LA-UR- 11-05235

Approved for public release; distribution is unlimited.

Title: Phase Transitions in Ferroic and Multiferroic Materials

Author(s): Avadh B. Saxena, 113324, T-4 LANL
Turab Lookman, 169767, T-4 LANL

Intended for: Meeting/Conference: Seminar at Beijing Computational Science Research Center, Beijing, China, 09/11/2011 - 09/13/2011
Harbin Institute of Technology, Harbin, China, 09/16/2011 - 09/17/2011

Los Alamos
NATIONAL LABORATORY
EST. 1943

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the Los Alamos National Security, LLC for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

Form 836 (7/06)

Phase Transitions in Ferroic and Multiferroic Materials

Avadh Saxena

Los Alamos National Lab, USA

Abstract:

Materials exhibiting ferroic phase transitions are ubiquitous in nature. Ferroic materials are those which possess two or more orientation states (domains) that can be switched by an external field and show hysteresis. Typical examples include ferromagnets, ferroelectrics and ferroelastics which occur as a result of a phase transition with the onset of spontaneous magnetization (M), polarization (P) and strain (e), respectively. A material that displays two or more ferroic properties simultaneously is called a 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, memory devices and shape memory elements in biomedical technology. First I will provide a historical perspective on this technologically important class of materials and then briefly illustrate the relevant concepts. I will discuss their properties, model the transitions at mesoscale and describe their microstructure. I will emphasize the role of long-range, anisotropic forces that arise from either the elastic compatibility constraints or the (polar and magnetic) dipolar interactions in determining the microstructure. Finally, I will discuss the role of color symmetry in multiferroic transitions and consider the effect of disorder on ferroic transitions.

Beijing and Harbin abstract

LA-UR-10-03487

PHASE TRANSITIONS IN FERROIC AND MULTIFERROIC MATERIALS

Avadh Saxena (Los Alamos National Lab)

1. Crystals (polar, strain, shuffle): space.

2. Interfaces and intrinsic inhomogeneity.

3. Magnetism: space and time; color symmetry.

4. Magnetoelectrics: P, M coupling; strain.

5. 1D, 2D vs 3D magnetic transitions.

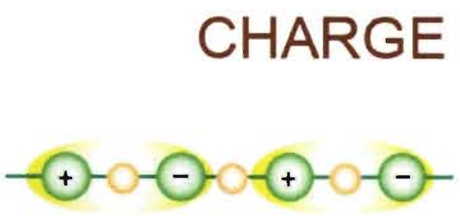
6. Magnetoelectric chains; Diperiodic (layer) magnetism: hexagonal manganites; $BiFeO_3$, $BaMnF_4$

Three Pillars of Functional Materials/Devices

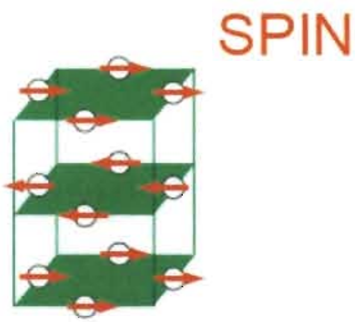
CHARGE SPIN LATTICE

Tholos Temple at Delphi, Greece, 300 BC

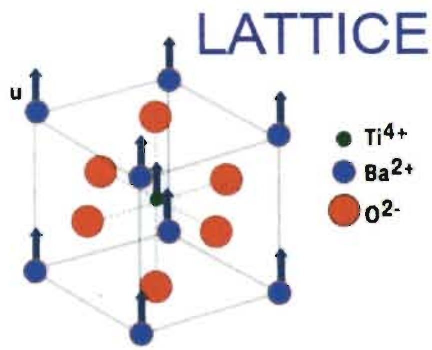
The Three Pillars of Functionality



Directional charge ordering



Antiferromagnetism

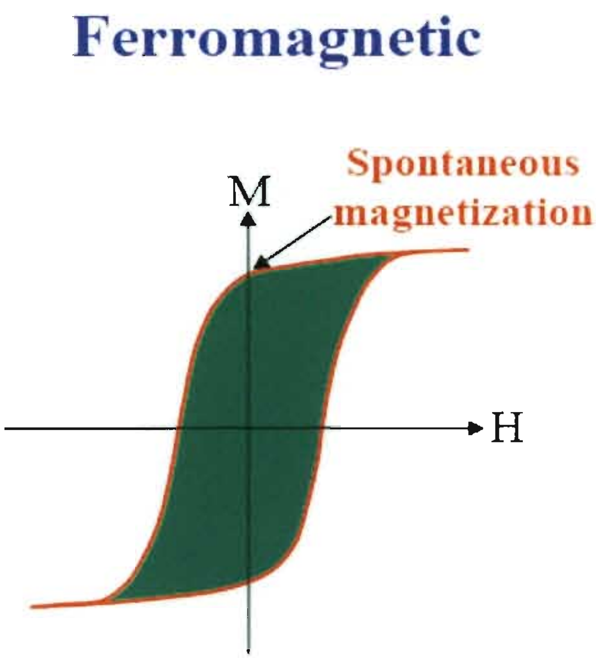


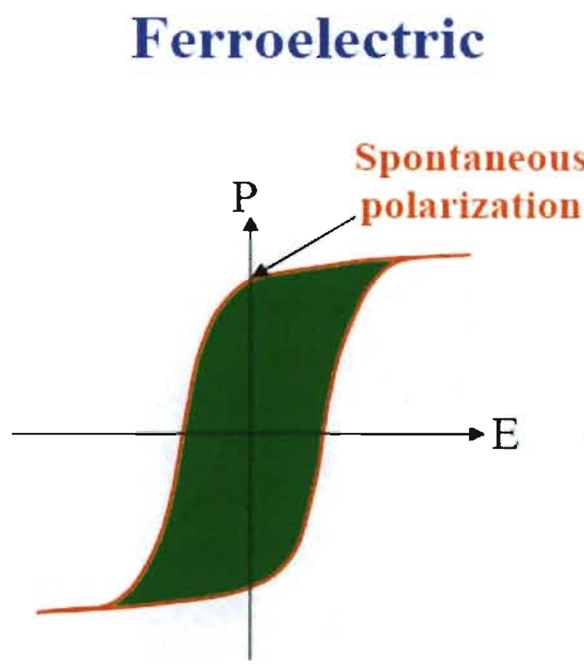
Tetragonal distortion

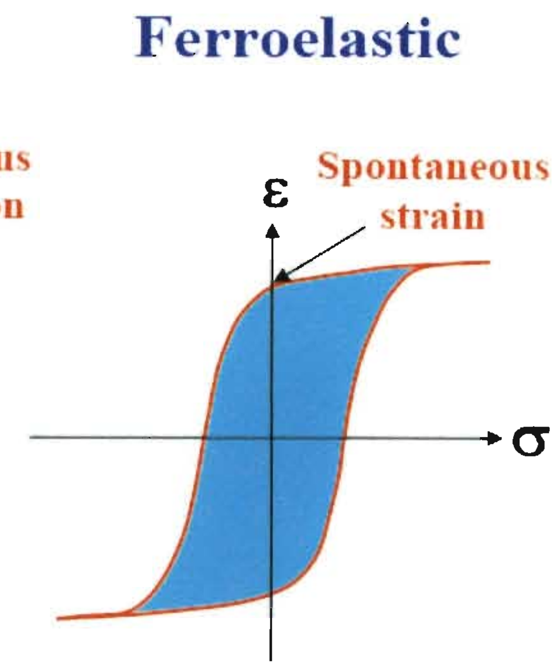
Orbitals: spatial distribution of charge

Ferroic phenomena

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

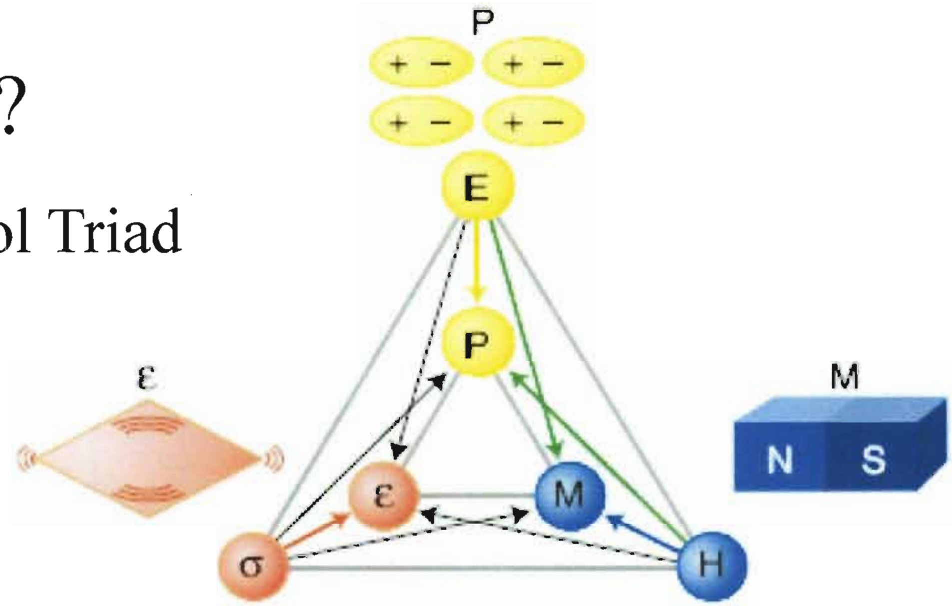






What is a multiferroic?

The Multiferroic phase-control Triad



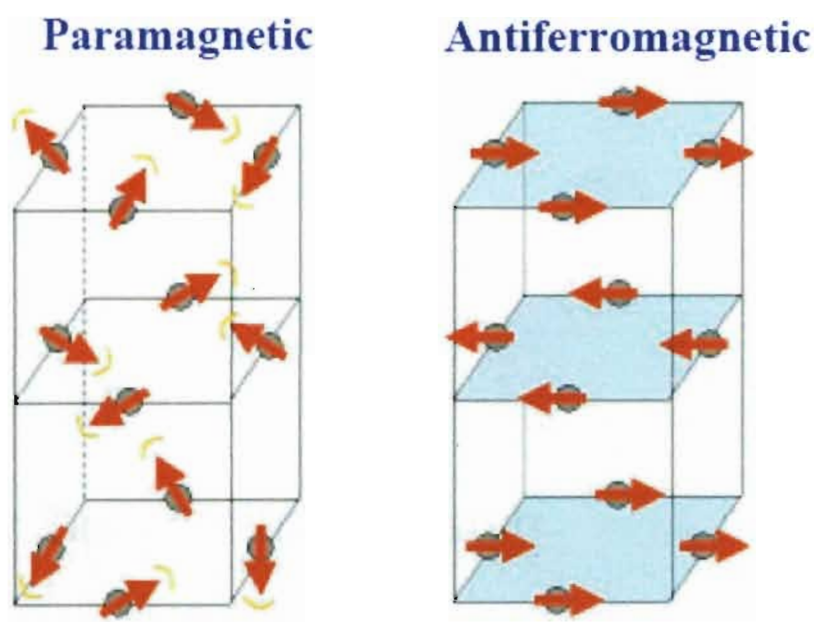
(Spaldin and Fiebig, Science 2005)

