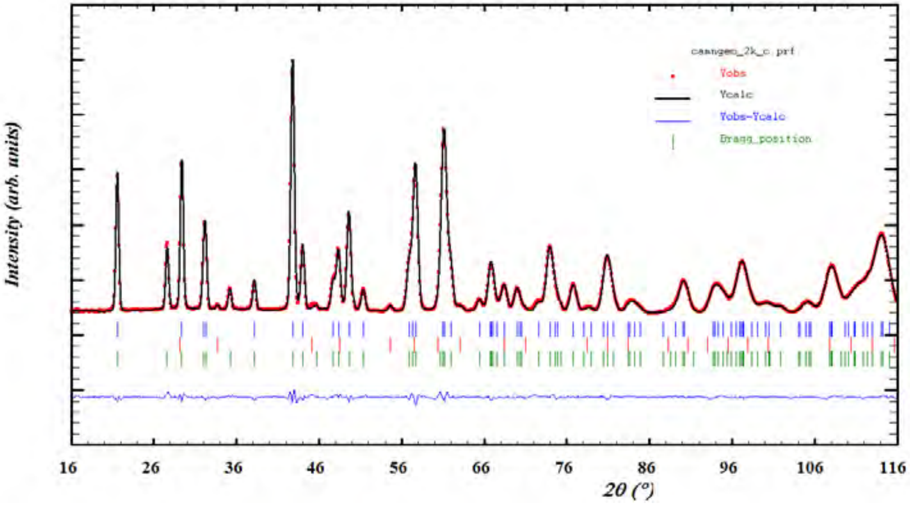
Representation analysis for Mn^{2+} in 4e site:

4e_1(0,y,0.25), 4e_2: (0,-y, 0.75)

#IrReps	Basis Function	Magn. S.G.
Γ_1	$(0,F_y,0)$	C2/c
Γ_2	$(0,A_y,0)$	C2/c’
Γ_3	$(F_x, 0, F_z)$	C2’/c’
Γ_4	$(A_x,0,A_z)$	C2’/c

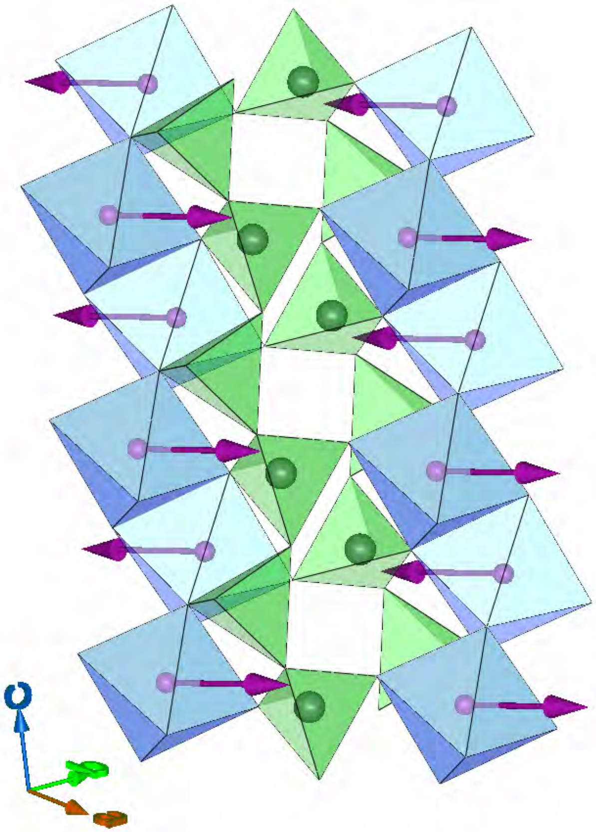
F=(++), A=(- -)

