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Title: Mesoscopic Modeling of ferroic and multiferroic phase transformations

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Form 836 (7/06)

Mesoscopic Modeling of Ferroic and Multiferroic Phase Transformations

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This talk will provide an overview of materials undergoing ferroic and multiferroic phase transformations. Materials exhibiting ferroic phase transformations are ubiquitous in nature. Ferroic materials possess two or more orientation states (domains) that can be switched by an external field and exhibit hysteresis. Typical examples include ferromagnets, ferroelectrics and ferroelastics, which occur as a result of a phase transformation with the onset of spontaneous magnetization (M), polarization (P) and strain (e), respectively. Materials that display two or more ferroic properties simultaneously are called multiferroic, e.g. magnetoelectrics (simultaneous P and M). Another novel class of ferroic materials called ferrotoroidics has been recently found. These materials find widespread applications as actuators, transducers, information storage and memory devices as well as shape memory elements in biomedical technology. We will discuss their properties, model the transformations at *mesoscale* and describe their microstructure. We will emphasize the role of both crystallographic and *magnetic symmetry* in determining the relevant order parameters and the resulting free energy. We will also discuss long-range, anisotropic forces that arise from either the elastic compatibility constraints or the (polar and magnetic) dipolar interactions in determining the microstructure. In addition, we will explore the importance of defects such as *dislocations in multiferroics*. Finally, we will focus on thermodynamic and *caloric effects* in these technologically important materials.

Collaborators: T. Lookman, A. Planes, T. Castan.

Osaka abstract

LA-UR-10-03487

MESOSCOPIC MODELING OF FERROIC AND MULTIFERROIC PHASE TRANSFORMATIONS

Avadh Saxena (Los Alamos National Lab)

1. Crystals (polar, strain, shuffle): space.
2. Magnetism: space and time; color symmetry.
3. Magnetoelectrics: P, M coupling; strain.
4. Ferrotoroidic materials: $LiCo(PO_4)_3$.
5. Caloric effects in ferrotoroidics; Experimental implications.

Collaborators: T. Lookman (Los Alamos),
A. Planes, T. Castan (Univ. Barcelona)

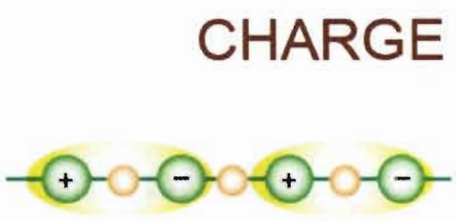
James A. KRUMHANSL

Gerhard R. BARSCH

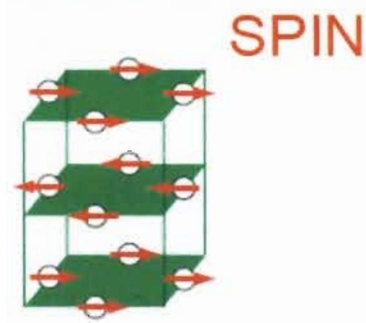
Aug. 2, 1919 – May 6, 2004

Jun. 22, 1927 – Jul. 10, 2011

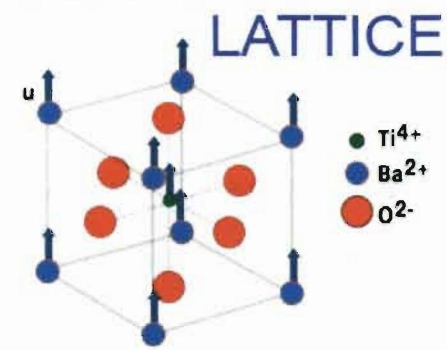
The Three Pillars of Functionality



Directional charge ordering



Antiferromagnetism

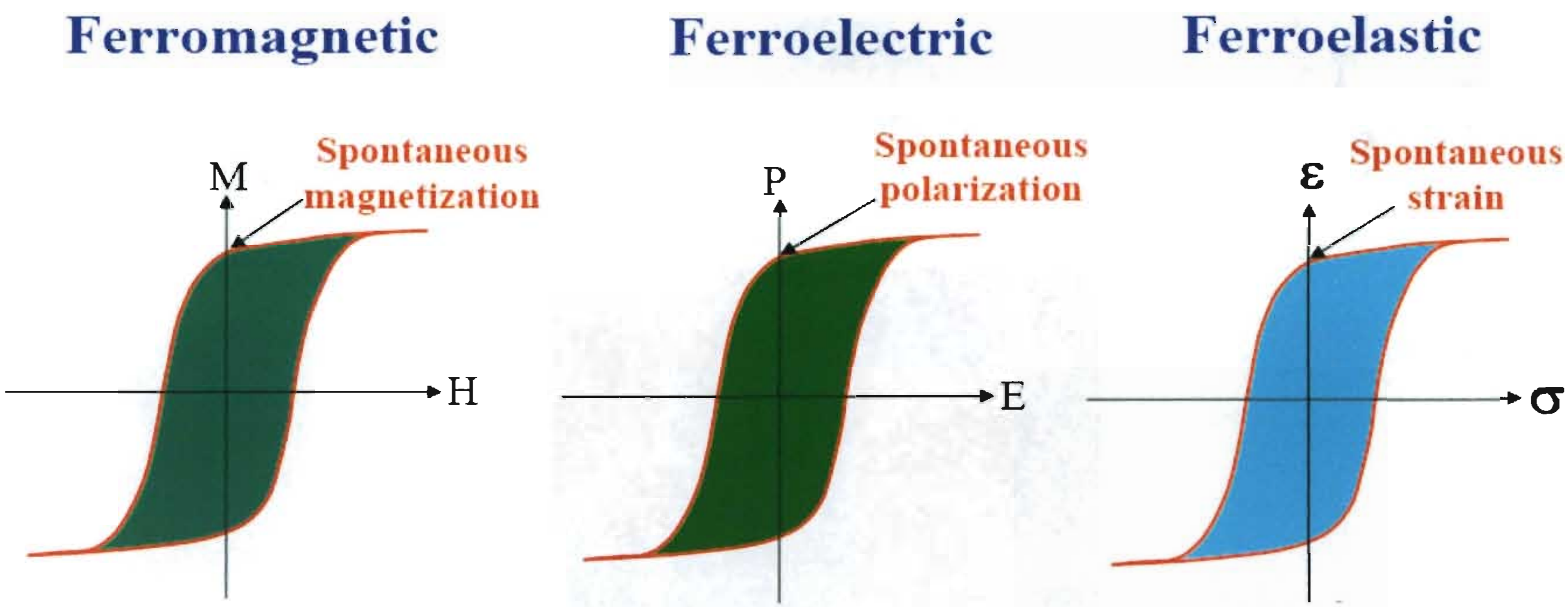


Tetragonal distortion

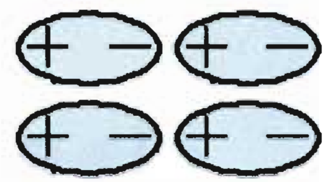
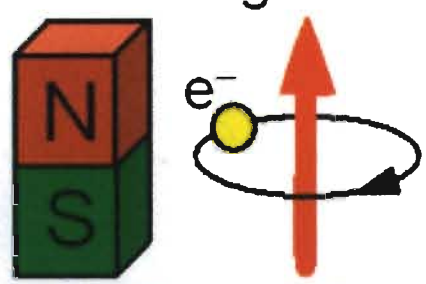
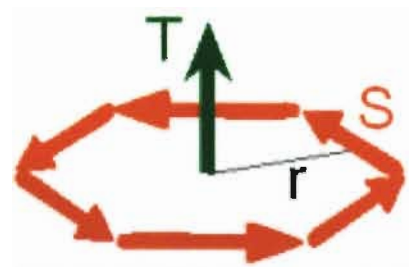
Orbitals: spatial distribution of charge