A compound that displays two or more ferroic states

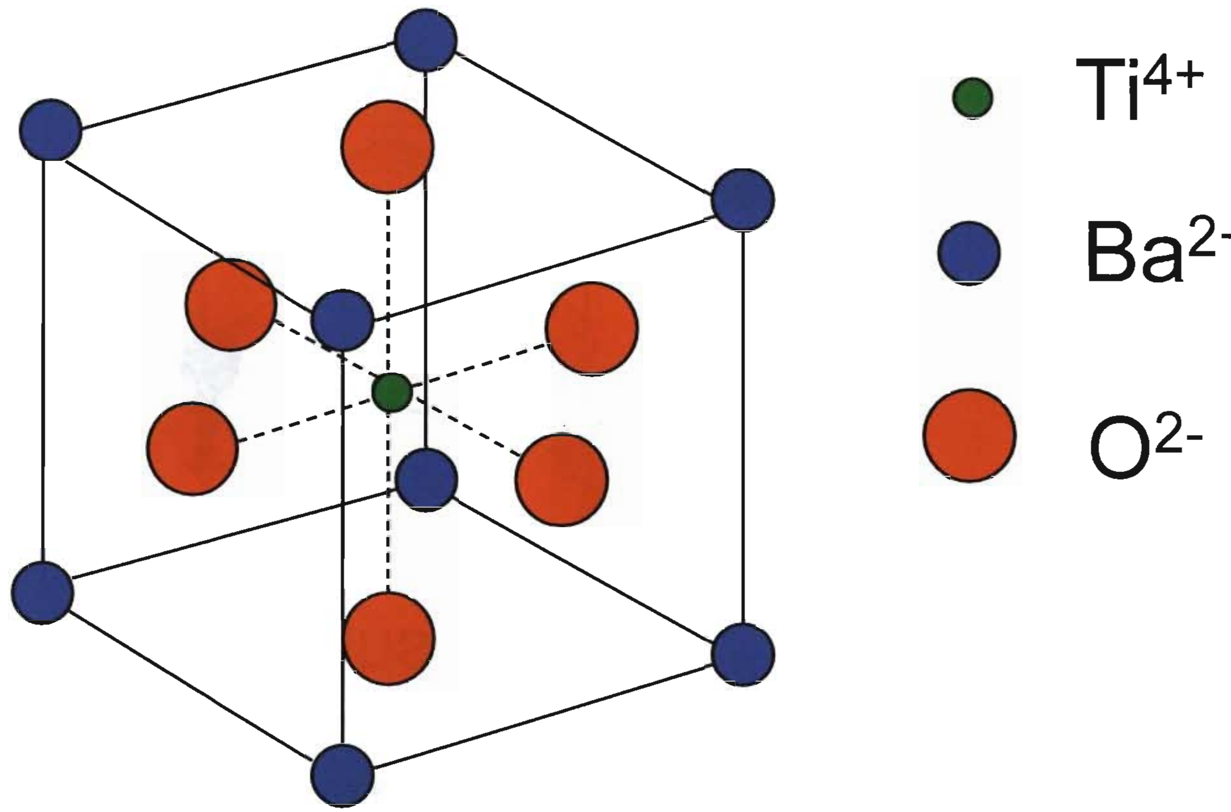
- Ferromagnetic – spontaneous magnetization M
- Ferroelectric – spontaneous polarization P
- Ferroelastic – spontaneous strain ε

Ferromagnetic phenomena

- Spontaneous polarization upon cooling
  - Spin polarization - (anti)ferromagnetic



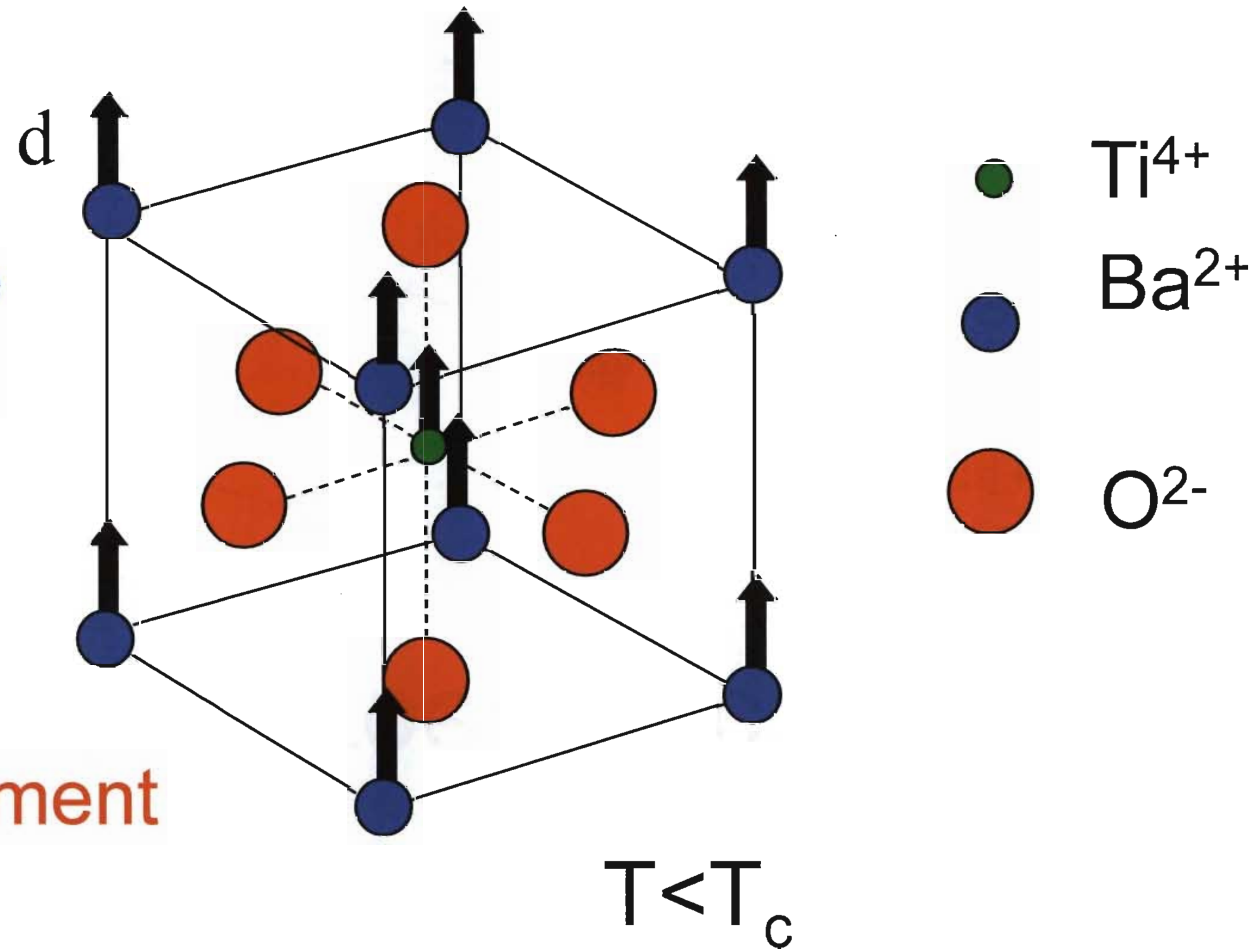
Textbook Ferroelectric: $BaTiO_3$



$T > T_c$

$BaTiO_3$

Structural Phase Transition



Effective charge

$$P = d\,Z^{*}$$

Dipole Moment

•Example: Cubic to Tetragonal

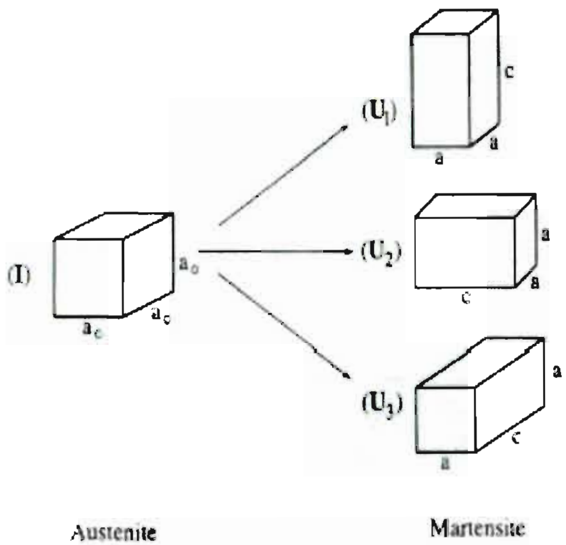


Figure 4.4: The three variants of martensite in a cubic to tetragonal transformation.

Ferroelastic

$Fe_{0.7}Pd_{0.3}$

AUSTENITE

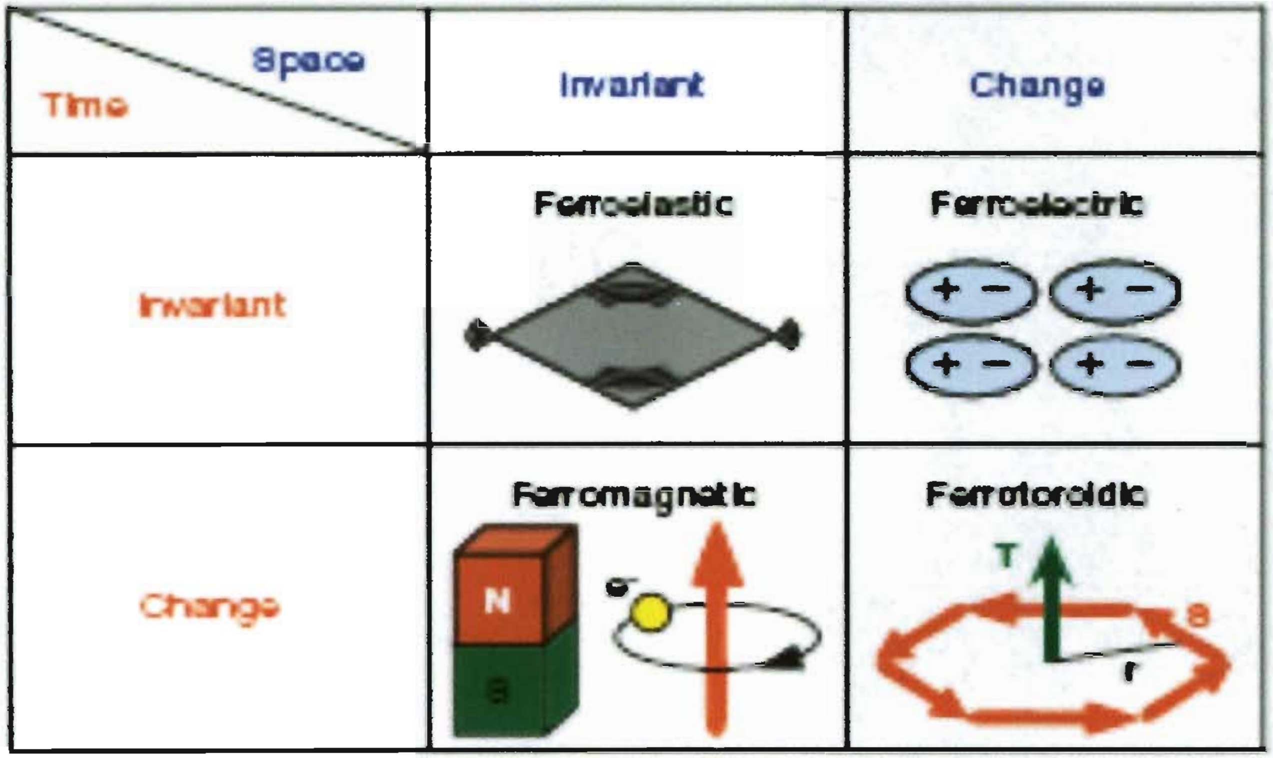
TWEED

$T_0 = 268\ K$

(TWINNED) MARTENSITE

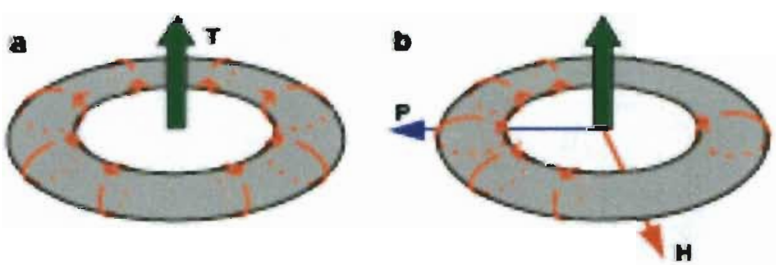
Sugiyama (1985)