<u>Γ4, @2K:</u>	m(a)	m(b)	m(c)	Mtot
	4.30	0.00	1.14	$4.17\mu_B$



-k=[0,0,0] → preserve C-centering ie interchain FM

- Γ_4 : intrachain AFM



→ C2’/c : allows for linear ME effect

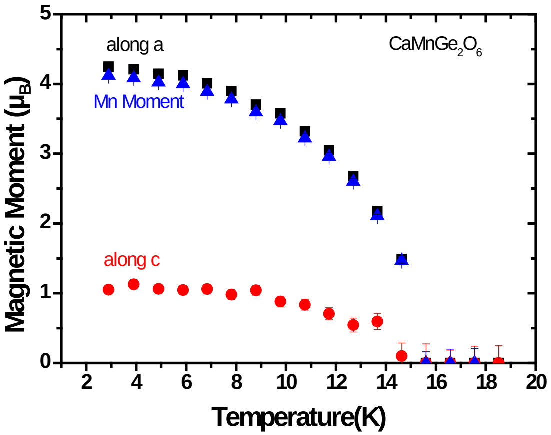
Linear ME effect in $CaMnGe_2O_6$

Magnetic space group: **C2’/c** allows for **linear ME**

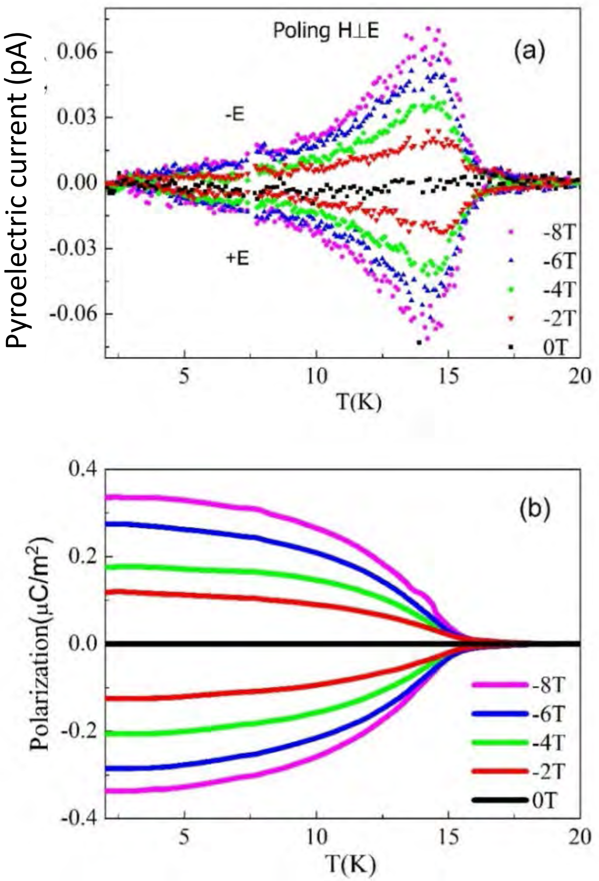
$$P_i = \alpha_{ij} H_j$$

- The form of tensor for linear ME effect:

$$\alpha_{ij} = \begin{pmatrix} 0 & \alpha_{12} & 0 \\ \alpha_{21} & 0 & \alpha_{23} \\ 0 & \alpha_{32} & 0 \end{pmatrix}$$



Pyroelectric current measurement:
ME annealing E⊥H (pressed pellet)