Ferroic phenomena

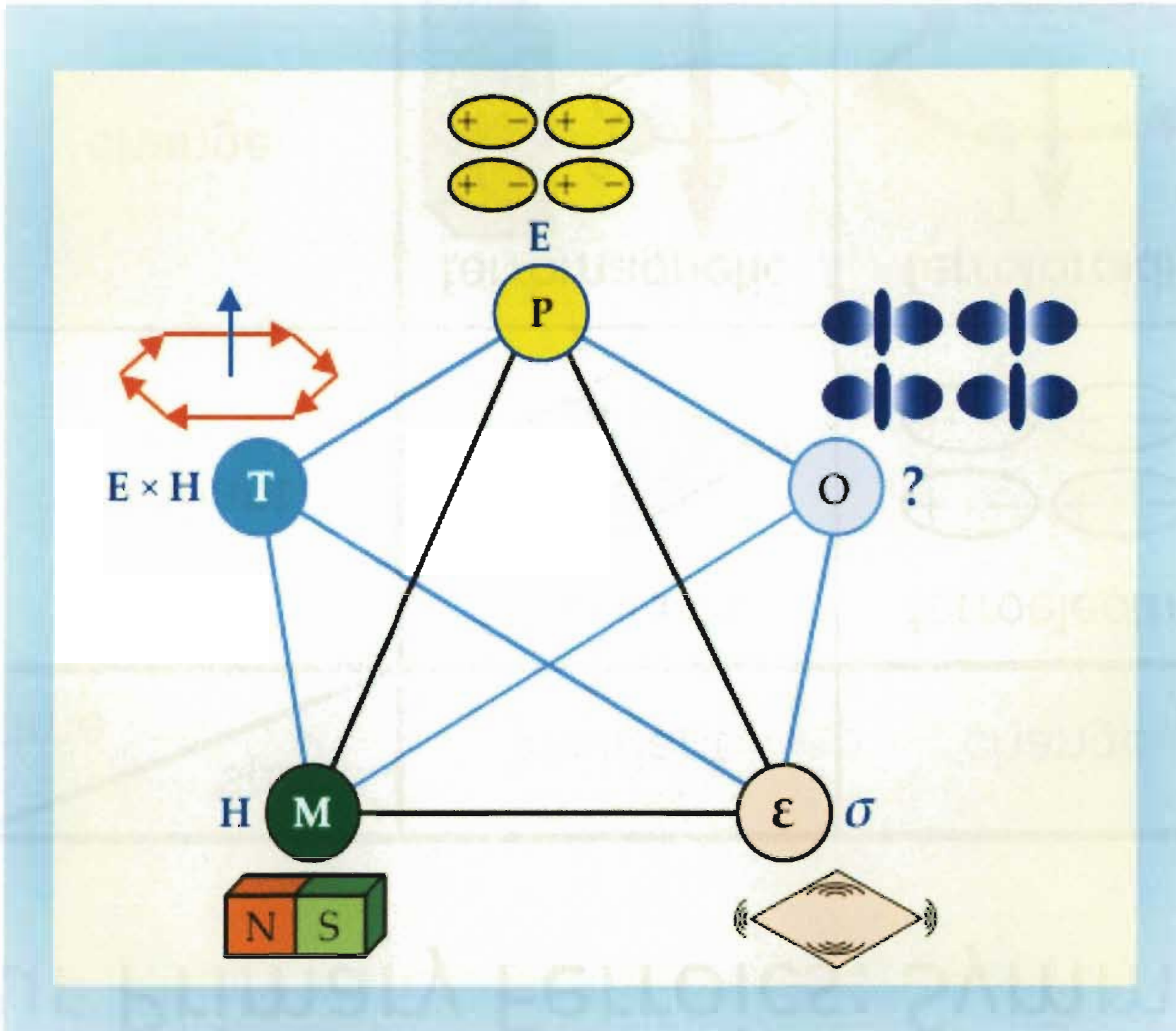
Ferroics is a family of materials exhibiting one or more multifunctional characteristics such as **ferroelectric, ferromagnetic, or ferroelastic** properties



Four Primary Ferroics: Symmetry

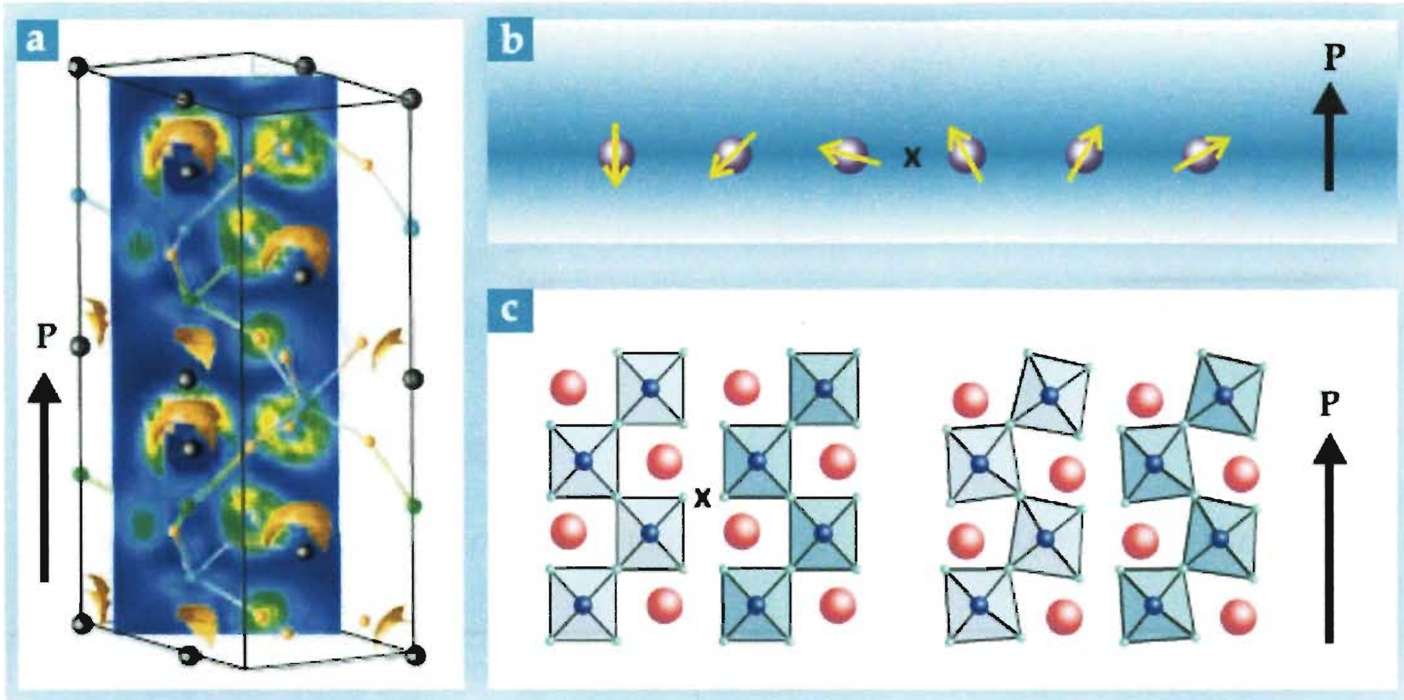
time \ space	invariant	change
invariant	ferroelastic 	ferroelectric 
change	ferromagnetic  	ferrotoroidic 

INTERACTIONS in MULTIFERROICS



Spaldin et al., Physics Today, Oct. 2010

$BiFeO_3$

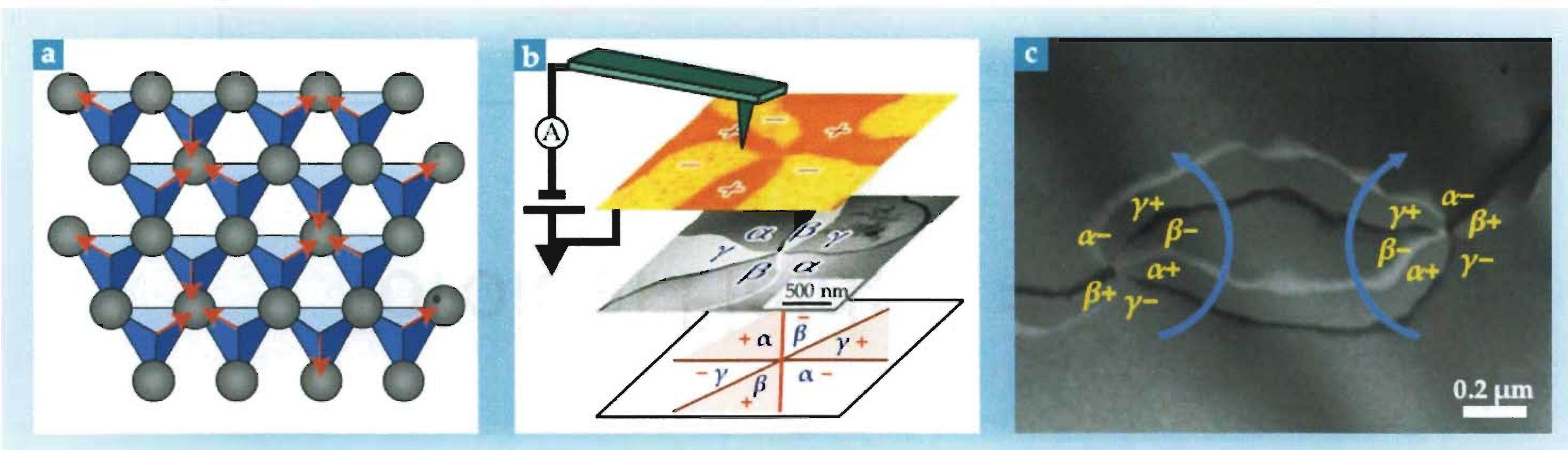


$TbMnO_3$

$BaNiF_4$

Spiral magnetism and multiferroic vortices

YMnO3



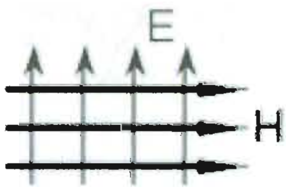
Toroidal Field: G = E x H

Type	Micro. property	Macro. property	Force field
Ferroelastic	Deformation	Strain	Stress
Ferromagnetic	Magnetic moment	Magnetization	Magnetic field
Ferroelectric	El. dipole moment	Polarization	Electric field
Ferrotoroidic	Magnetic vortex	Toroidization	Toroidal field