Ferrotoroidics



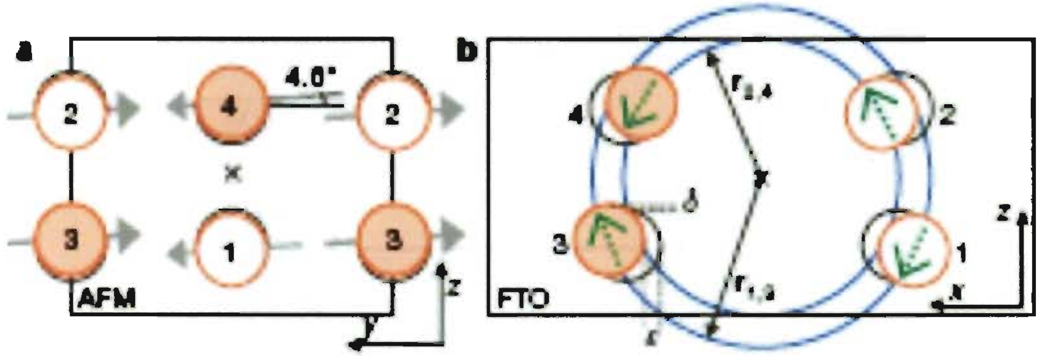
$$M = T \times E$$

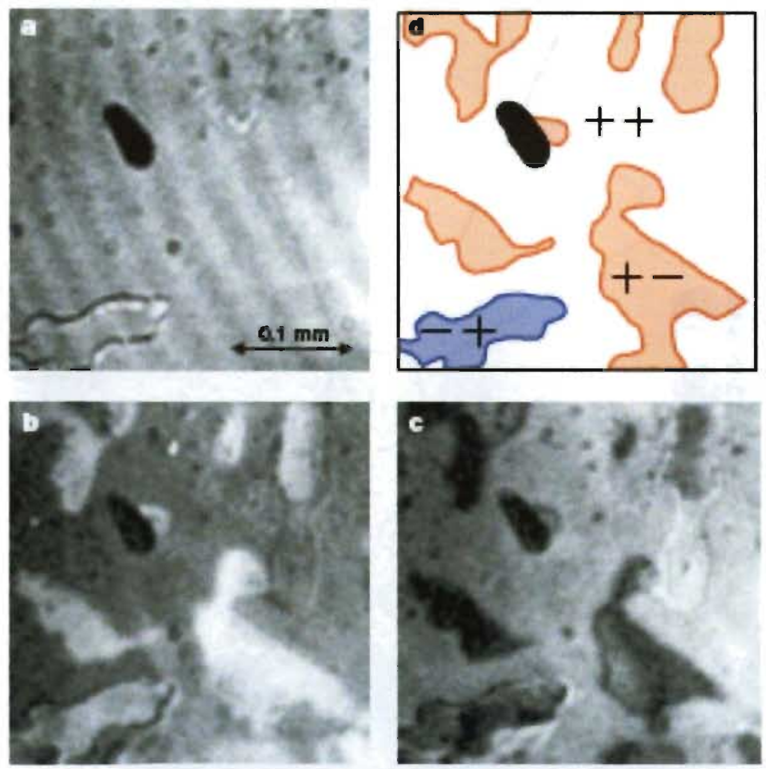
$$P = -T \times H$$



1	$\bar{1}$	1′	$\bar{1}'$	Basis	
1	1	1	1	ε_{ij}	Strain
1	−1	1	−1	P	Polarization
1	1	−1	−1	M	Magnetization
1	−1	−1	1	T	Toroidal moment

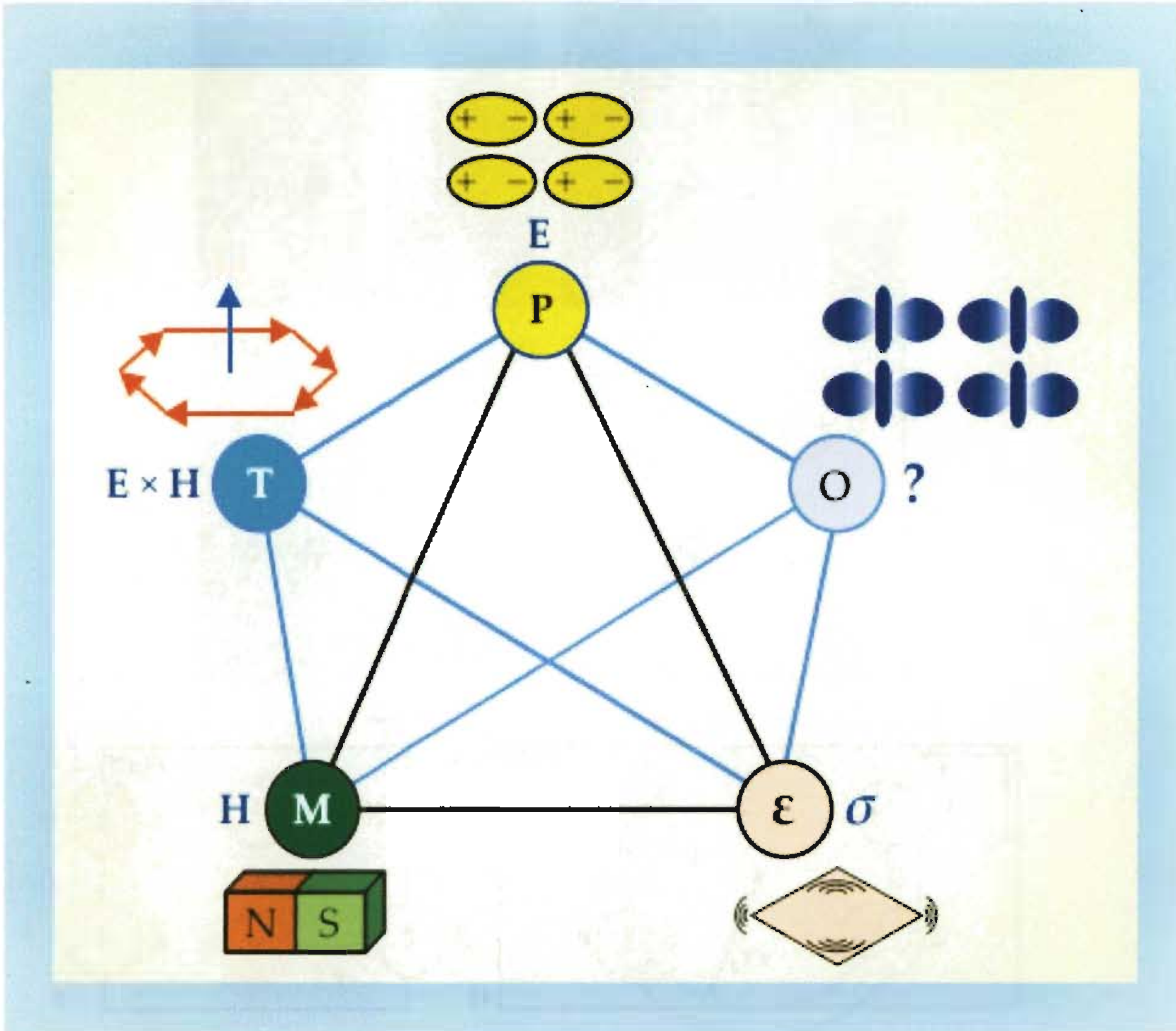
Ferrotoroidic Domain Walls





Van Eken et al., Nature 449, 702 (2007): LiCoPO$_4$

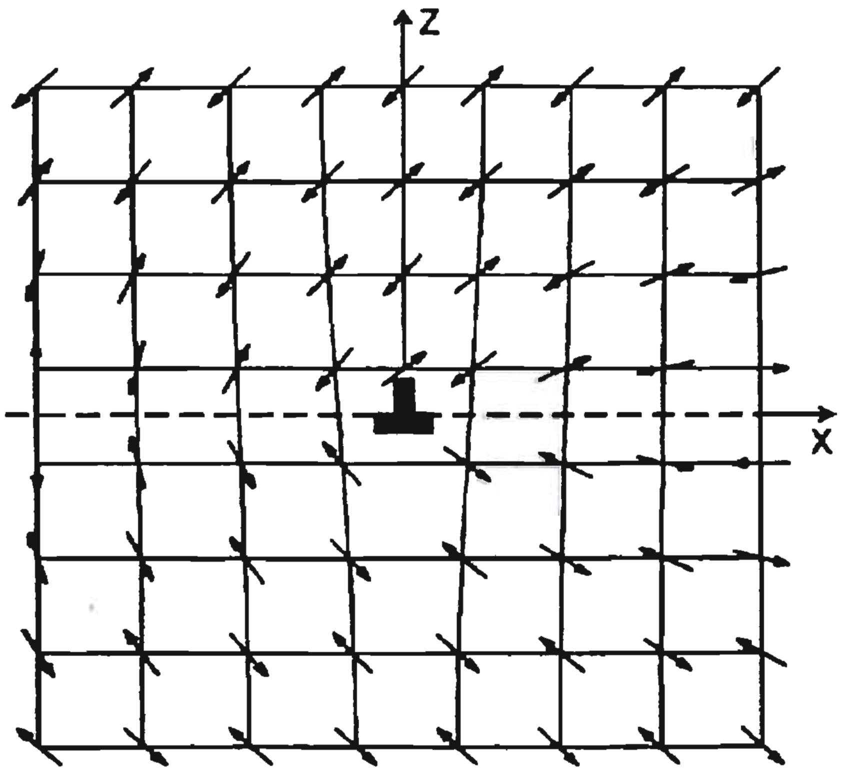
INTERACTIONS in MULTIFERROICS



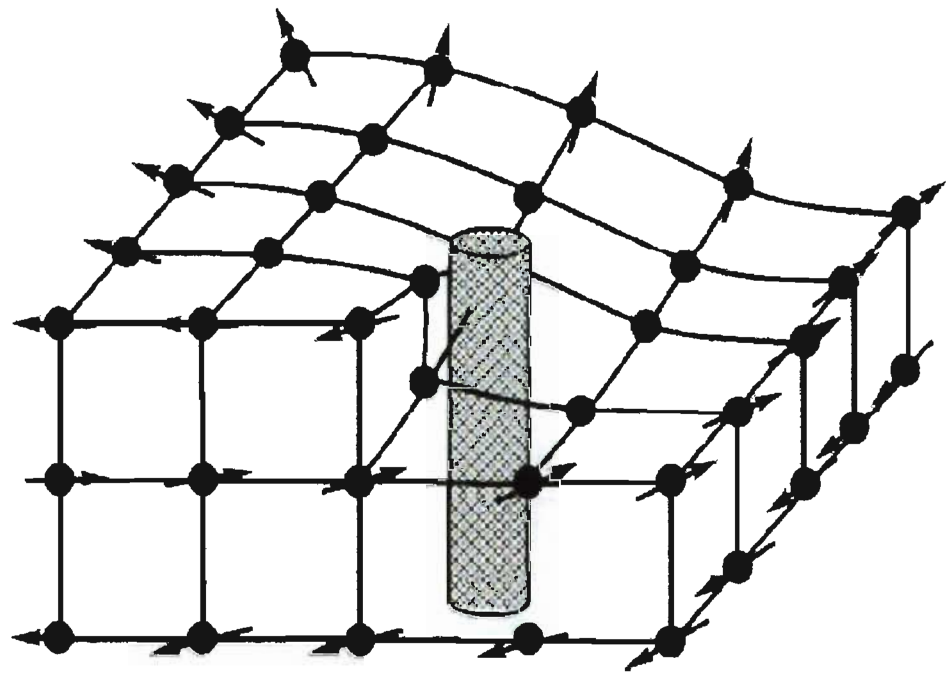
Spaldin et al., Physics Today, Oct. 2010

DISLOCATIONS IN MAGNETIC CRYSTALS

EDGE: AFM spin ordering



SCREW: spiral spin distribution



MICROSTRUCTURE

&

INTRINSIC INHOMOGENEITY

•**First half of 20th. Century**:-uniform, defect free single crystals

W. Pauli, 1931

"One should'nt work with semiconductors, that is a filthy mess: who knows whether they really exist".