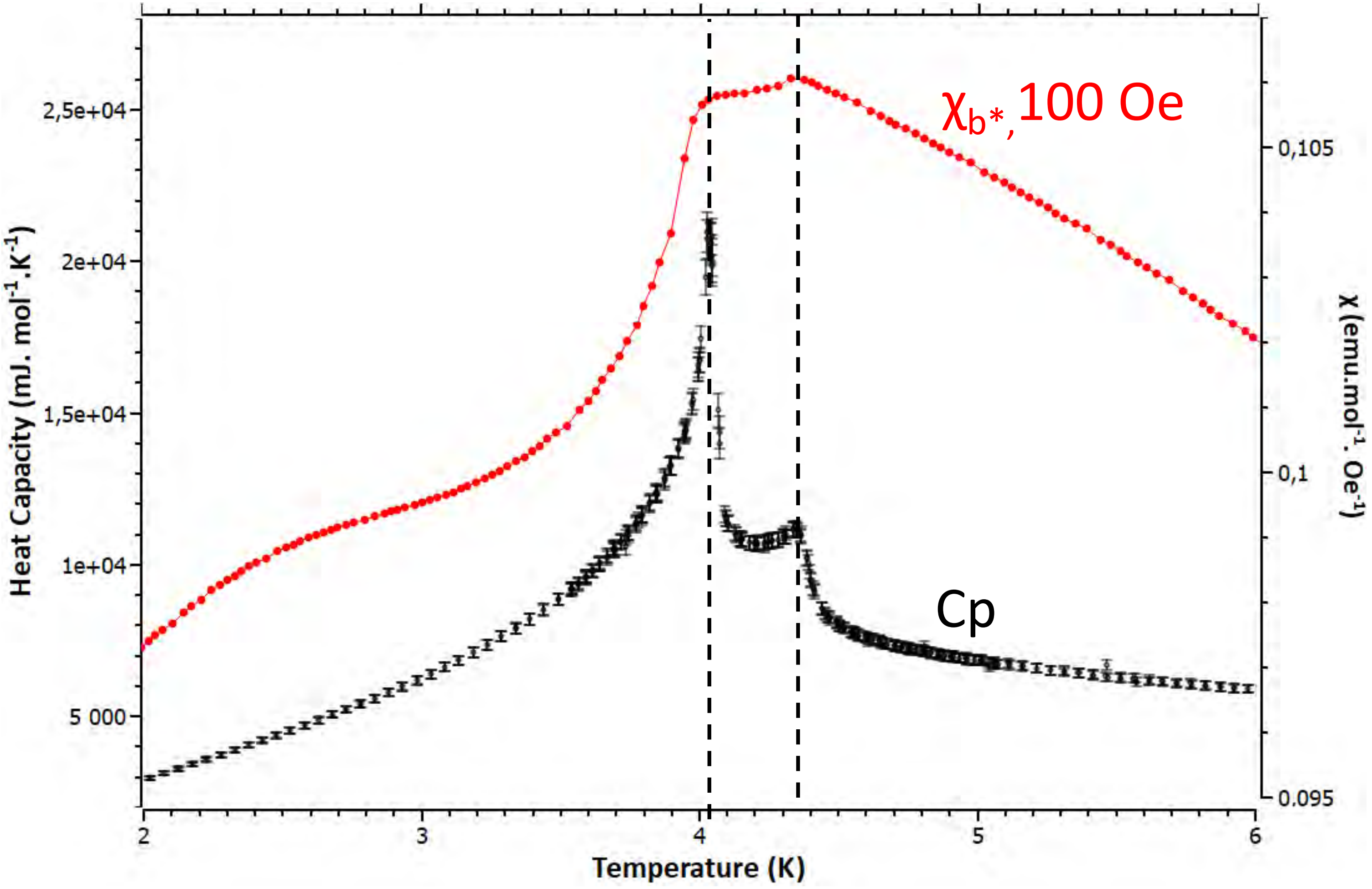


L. Ding, C. V. Colin, C. Darie, J. Robert, F. Gay, and P. Bordet, Phys. Rev. B 93, 064423, 2016

No electrical polarization in the absence of an applied magnetic field!