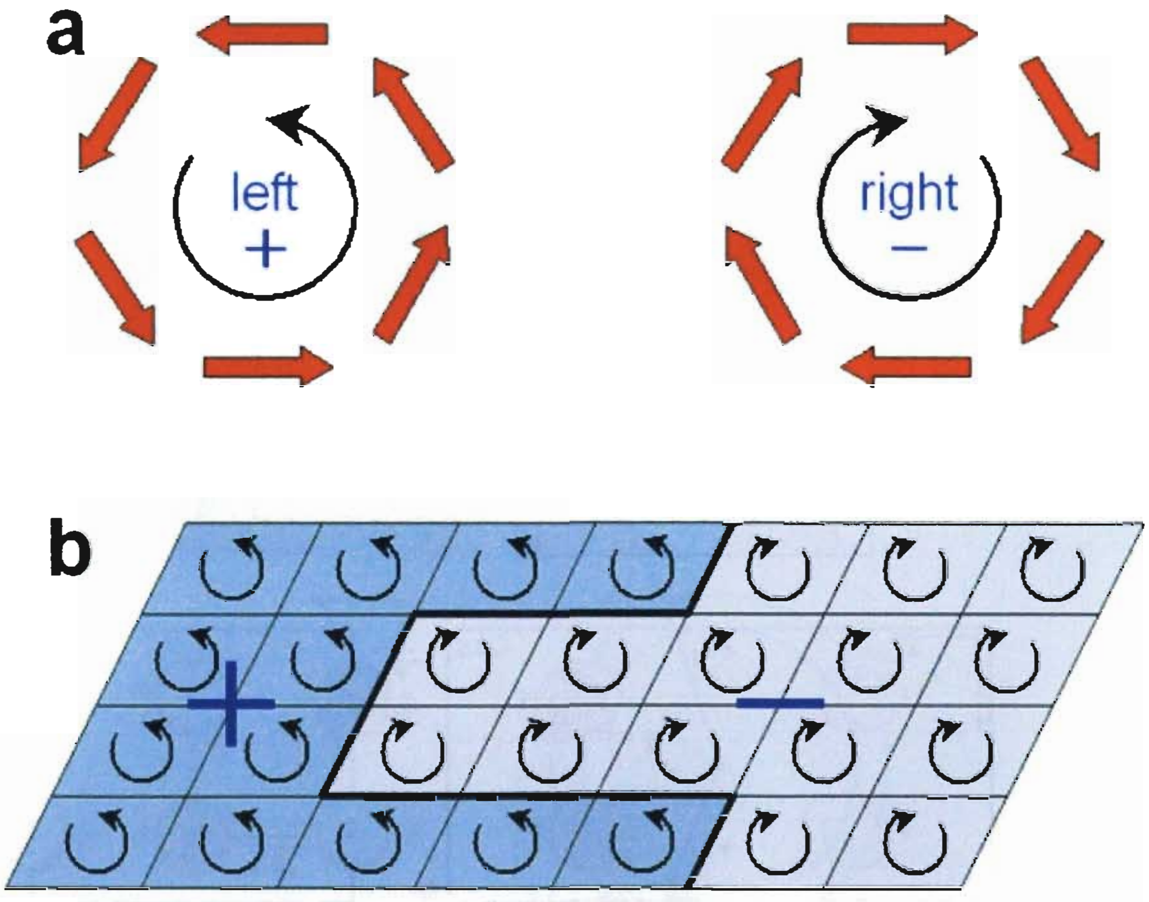
"Toroidal field": A field asymmetric under space inversion and time reversal

(1) A magnetic vortex field $\nabla \times \mathbf{H} \neq 0$

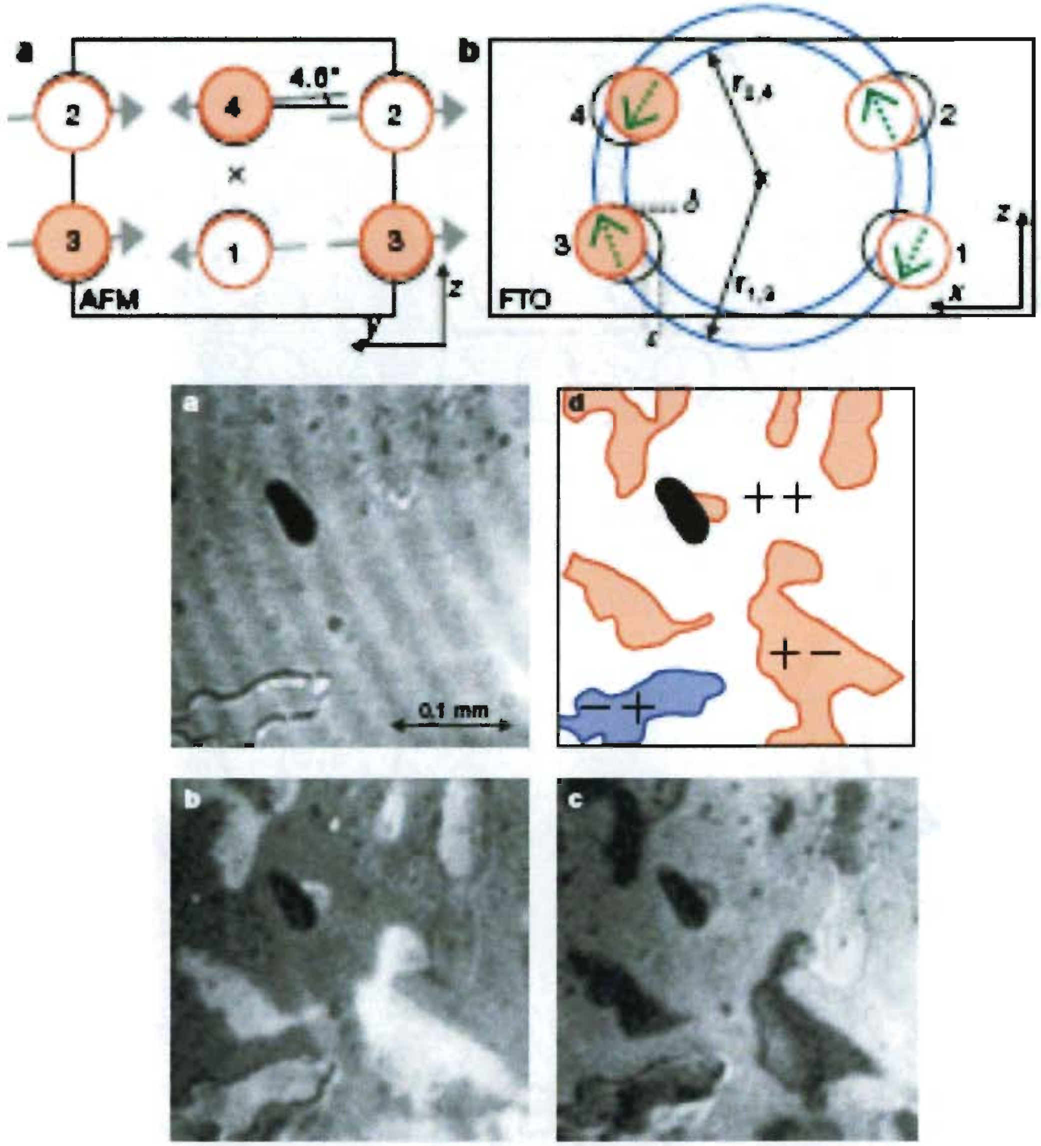
(2) Crossed magnetic and electric fields $\mathbf{E} \perp \mathbf{H}$