R. Feynman, ~ 1955

"Its the dirt that we need to control and engineer".

•**Second half of 20th. Century**:-

defects

---synthesis of large and pure Si crystals

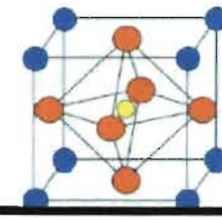
disorder

---- notions of Anderson localization, mobility edge, spin glasses

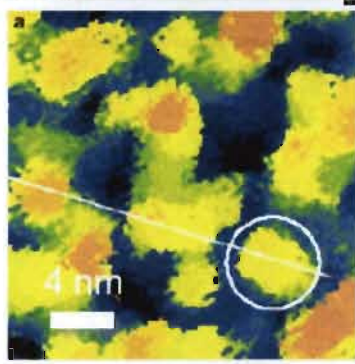
Impact

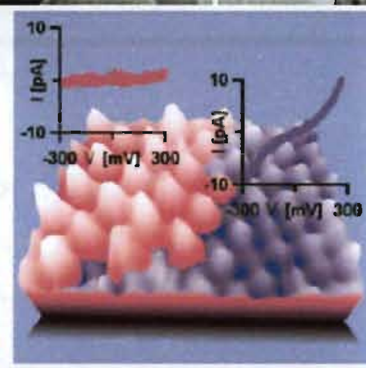
---transistor era, semiconductor electronics, computer industry

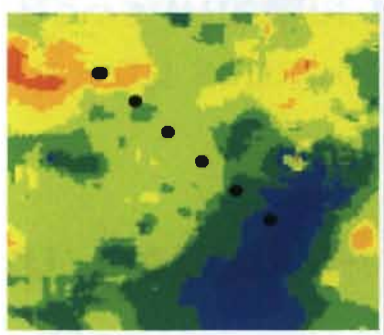
- **21st Century:- many-atom unit cells**

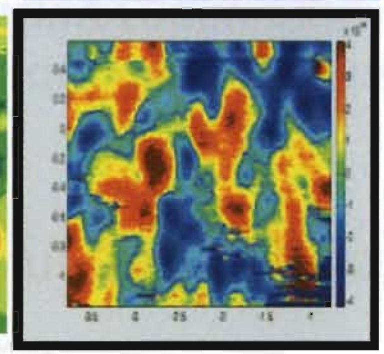


Materials ⇨ Intrinsic inhomogeneity ⇨ Function



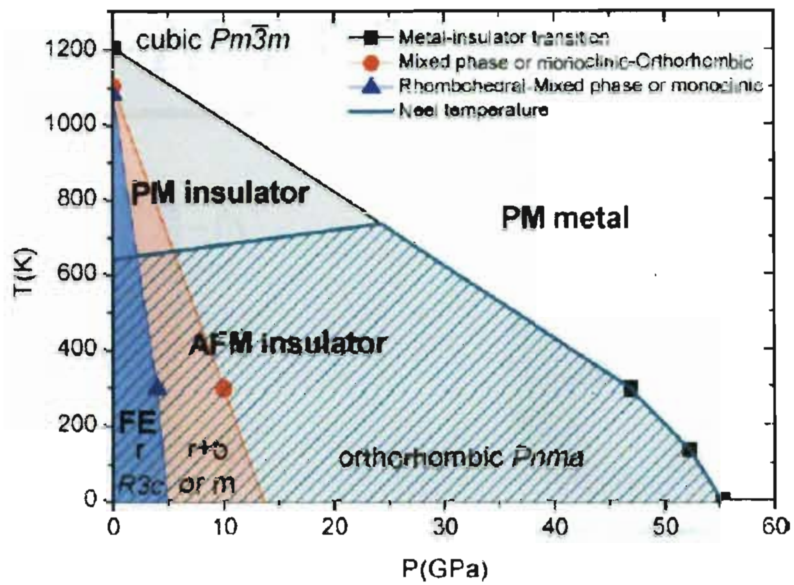




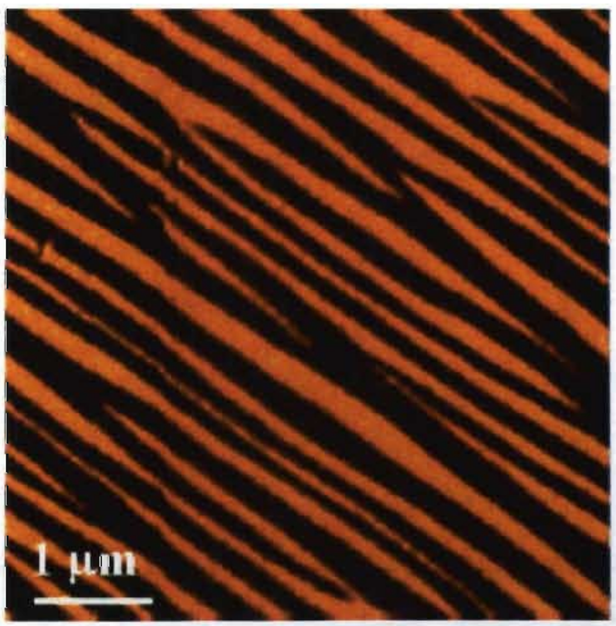


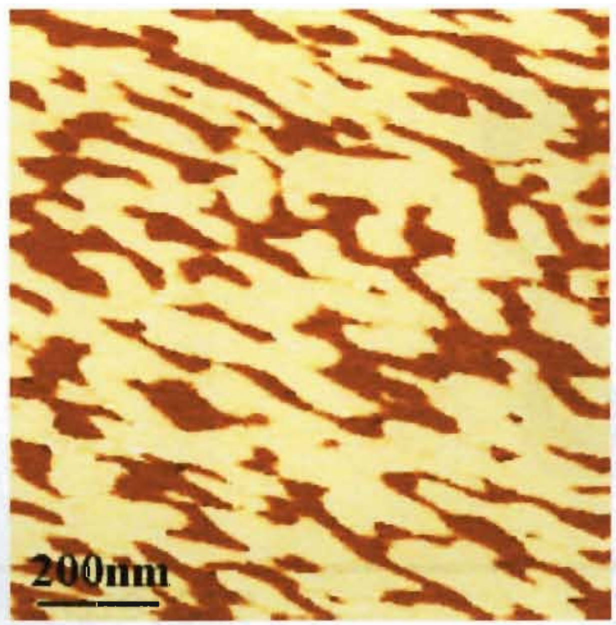
Materials	Function
• Shape Memory Alloys	• Residual strain
• Ferroelectrics	• Polarisation
• Ferromagnetics / Magnetoelastics	• Magnetism/ Magnetostriction
• Magnetoelectrics	• Polarization/ Magnetization
• Manganites	• Collosal Magneto-Resistance
• Cuprates Pnictides	• High Tc Superconductivity

Intrinsic inhomogeneity in $BiFeO_3$ thin films



G. Catalan, J.F. Scott, Adv. Mater. 21, 2463 (2009)

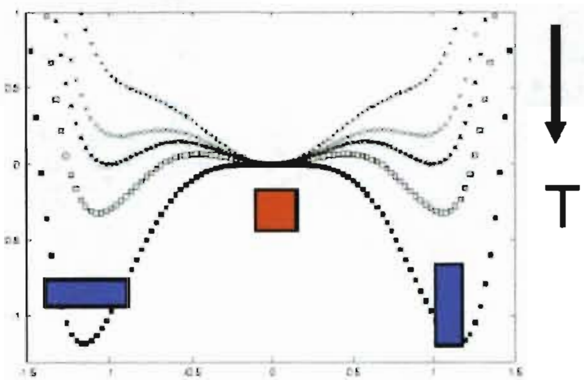




Order Parameters

Functionalities ε, P, M, ψ

Free energy



Landau, 1937

+

Spatial variations

$+\psi_o$

$|\nabla \psi|^2$

$-\psi_o$

$+\psi_o$

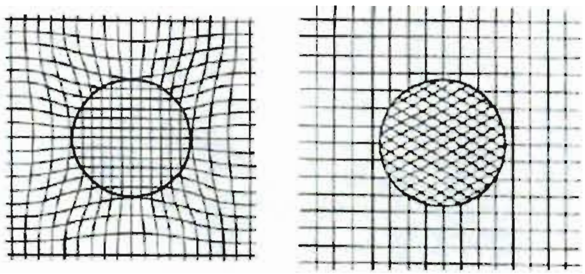
$-\psi_o$

Ginzburg, 1955

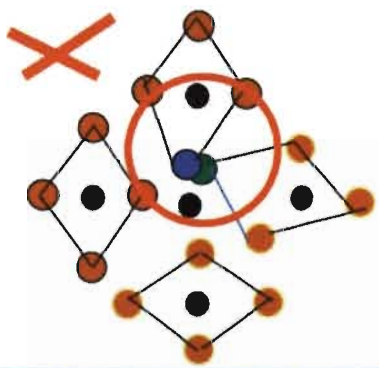
Free Energy : $F(\varepsilon, P, M, \psi : \nabla\varepsilon, \nabla\psi ..)$

Strain: lattice as an elastic template

coherent incoherent



Saint Venant Compatibility, 1864



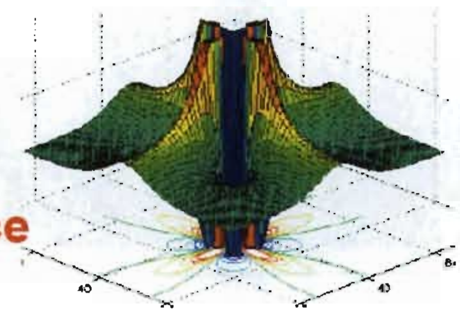
Lookman et al, PRB, 2003; 2004

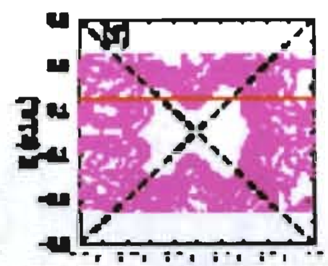
$$\nabla \times (\nabla \times \vec{\varepsilon})^T = 0$$

Strains not unique

$$\varepsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)$$

⇩





Lookman, Fellows

Constraint ⟶ **anisotropic long-range force**

•Example: Cubic to Tetragonal

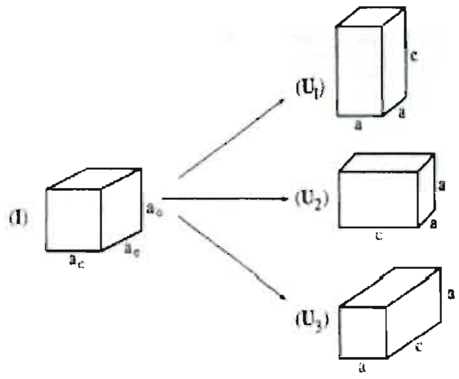
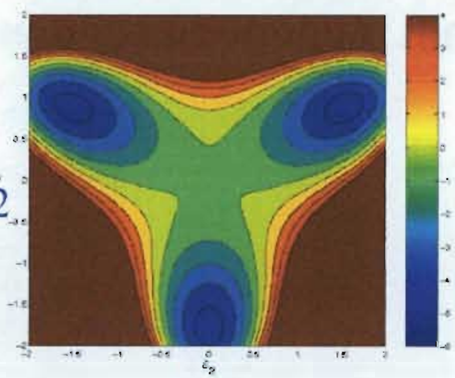


Figure 4.4: The three variants of martensite in a cubic to tetragonal transformation.