$SrMnGe_2O_6$: magnetic properties

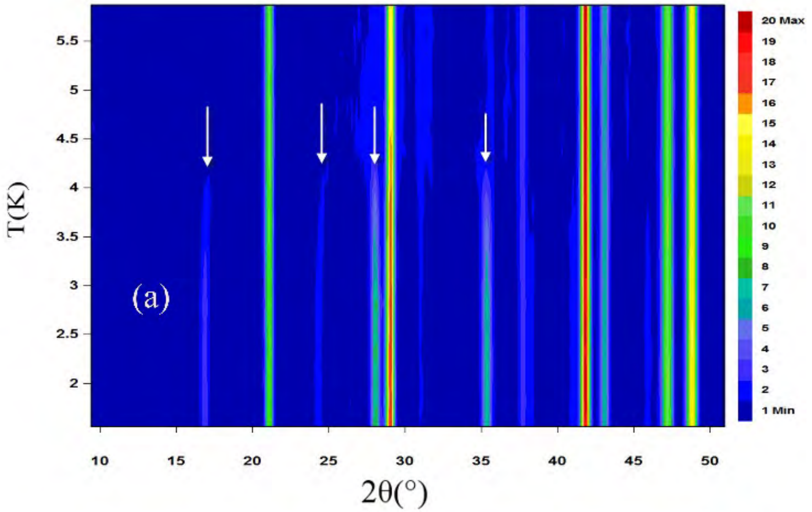
T_{N2}=4,05(2)K T_{N1}= 4,36(2)K

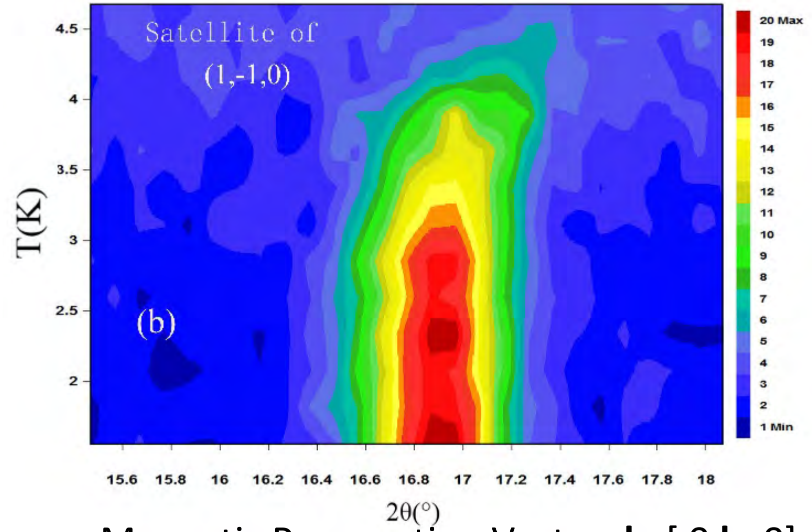


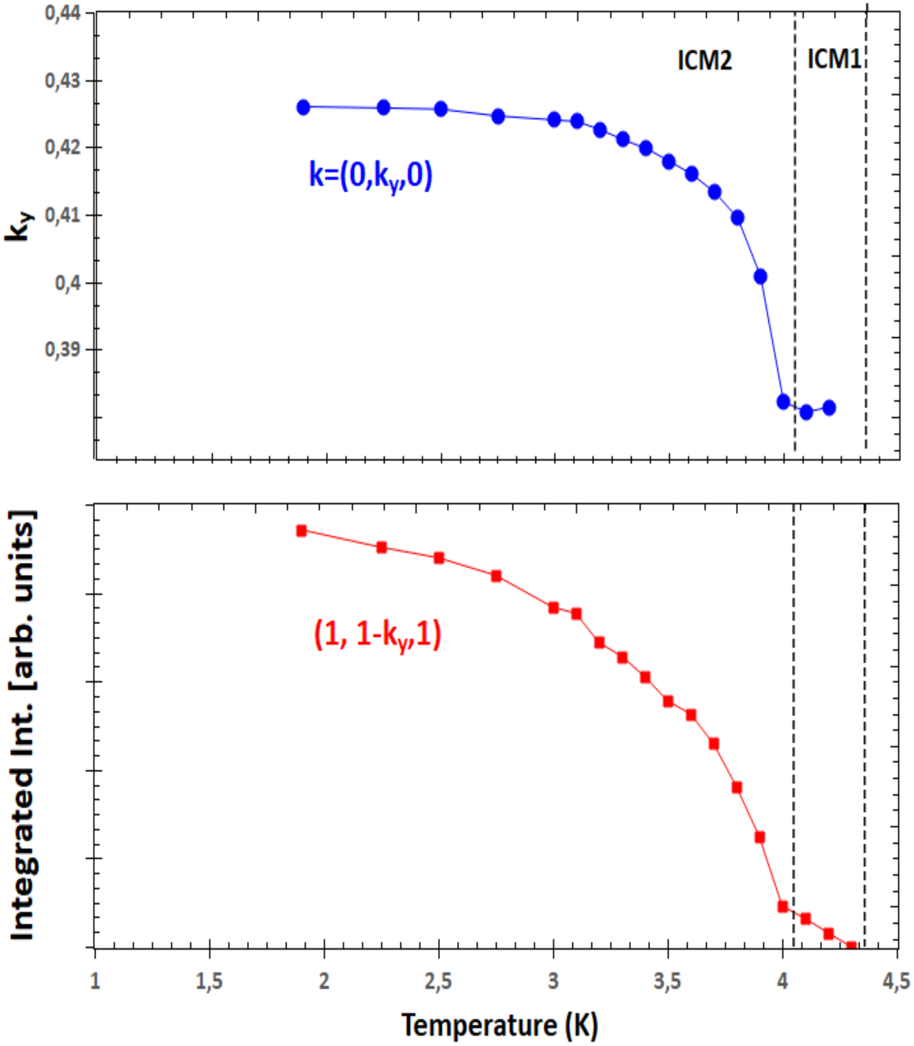
$SrMnGe_2O_6$: incommensurate magnetic structures