Toroidal domains

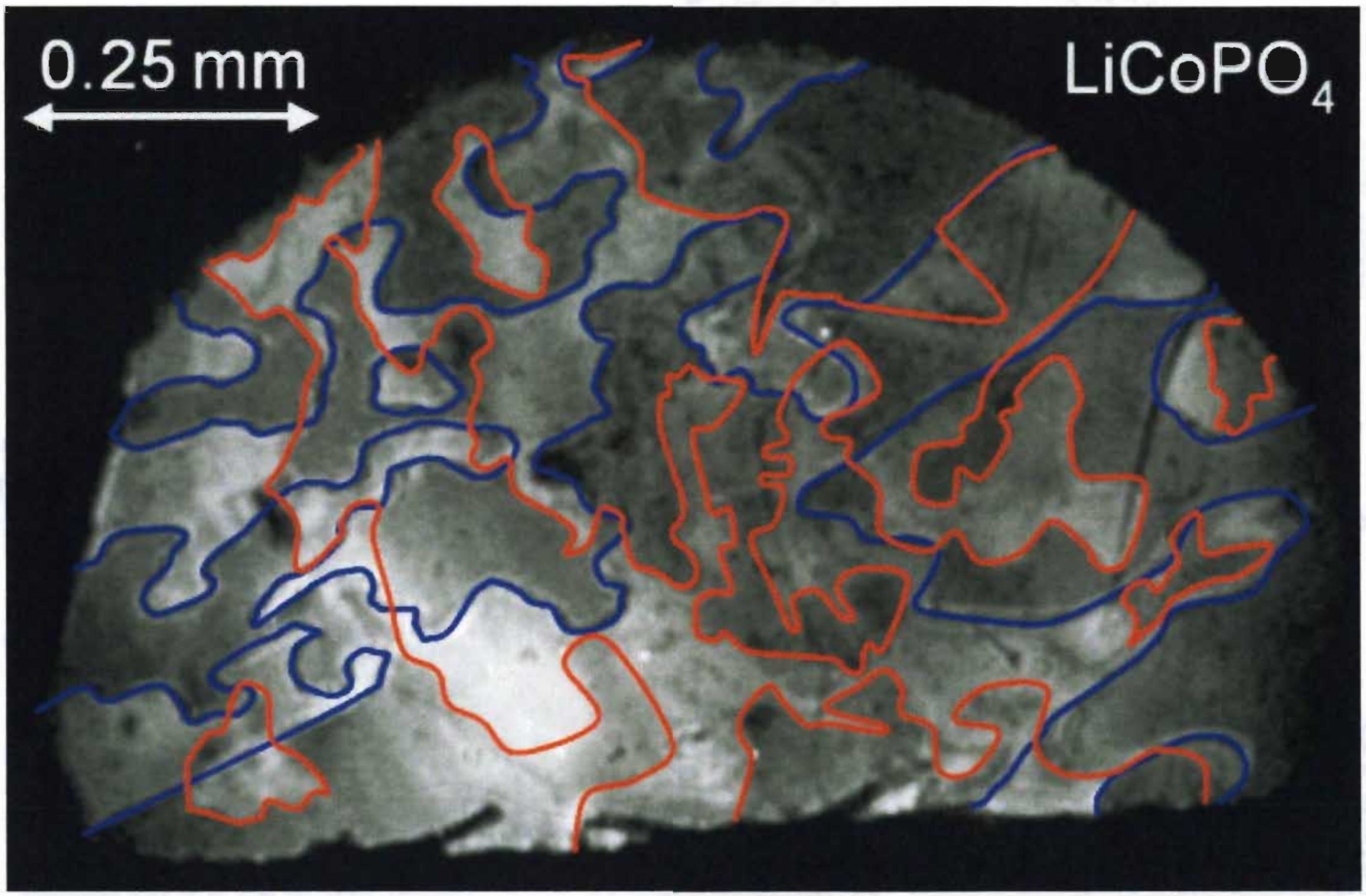


Ferrotoroidic Domain Walls

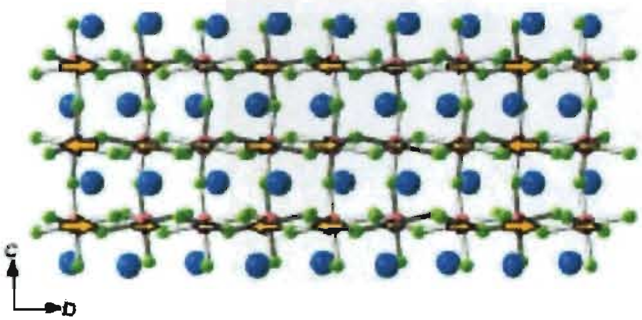


Van Eken et al., Nature 449, 702 (2007): $LiCoPO_4$

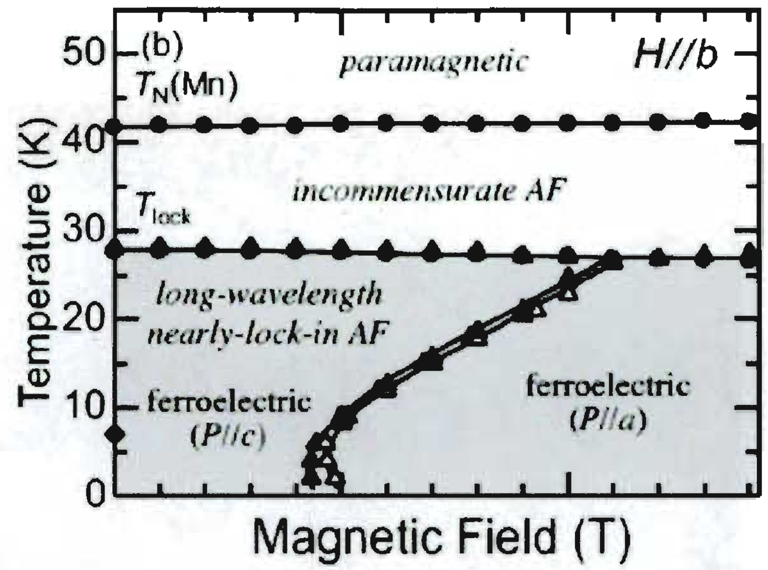
Coexisting AFM and Ferrotoroidic walls



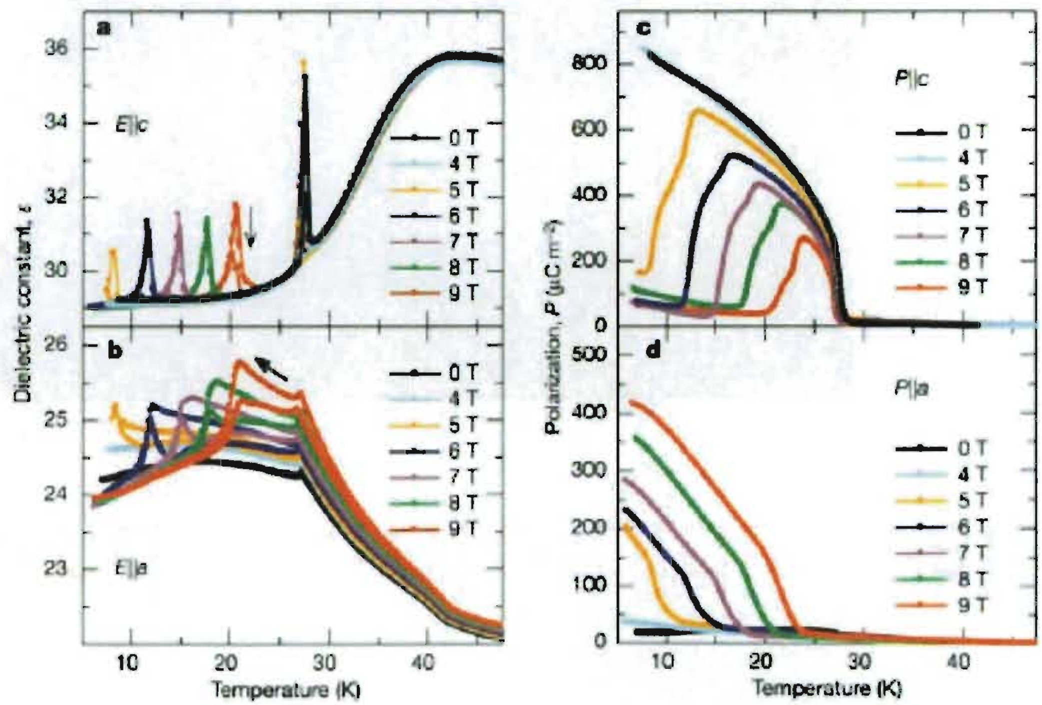
M control of P (H)



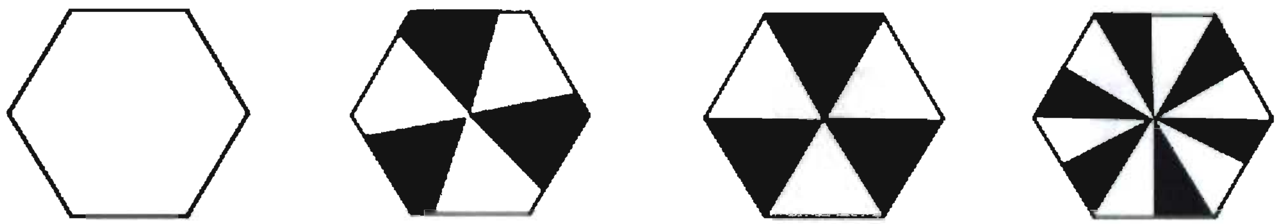
$TbMnO_3$



Kimura et al.,03-05



2D Magnetic Point Groups

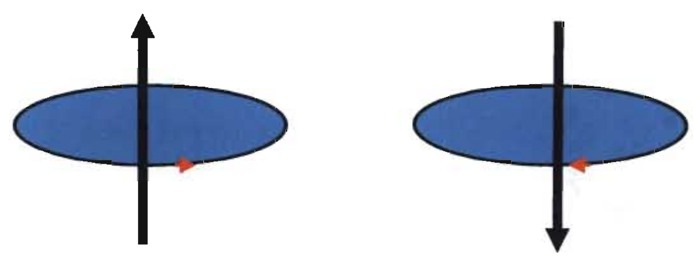


6mm 6' 6'm'm 6m'm'

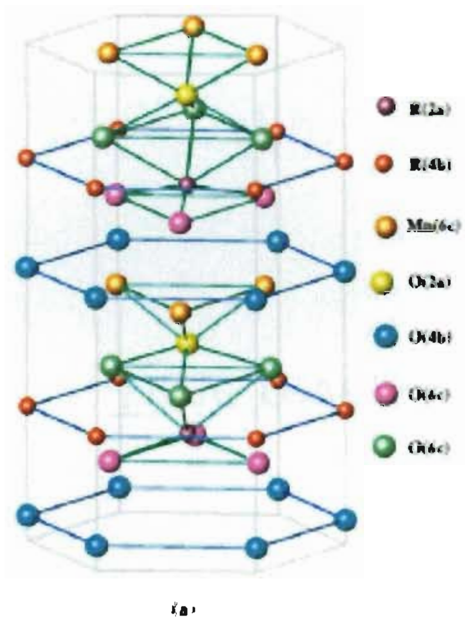
Symmetry of uncolored and colored hexagons

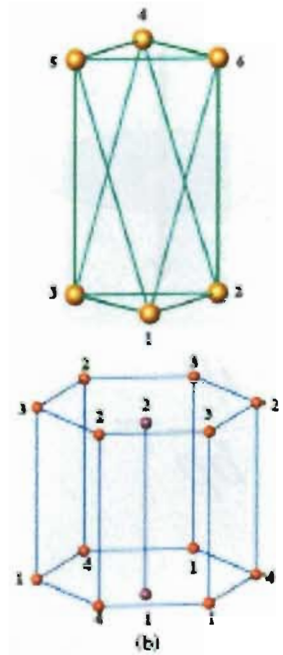
Time reversal: $i = \frac{dq}{dt}$ $-i = \frac{dq}{d(-t)}$

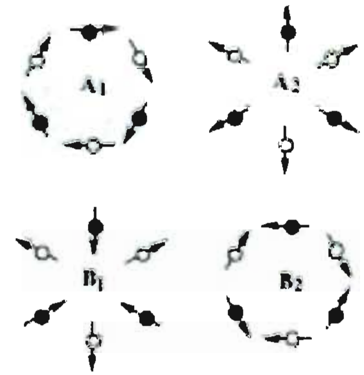
Spin flip:

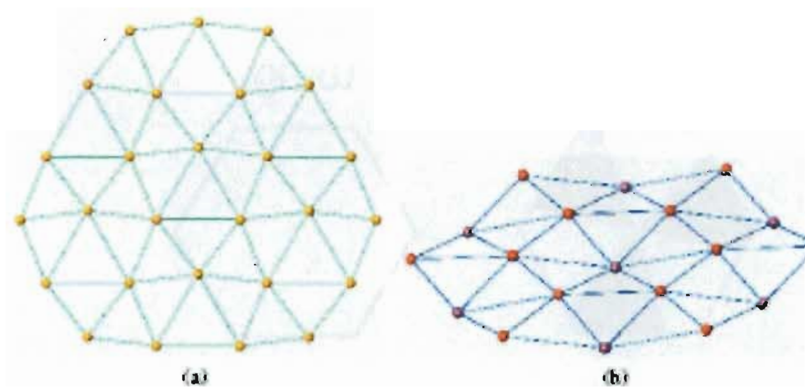


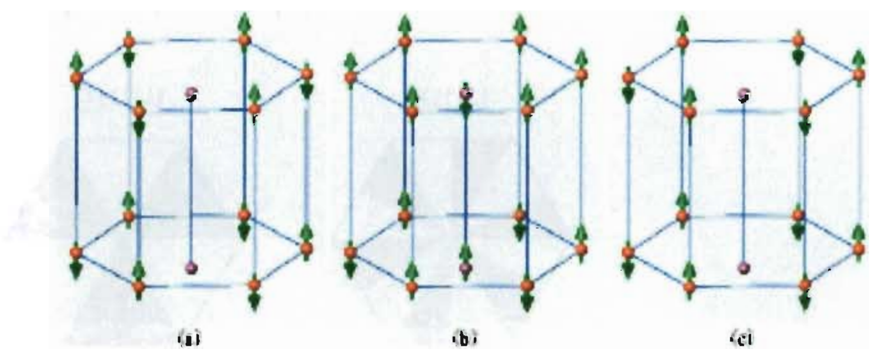
RMnO$_3$: R=Ho, Er, Tm, Yb, Lu, Y, Sc











I. Munawar, S.S. Curnoe, J. Phys. Cond. Matt. 18, 9575 (2006)

Th. Lonkai et al., JAP 93, 8191 (2003): Weak interlayer coupling

Conclusions

- Multiferroics: simultaneously ferromagnetic (M), ferroelectric (P), ferroelastic (e).
- Ferrotoroidic materials.
- Magnetoelectrocaloric effect.
- Toroidocaloric effect.
- 2D multiferroic and toroidic materials.
- Synthesis of new materials.
- Notion of color symmetry.
- Phase transitions within toroidic subgroups.
- Free energy: F(P,M,T,e), domain walls, microstructure simulation.

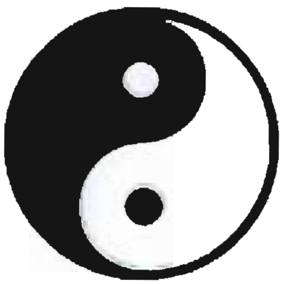


Fig. 1. T'ai-chi T'u.

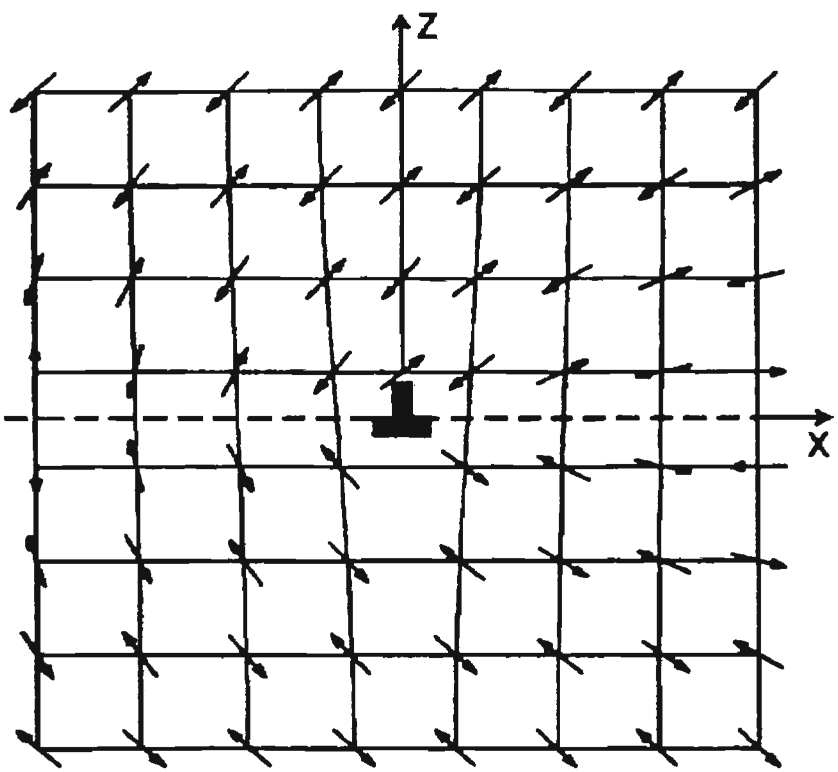
REMARKS

- Multiferroics as metamaterials (NIM).
- Spintronics and "Straintronics".
- Ferroic glasses: strain glass, toroidic glass.
- Multiferroic & magnetoelectric tweed.
- Quantum paraelectrics, paraferroics.
- Quantum criticality in multiferroics.
- Metamagnets: metaferroics, metaelectrics.

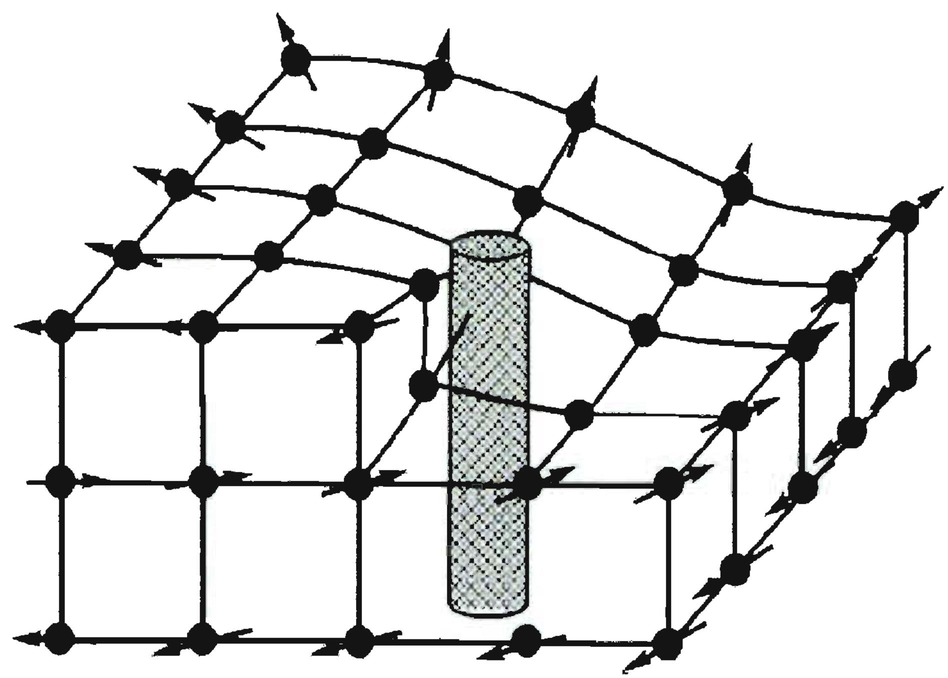
(J.W. Kim, PNAS 106, 15573, 2009).