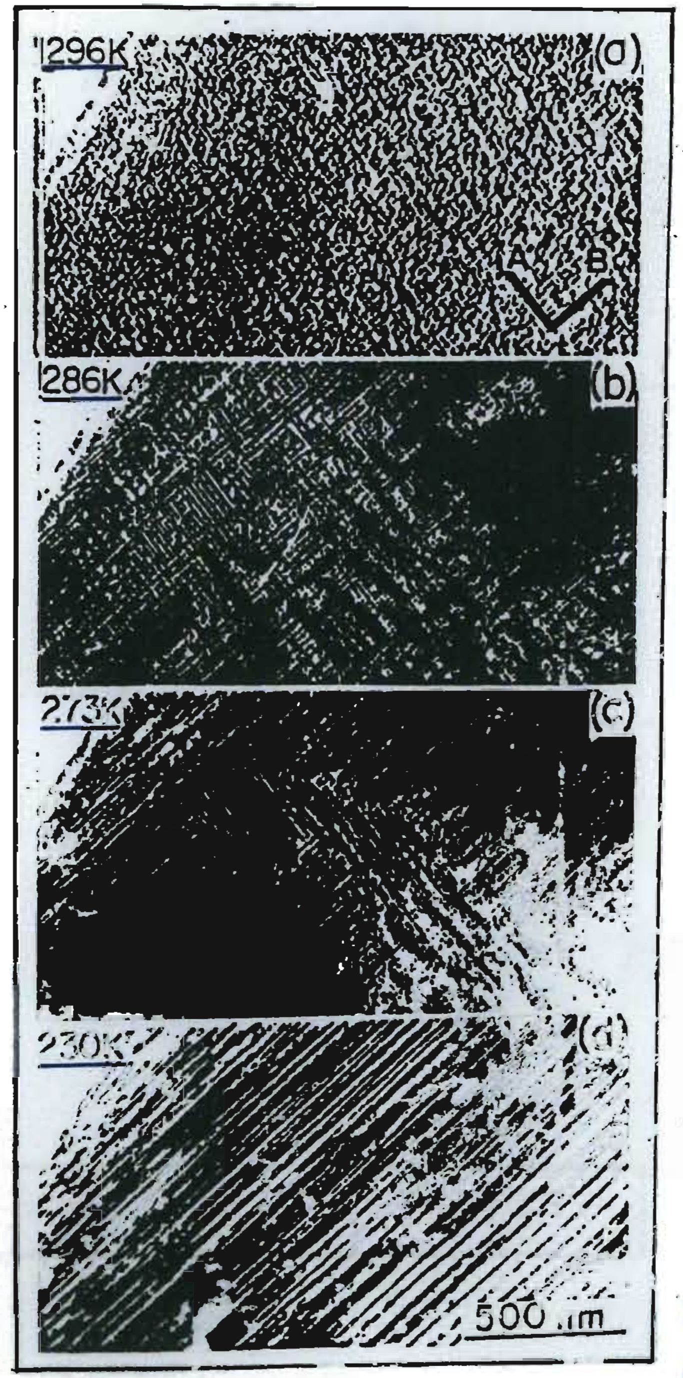
$$F\left(e_2, e_3\right)$$



Order parameter

$$\left(e_2 = \frac{\varepsilon_{xx} - \varepsilon_{yy}}{\sqrt{2}}, e_3 = \frac{\varepsilon_{xx} + \varepsilon_{yy} - 2\varepsilon_{zz}}{\sqrt{6}} \right)$$

Barsch &Krumhansl, 84, Falk, 83



$Fe_{0.7}Pd_{0.3}$

AUSTENITE

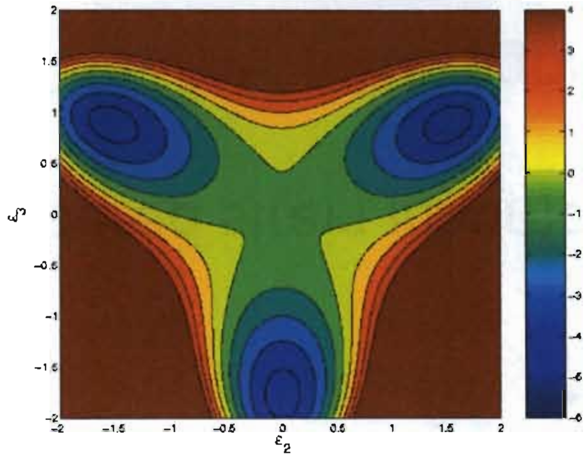
TWEED

$T_0 = 268$ K

(TWINNED) MARTENSITE

Sugiyama (1985)

Free energy: Triangle



Order parameter:
two-component shear

$$F_{struct}(e_2, e_3) = \mathbf{A_o}(T - T_0)(e_2 + e_3)^2 + \mathbf{B}e_3(e_3^{\ 2} - 3e_2^{\ 2}) + \mathbf{C}(e_2 + e_3)^4$$

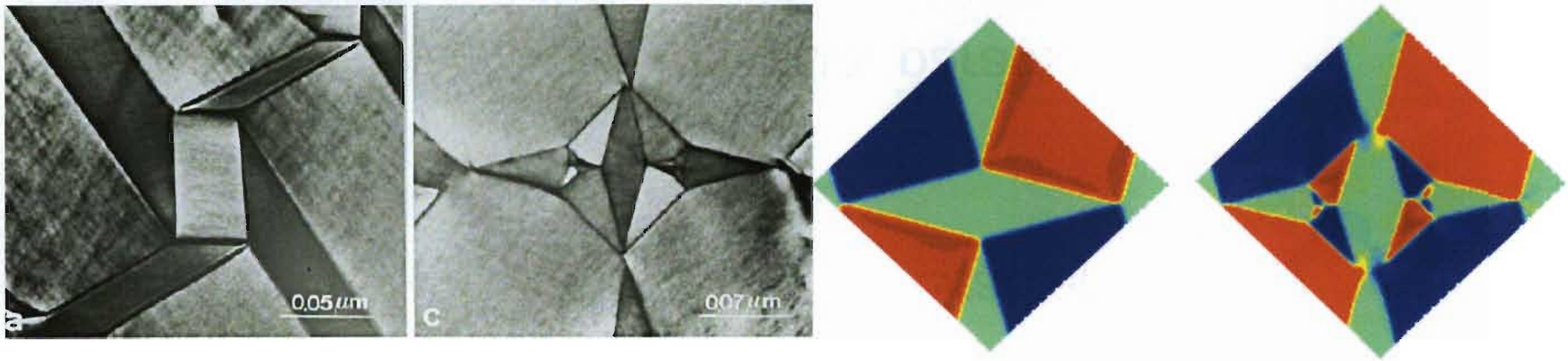
$$+\frac{\mathbf{g}}{2}(|\nabla e_2|^2 + |\nabla e_3|^2)$$