ND on powder: D1B @ ILL

ND on single crystal: D23 @ ILL







Magnetic Propagation Vector **k**=[0 $\mathbf{k_y}$ 0]

L. Ding, C. V. Colin, C. Darie, and P. Bordet, J. Mater. Chem. C 4, 4236 (2016).

$SrMnGe_2O_6$: IMC 1

@4.1K, k_y= 0.381

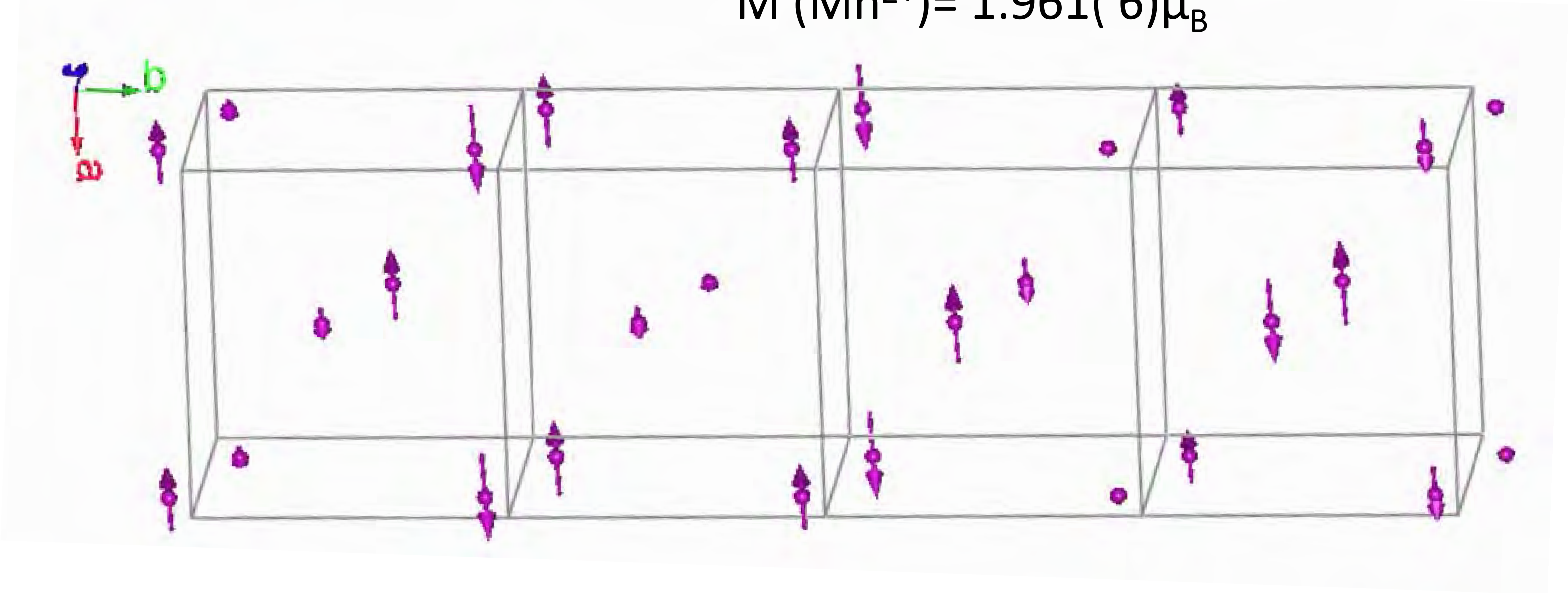
290 reflections

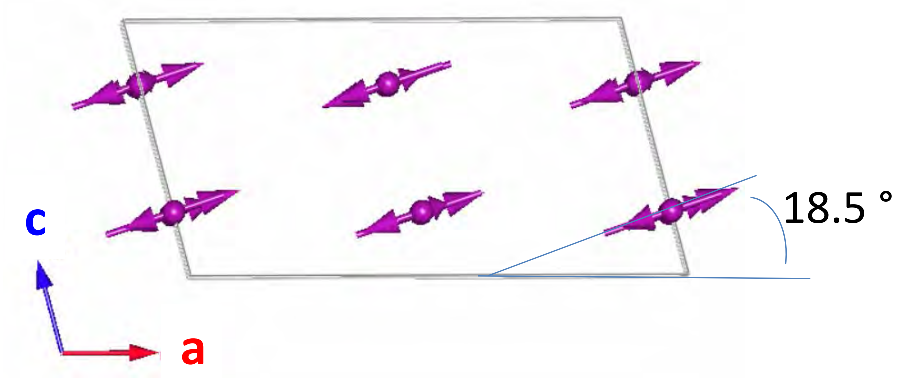
RF -factor :   11.02%