DISLOCATIONS IN MAGNETIC CRYSTALS

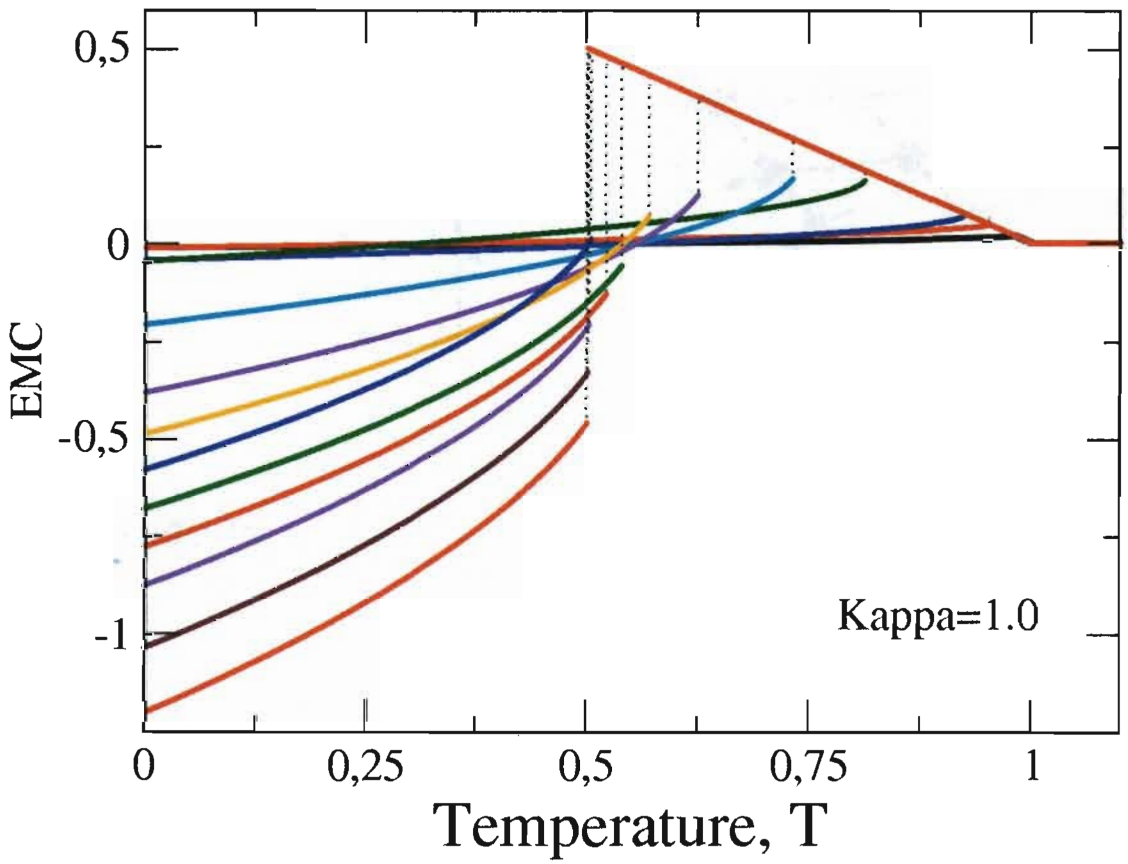
EDGE: AFM spin ordering



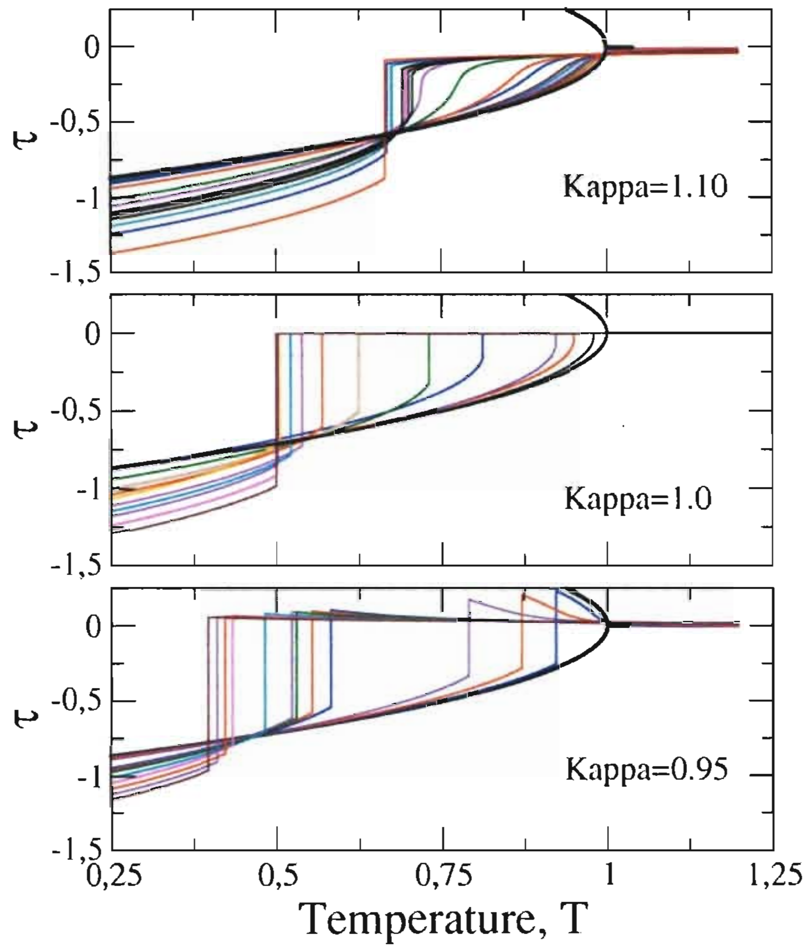
SCREW: spiral spin distribution



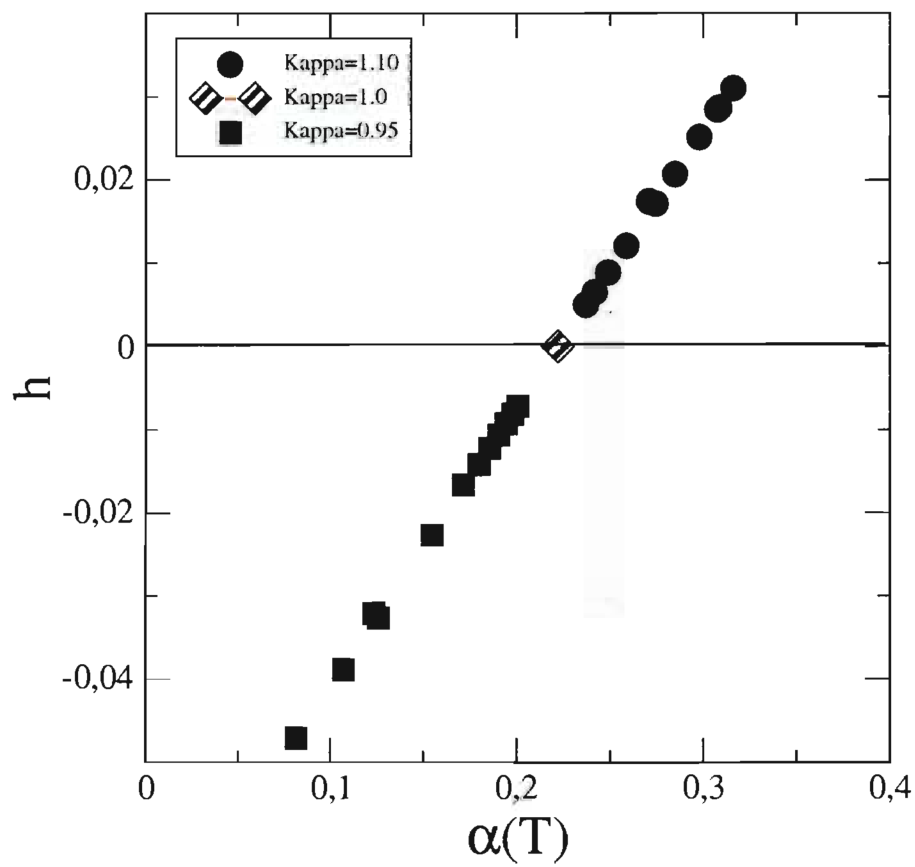
TOROIDOCALORIC EFFECT



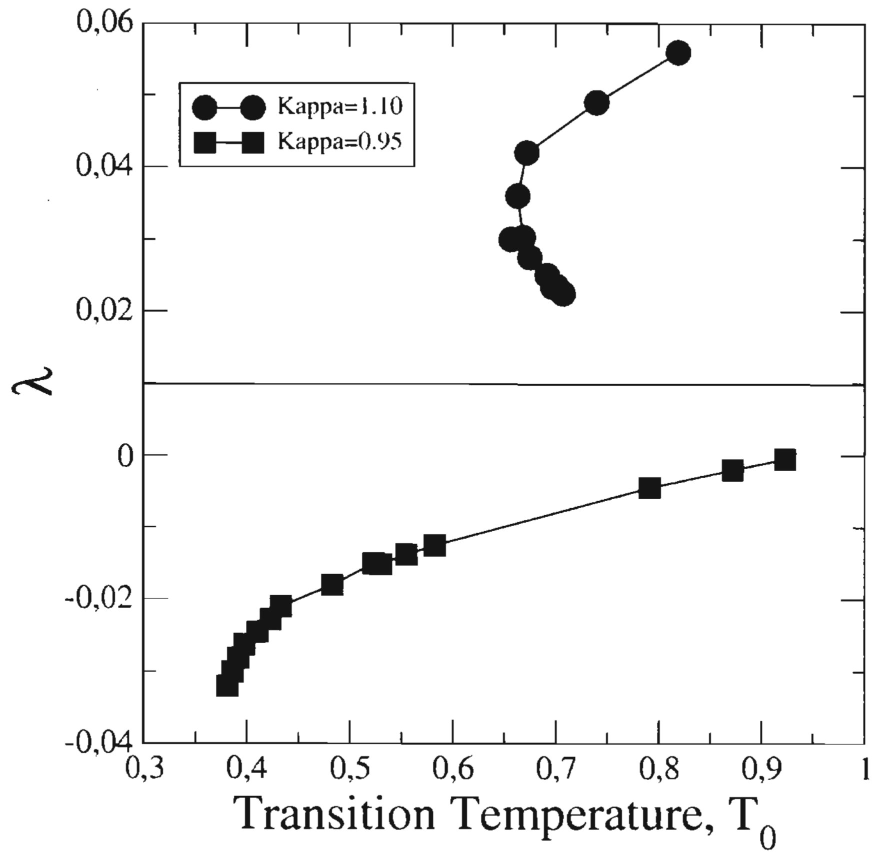
TOROIDAL ORDER PARAMETER



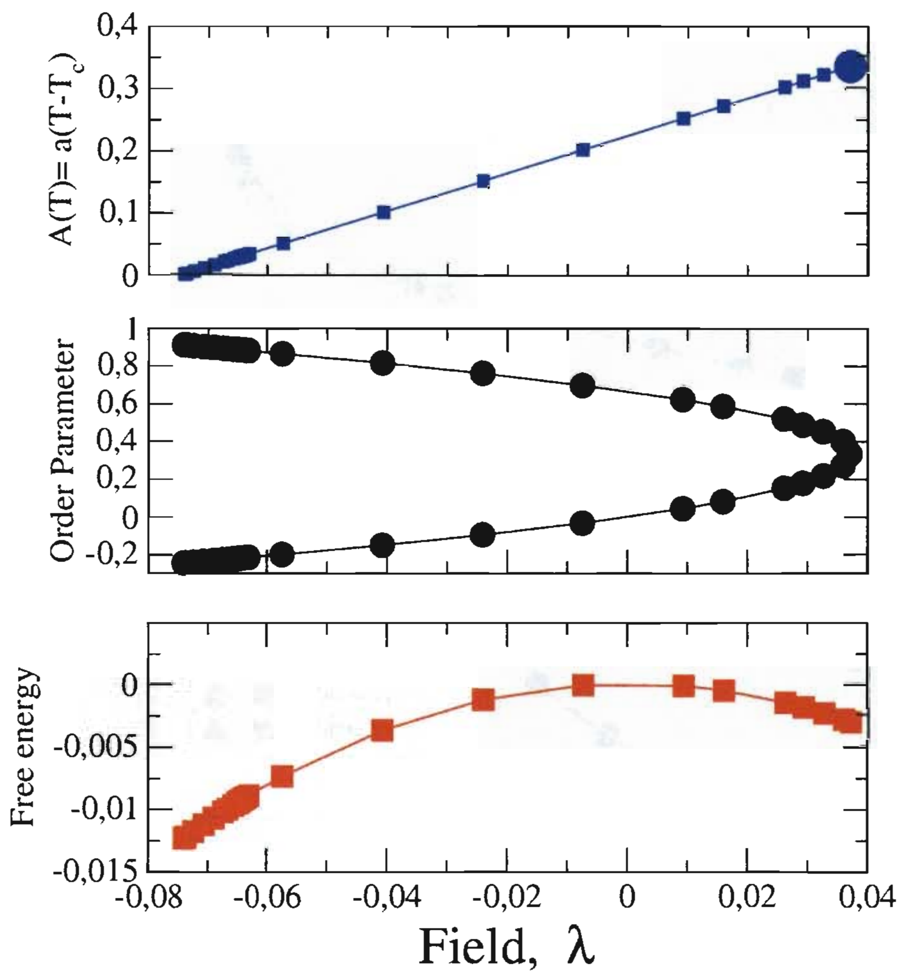
RESCALED PHASE DIAGRAM



FIELD DEPENDENCE



PHASE DIAGRAM



LANDAU FREE ENERGY FOR FERROTOROIDICS:

$$F(T, \mathbf{T}, \mathbf{P}, \mathbf{M}) = \frac{1}{2}a_0(T - T_c^0)\tau^2 + \frac{1}{4}b\tau^4 + \frac{1}{2}\chi_p^{-1}P^2 + \frac{1}{2}\chi_m^{-1}M^2 + \kappa\mathbf{T}\cdot(\mathbf{P}\times\mathbf{M}) - \mathbf{G}\cdot\mathbf{T} - \mathbf{H}\cdot\mathbf{M} - \mathbf{E}\cdot\mathbf{P}$$

$$\frac{\partial G}{\partial \mathbf{P}} = \chi_p^{-1}\mathbf{P} - \mathbf{E} + \kappa(\mathbf{M}\times\mathbf{T}) = 0$$

$$\frac{\partial G}{\partial \mathbf{M}} = \chi_m^{-1}\mathbf{M} - \mathbf{H} + \kappa(\mathbf{T}\times\mathbf{P}) = 0$$

TOROIDOCALORIC EFFECT:

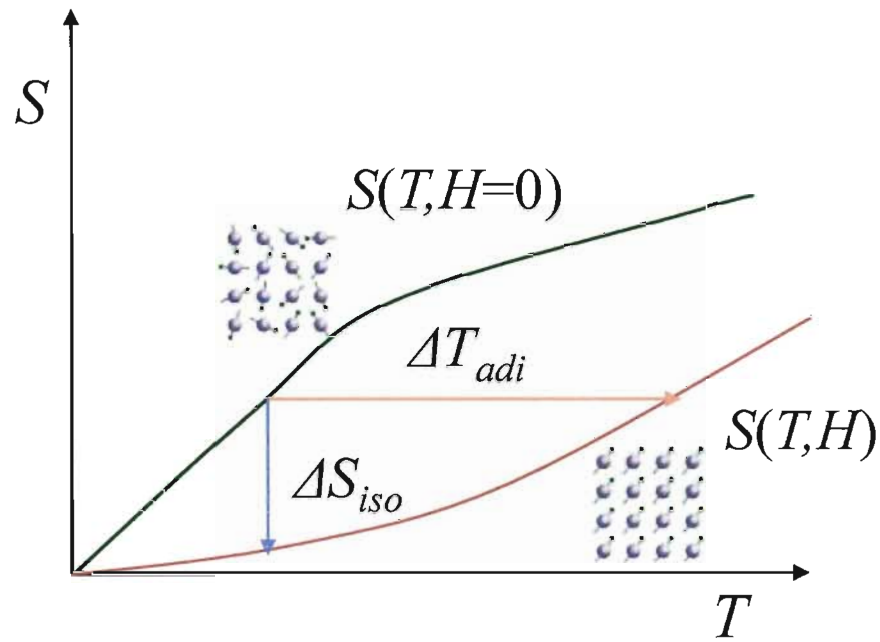
$$\Delta S(T, 0 \rightarrow \mathbf{H}) = \int_0^{\mathbf{H}} \left(\frac{\partial \mathbf{M}}{\partial T}\right)_{T,\{\mathbf{H}\}} d\mathbf{H}$$

$$\Delta T(T_{in}, 0 \rightarrow \mathbf{H}) = -\int_0^{\mathbf{H}} \frac{T}{C} \left(\frac{\partial \mathbf{M}}{\partial T}\right)_{T,\{\mathbf{H}\}} d\mathbf{H}$$

$$\Delta S(T, 0 \rightarrow \mathbf{E}) = \int_0^{\mathbf{E}} \left[\left(\frac{\partial \mathbf{P}}{\partial T}\right)_{\mathbf{E},\mathbf{H}} + \mathbf{H} \times \left(\frac{\partial \mathbf{T}}{\partial T}\right)_{\mathbf{E},\mathbf{H}}\right] \cdot d\mathbf{E}$$