Gradient energy

$$+\frac{A_1}{2}e_1^{\ 2}$$

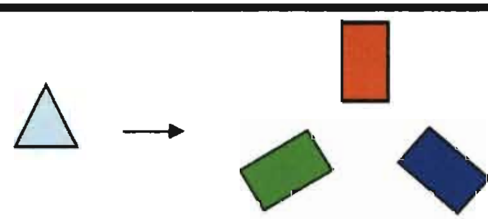
Non-order parameter

Ordered Microstructure in Elastic Materials



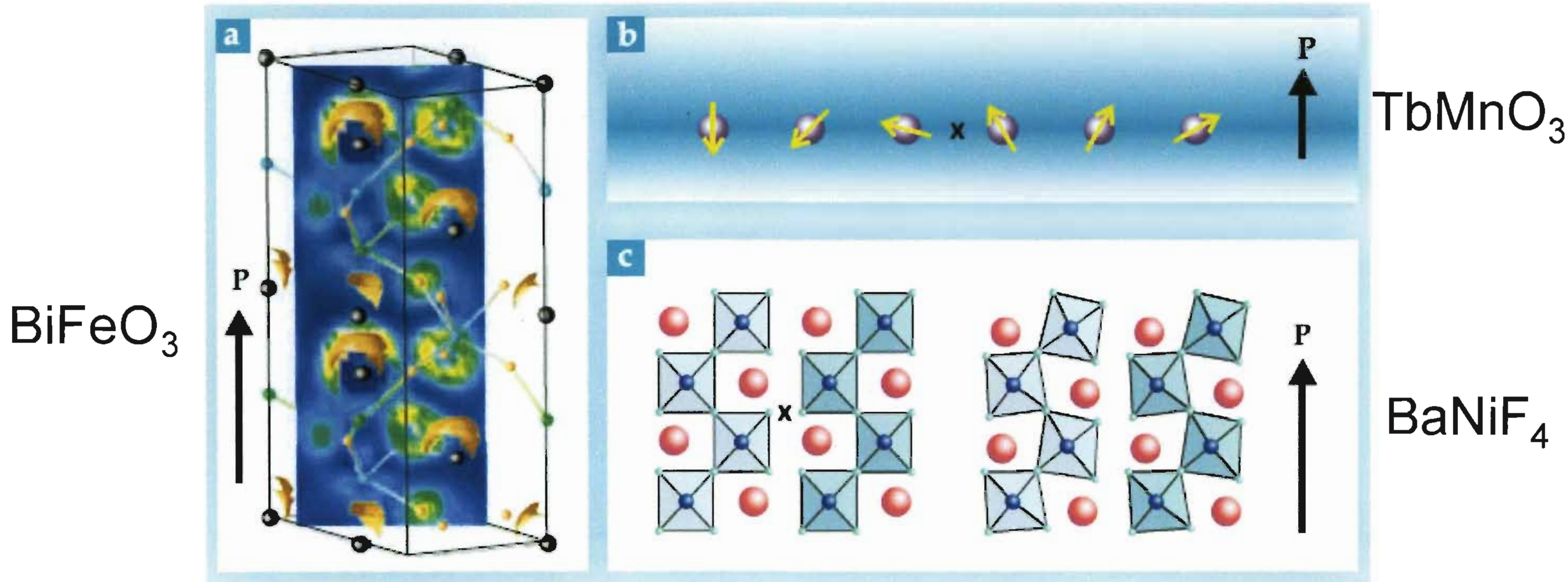
Amelincx et al. 1982

Lookman et al., PRB, 2003



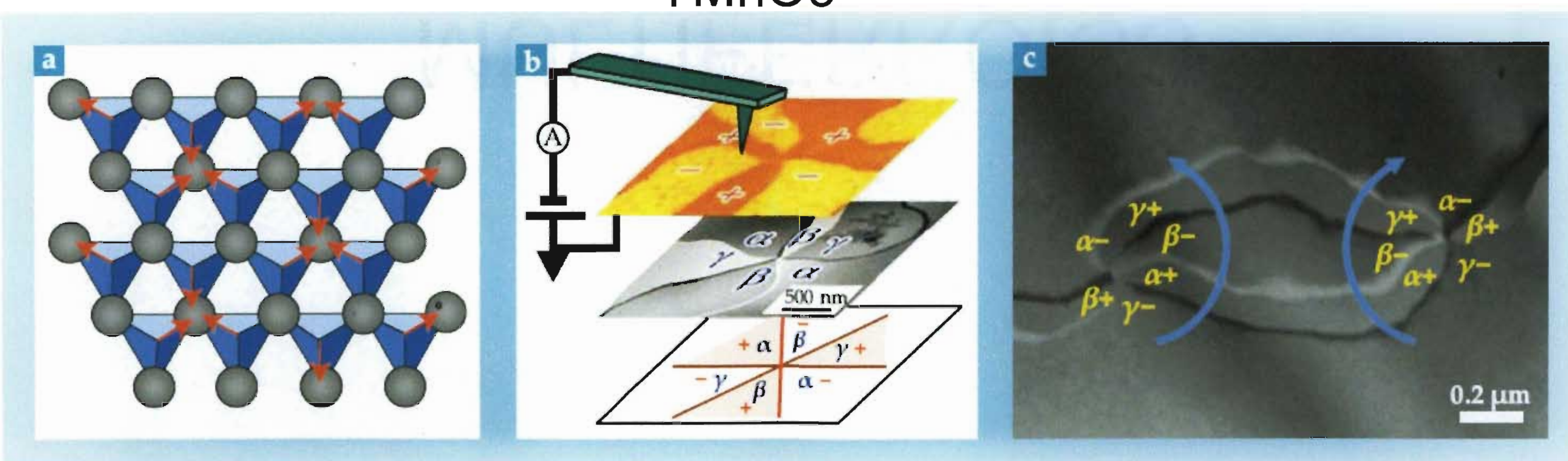
- Ordered strain inhomogeneity in a structural transformation
- $Pb_3(VO_4)_2$: Hexagonal to Orthorhombic transformation

MULTIFERROICS



Spiral magnetism and multiferroic vortices

YMnO3



History of Magnetoelectrics

Single phase

1894 Proposed (Curie)

1927 Magnetoelectric coined by Debye

1960 Cr_2O_3 (M with E) $\alpha_{zz} \sim 4.13\,psm^{-1}$

1964 Cr_2O_3 (P with H)

1963-66 $Ti_2O_3, GaFeO_3$ boracites, phosphates, garnet films

1984 $TbPO_4, \alpha_{aa} \sim 36.7\,psm^{-1}$

1995 Yttrium iron garnet films, $30\,psm^{-1}$

1993 $LiCoPO_{3,} \alpha_{yx} \sim 30.6\,psm^{-1}$

1997 $YMnO_3$

Applications: switching, actuation, coexisting P,M

Two-phase composites

1949 Proposed

1972-76 $BaTiO_3$ $CoFe_2O_4$ $\alpha \sim 720\,psm^{-1}$

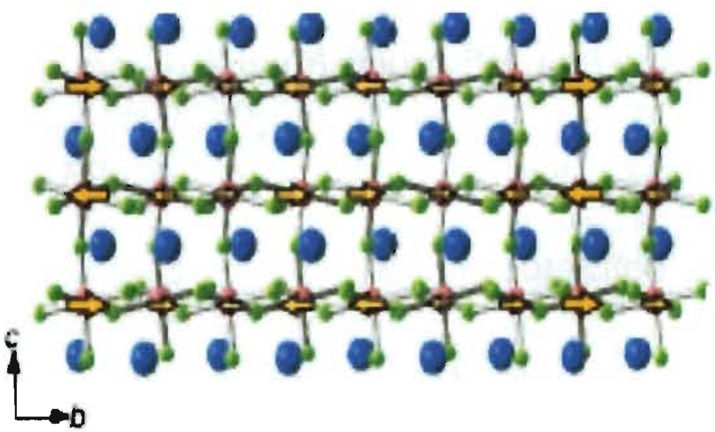
1985 Titanate/Ferrite

↓ PZT/Terfenol-D

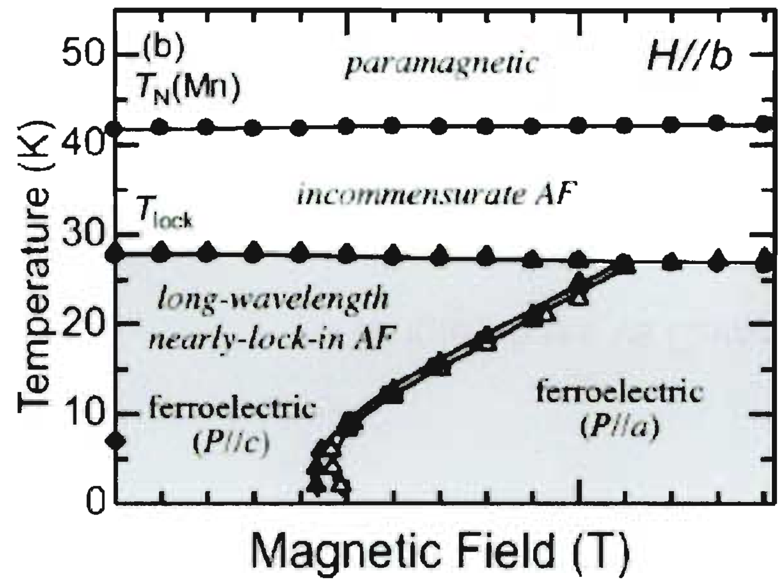
$PbZr_{1-x}Ti_xO_3 / Tb_{1-x}Dy_xFe_2$

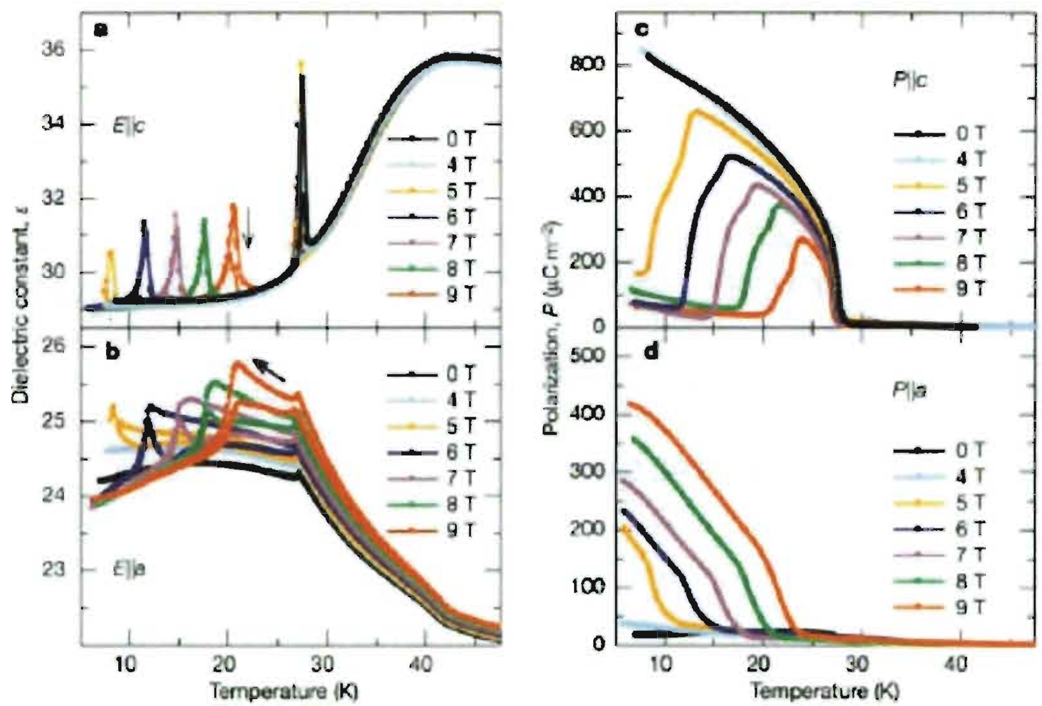
Single phase vs Composites

M control of P (H)



TbMbO$_3$

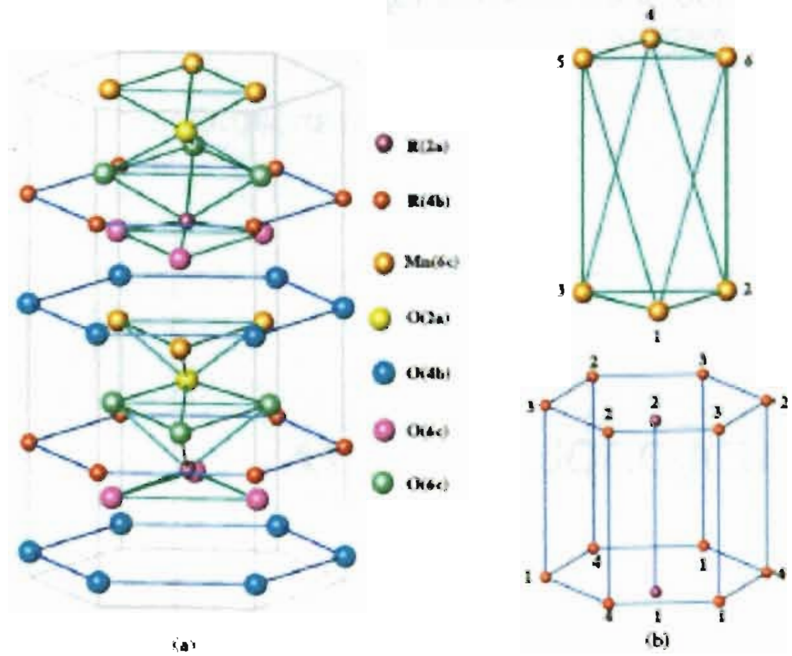


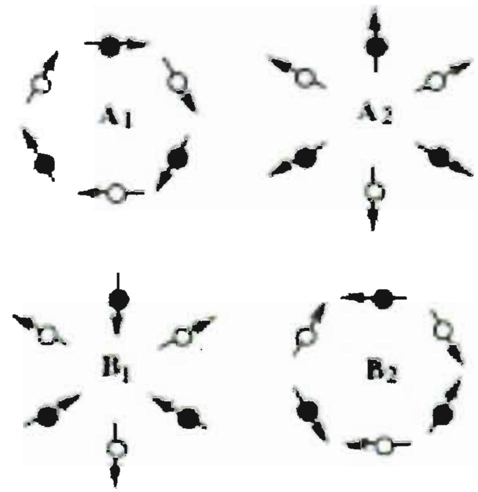


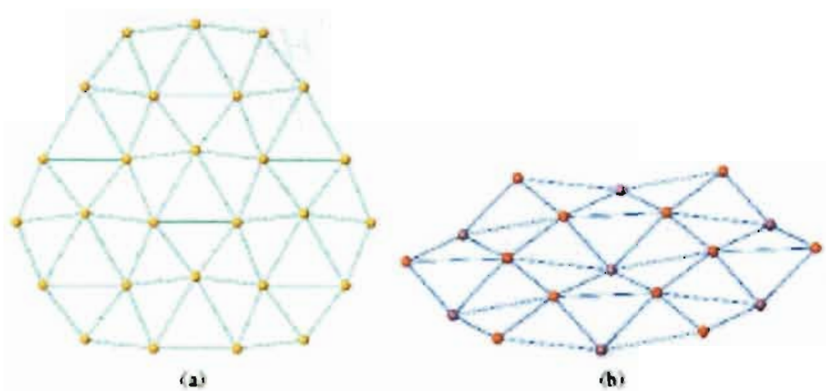
Dielectric constant
& Polarization vs. T