Sinusoidally modulated structure

Moments in the (a,c) plane

M (Mn^{2+})= 1.961(6)μ_B





IR: mLD2

P (a,0) 15.1.7.3.m86.? B2/b1'(0,0,g)s0s

Centrosymmetric Magnetic Point group: **2/m1'**

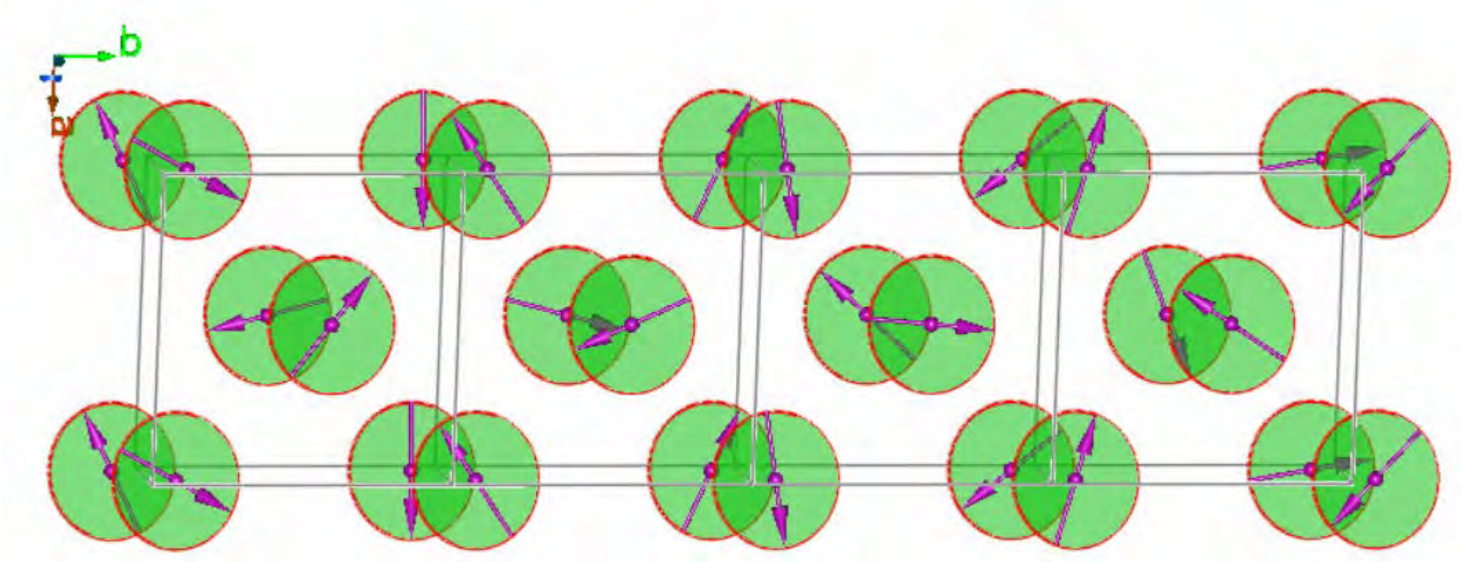
$SrMnGe_2O_6$: IMC 2

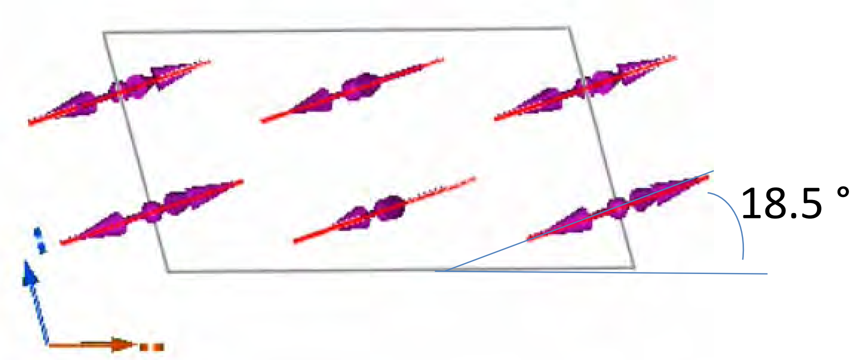
@2.0K, k_y= 0.485

290 reflections
RF -factor :   3.54%

Elliptical cycloïd