$$\Delta S(T, 0 \rightarrow \mathbf{H}) = \int_0^{\mathbf{H}} \left[\left(\frac{\partial \mathbf{M}}{\partial T}\right)_{\mathbf{H},\mathbf{E}} + \left(\frac{\partial \mathbf{T}}{\partial T}\right)_{\mathbf{H},\mathbf{E}} \times \mathbf{E}\right] \cdot d\mathbf{H}$$

MAGNETOCALORIC EFFECT:



Equations:

$$\Delta S_{iso} = \int_0^H \left(\frac{\partial S}{\partial H}\right)_T dH$$

$$\Delta T_{adi} = -\int_0^H \frac{T}{C}\left(\frac{\partial S}{\partial H}\right)_T dH$$

GIBB'S FREE ENERGY:

$$\mathbf{G} = \mathbf{E} \times \mathbf{H}, \quad \mathbf{P} = -\mathbf{T} \times \mathbf{H}, \quad \mathbf{M} = \mathbf{T} \times \mathbf{E}$$

$$dU = TdS + \mathbf{E} \cdot d\mathbf{P} + \mathbf{H} \cdot d\mathbf{M} + \mathbf{G} \cdot d\mathbf{T}$$

$$G = U - TS - \mathbf{E} \cdot \mathbf{P} - \mathbf{M} \cdot \mathbf{H} - \mathbf{T} \cdot \mathbf{G}$$

$$dG = -SdT - [\mathbf{P} + (\mathbf{H} \times \mathbf{T})] \cdot d\mathbf{E} - [\mathbf{M} + (\mathbf{T} \times \mathbf{E})] \cdot d\mathbf{H}$$

$$\frac{d\mathbf{E}}{dT} = -\frac{\Delta S}{\Delta \mathbf{P} + \mathbf{H} \times \Delta \mathbf{T}}$$

$$\frac{d\mathbf{H}}{dT} = -\frac{\Delta S}{\Delta \mathbf{M} + \mathbf{E} \times \Delta \mathbf{T}}$$

Thermodynamics

Thermodynamic description of system *K*: take temperature and generalized forces $[T, \{y_i\}]_{i=1\ldots N}$ as independent variables. Then:

$$dS = \left(\frac{\partial S}{\partial T}\right)_{y_{i=1\ldots N}} dT + \sum_{j=1}^{N}\left(\frac{\partial S}{\partial y_j}\right)_{T, y_{i\neq j}} dy_j,$$