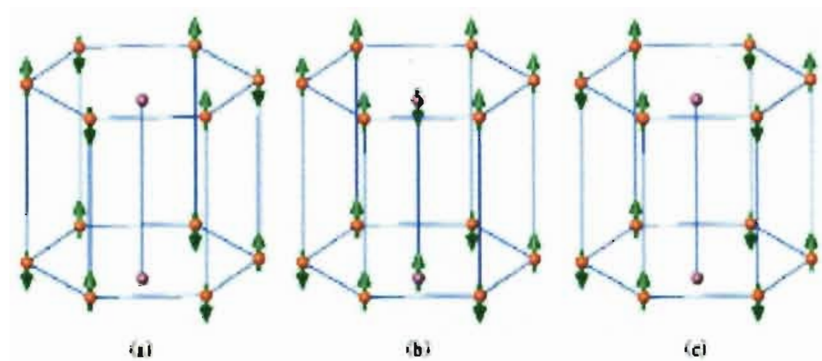
T. Kimura, …, Y. Tokura, PRL, 2003

Hexagonal $RMnO_3$: R=Ho, Er, Tm, Yb, Lu, Y, Sc









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

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

Magnetoelectric effect

$$F(\vec{E},\vec{H}) = F_o - P_i^s E_i - M_i^s H_i - \frac{1}{2}\epsilon_o \epsilon_{ij} E_i E_j - \frac{1}{2}\mu_o \mu_{ij} H_i H_j - \alpha_{ij} E_i H_j - \frac{1}{2}\beta_{ijk} E_i H_j H_k - .....$$

$$P_i(\vec{E},\vec{H}) = -\frac{\partial F}{\partial E_i} = P_i^s + \epsilon_o \epsilon_{ij} E_j + \alpha_{ij} H_j + ...$$

$$M_i(\vec{E},\vec{H}) = -\frac{\partial F}{\partial H_i} = M_i^s + \epsilon_o \epsilon_{ij} H_j + \alpha_{ij} E_j + ...$$

$\hat{\alpha}$ $\equiv$ Induction of P by H, M by E

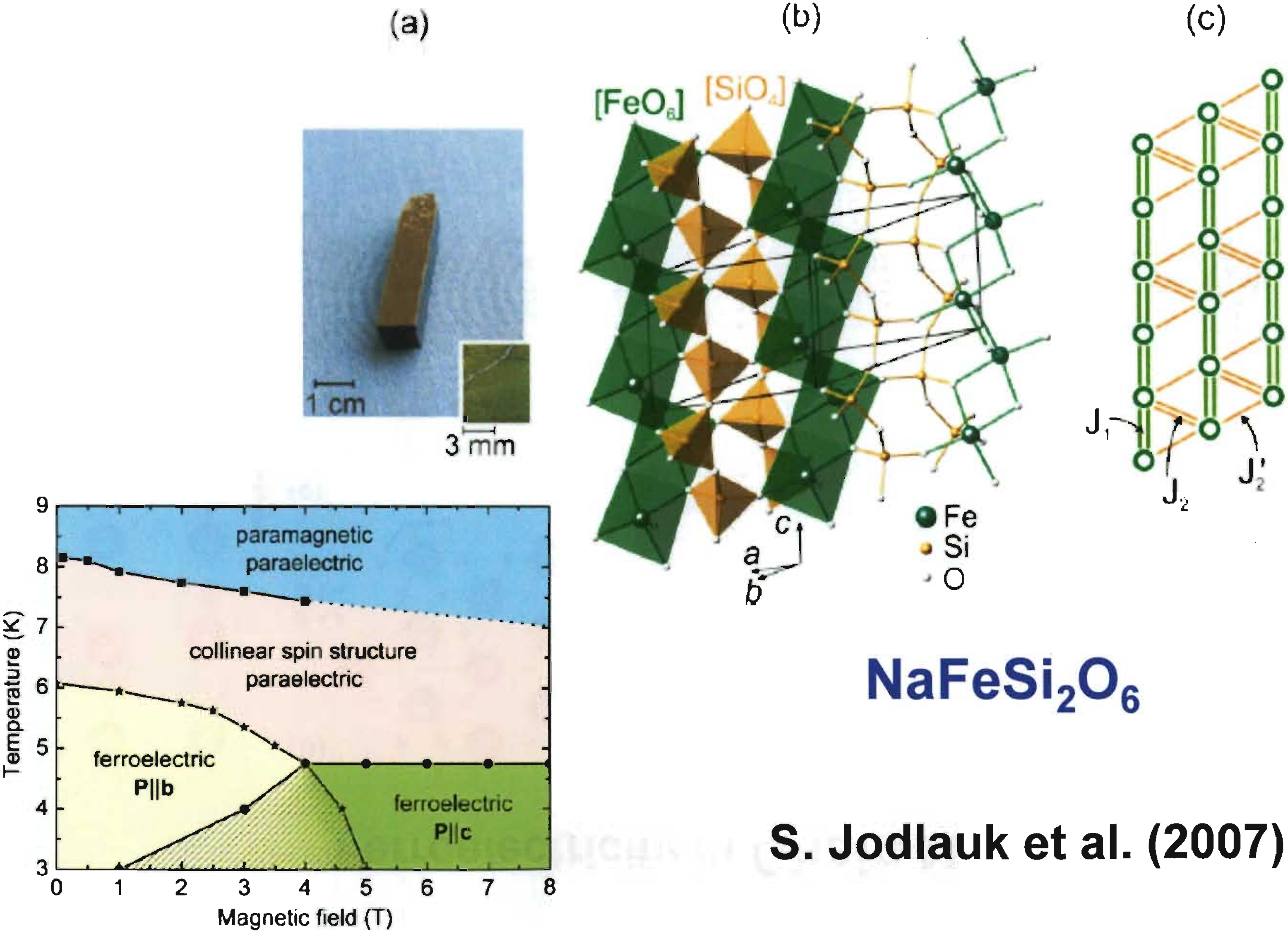
linear ME

For homogeneous materials, $\alpha_{ij}^{2} < \epsilon_{ii}\, \mu_{jj}$ (or $\chi_{ME}^{2} < \chi_M \chi_E$)

Expected to be large for systems developing magnetic, ferroelectric order at same T

Multiferroic chains: Pyroxenes

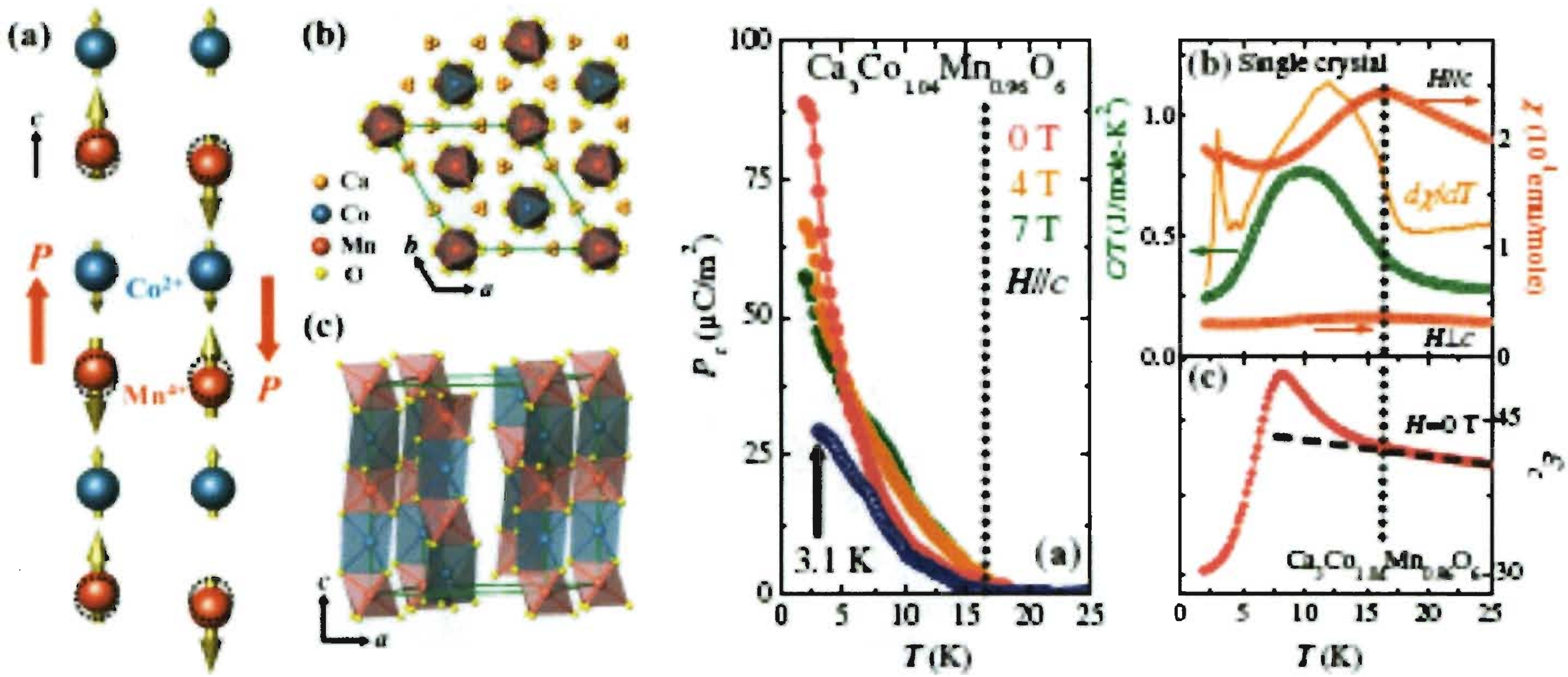
J. Phys.: Condens. Matter 19 (2007) 432201 Fast Track Communication