Moments in the (a,c) plane
M (Mn^{2+})= 4.08(2)μ_B



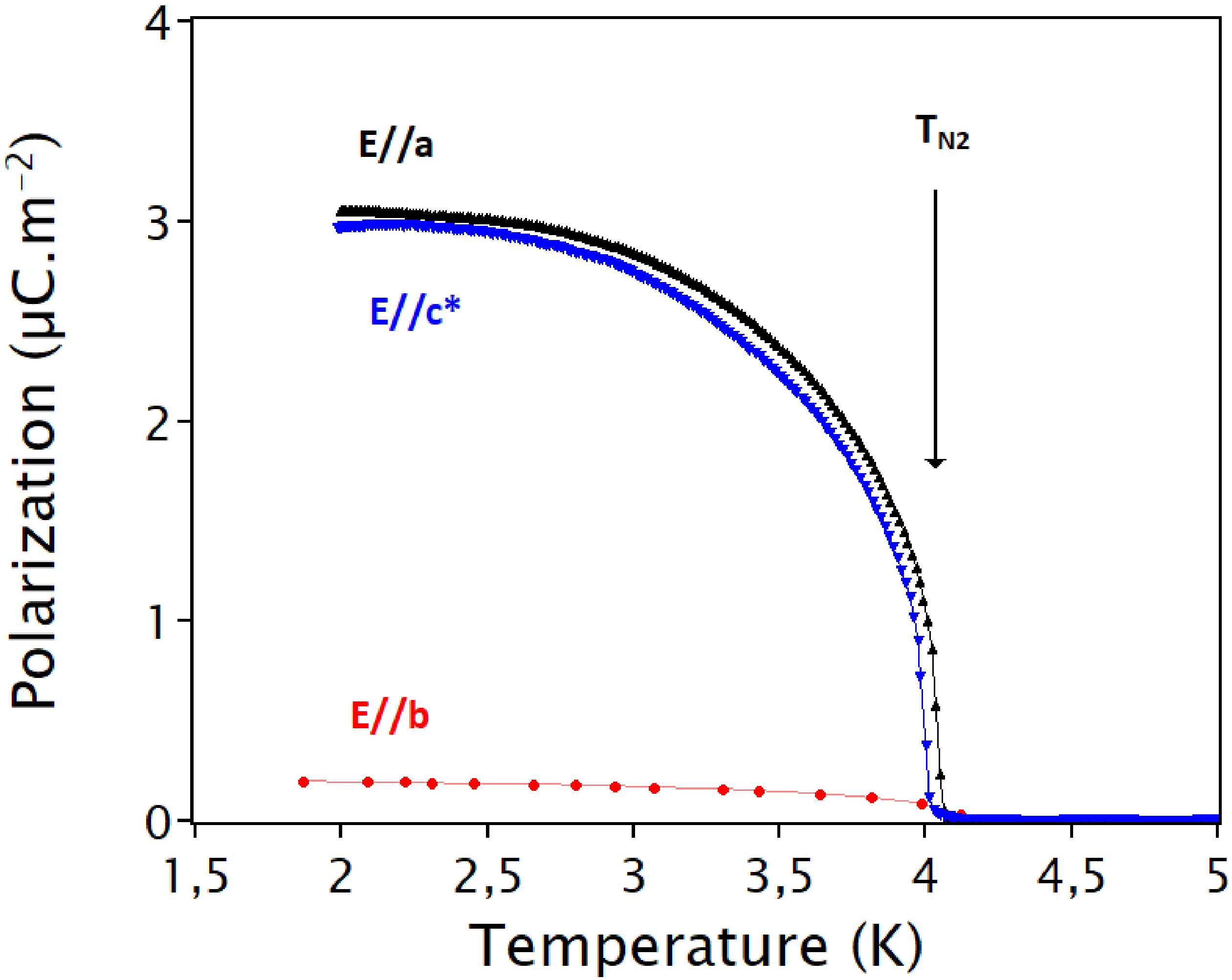


2 IR: mLD1 and mLD2
P-P (a,0|0,b) 9.1.7.2.m38.? Bb1'(0,0,g)0s
Polar Magnetic Point group: **m1’**

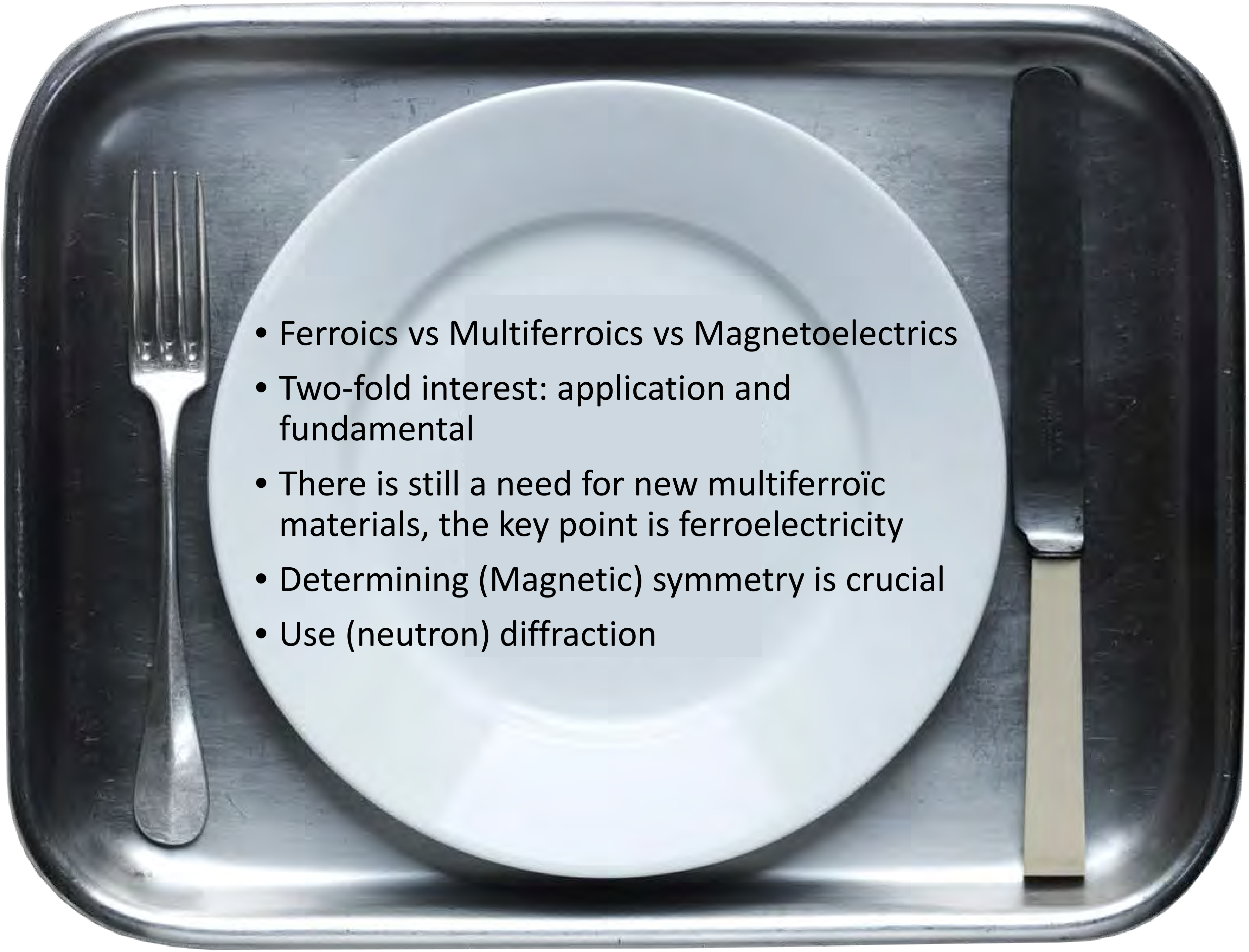
→ P allowed in the (a,c) plane

$SrMnGe_2O_6$: ferroelectricity driven by the magnetic order

Pyroelectric current measurement, E= 500kV.m^{-1}



In agreement with the determined polar magnetic structure below T_{N2}



- Ferroics vs Multiferroics vs Magnetoelectrics
- Two-fold interest: application and fundamental
- There is still a need for new multiferroïc materials, the key point is ferroelectricity
- Determining (Magnetic) symmetry is crucial
- Use (neutron) diffraction

Thank you!