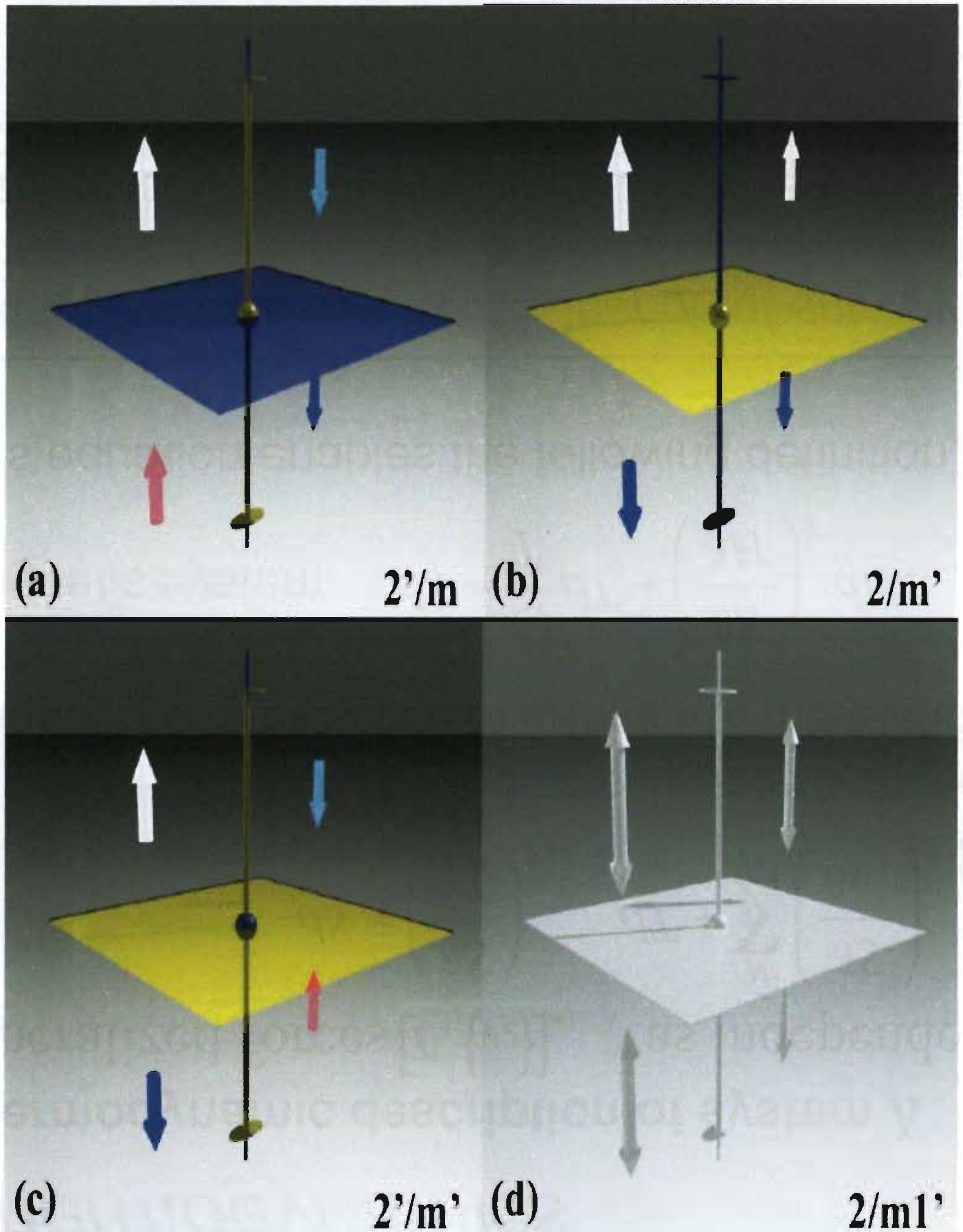
where $(\partial S/\partial T) = C/T$ and y_i són *external fields* (or generalized forces) that couple to the system (pressure, magnetic field, electric field,...).

Magnetic system: $$dS = \frac{C}{T}dT + \left(\frac{\partial S}{\partial H}\right)_T dH.$$

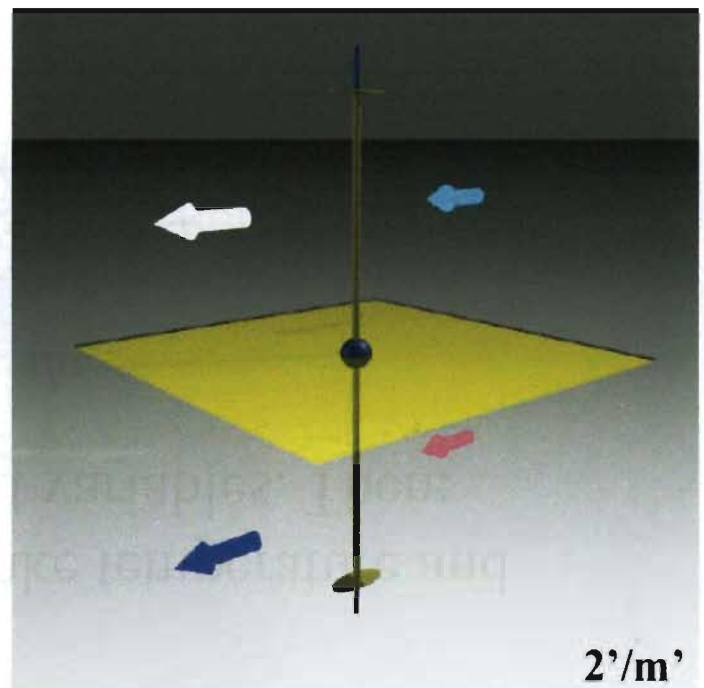
This equation enables the following definition,

Magnetocaloric effect: *Change of entropy or change of temperature of a magnetic system arising respectively from the isothermal or adiabatic application/removal of an external magnetic field*

MAGNETIC POINT GROUPS DERIVED FROM: 2/m

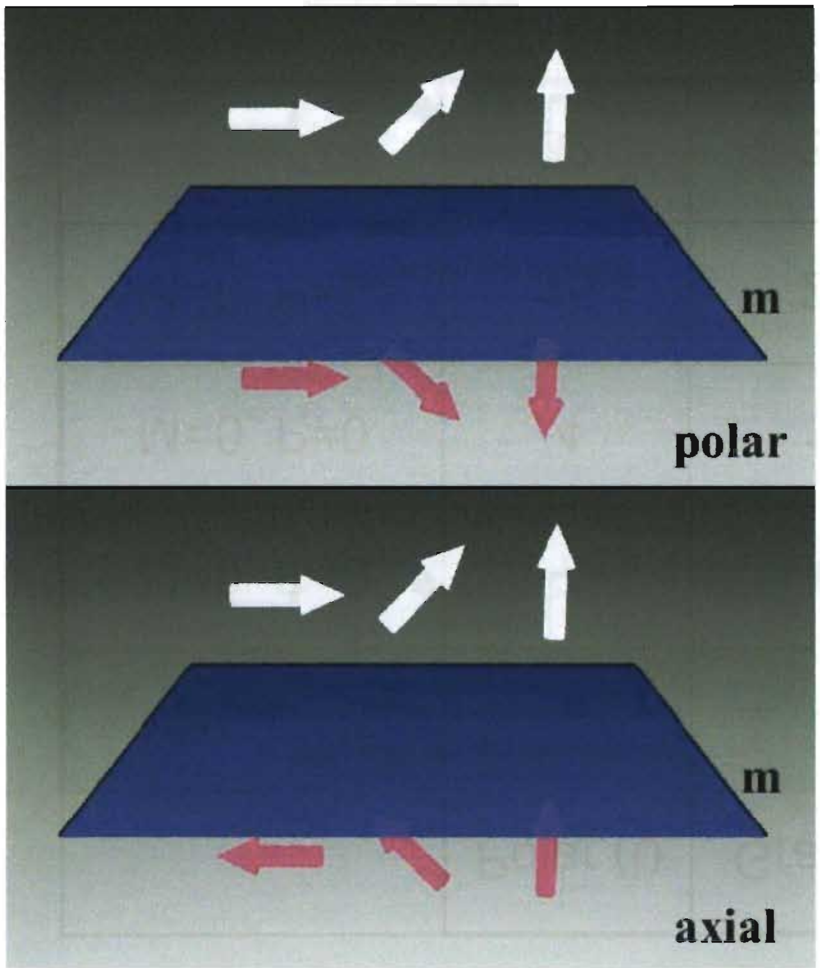


Ferromagnetic state

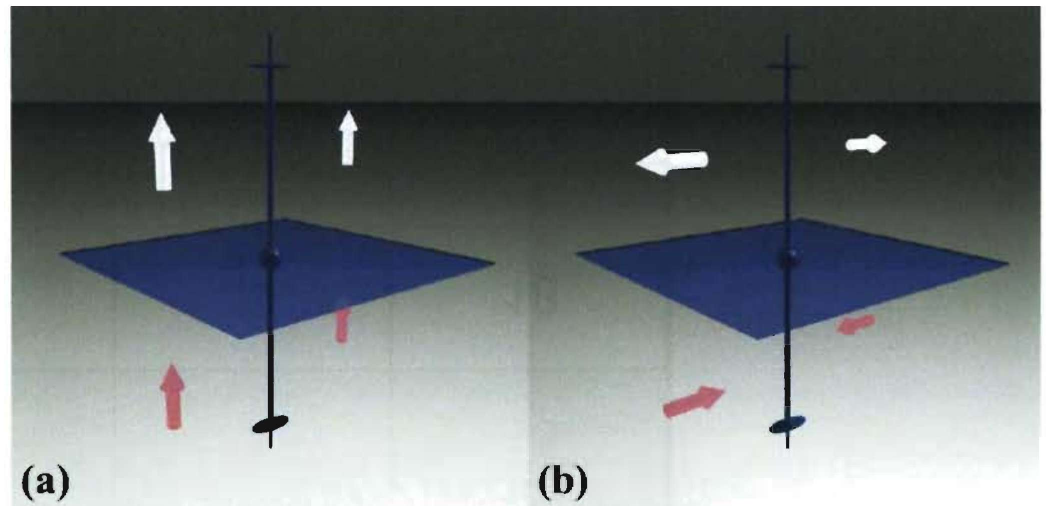


MAGNETIC SYMMETRY

MIRROR PLANE



POINT GROUP: 2/m



M. De Graef, 2009

3D Magnetic Point Groups

	Polar (I)	Gray (II)	Mixed (III)	Total
M≠0, P≠0	6	0	7	13
M≠0, P=0	7	0	11	18
M=0, P≠0	4	10	4	18
M=0, P=0	15	22	36	73
	32	32	58	122

AFE/Chiral

AFE/Chiral

AFM/Chiral

AFM/Chiral

1651