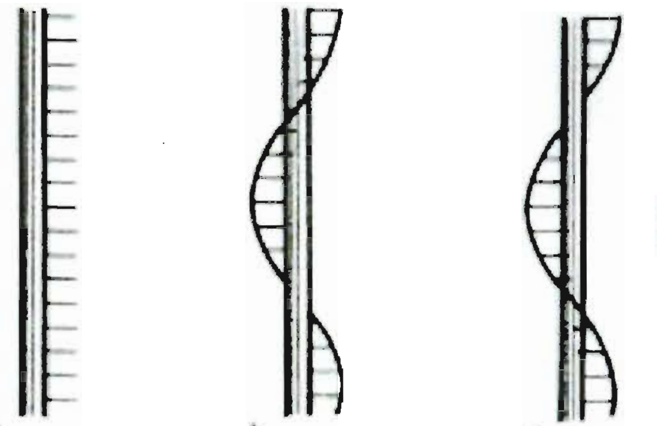
$NaFeSi_2O_6$

S. Jodlauk et al. (2007)

Ferroelectricity in Chain Magnets

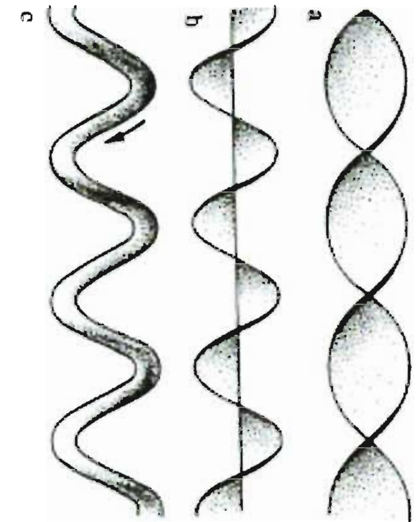


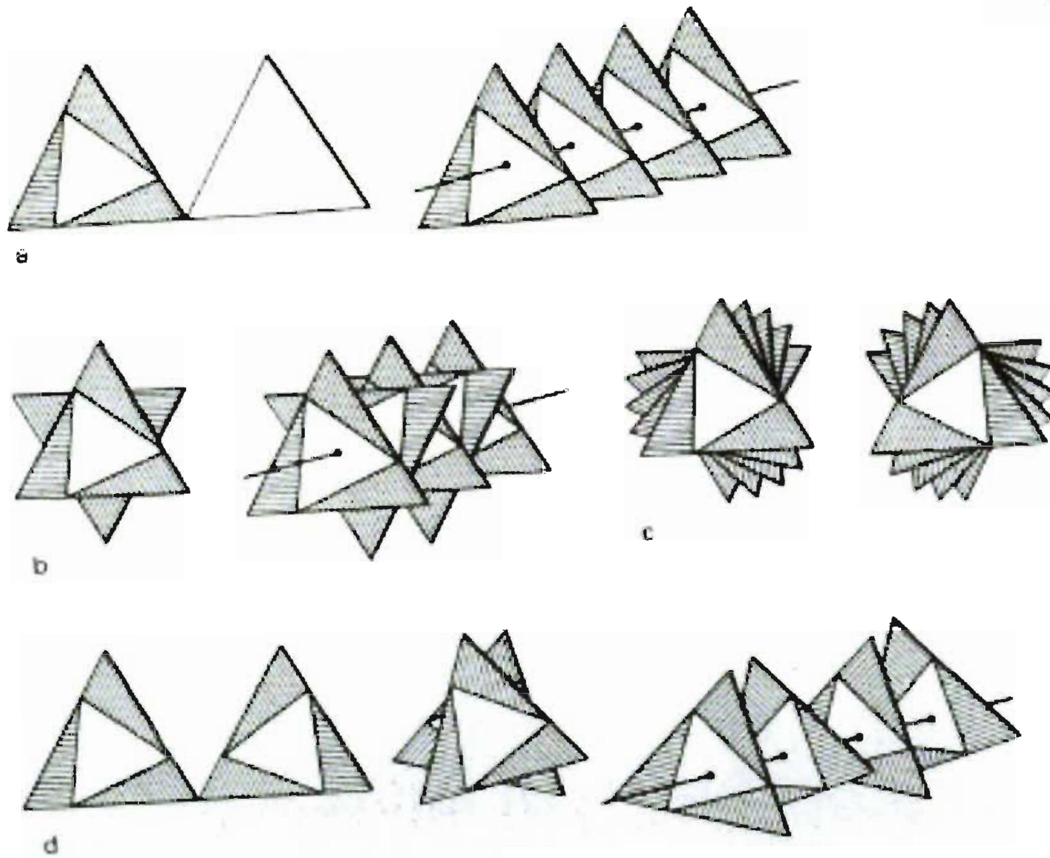
Y.J. Choi et al., PRL 100, 047601 (2008)



a b c

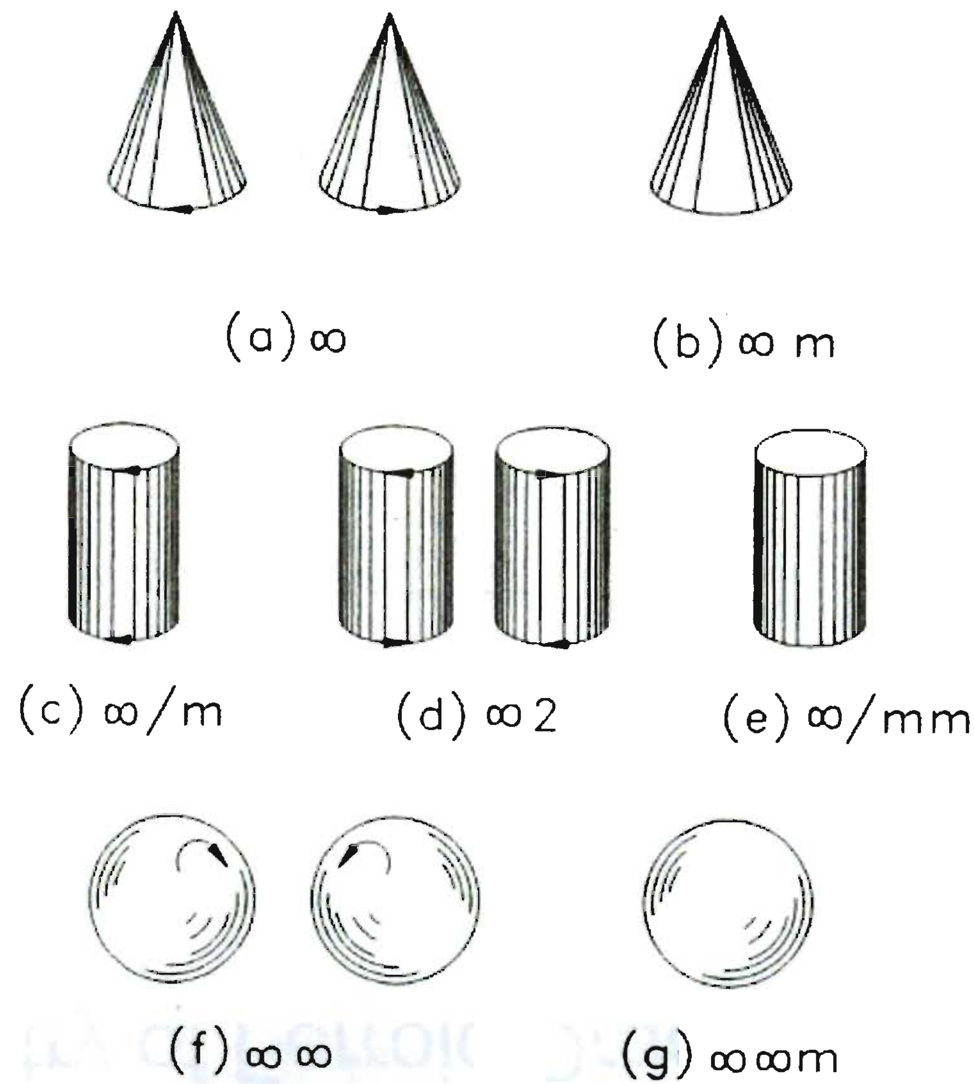
SYMMETRY OF RODS



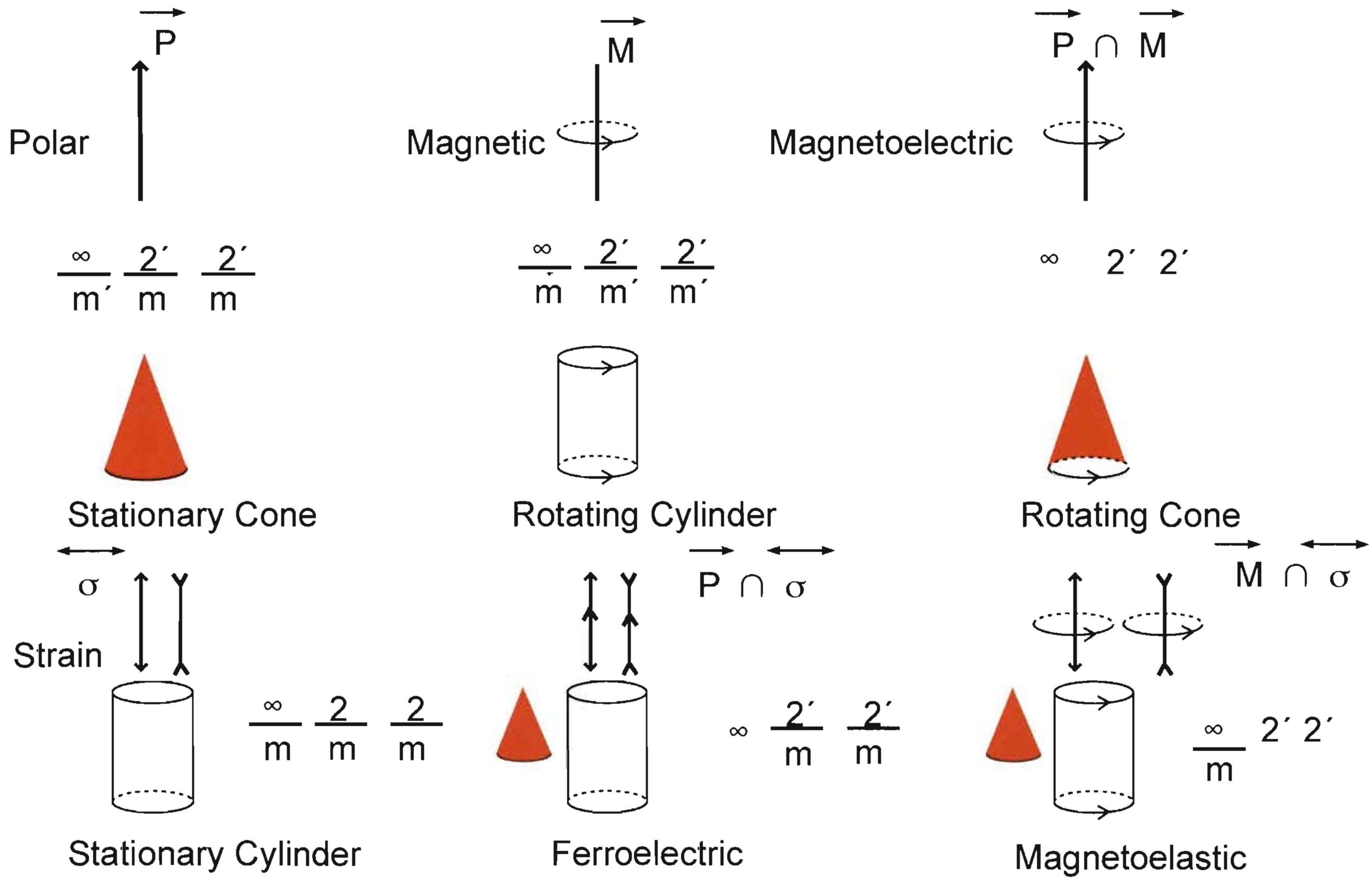


MAGNETIC SYMMETRY

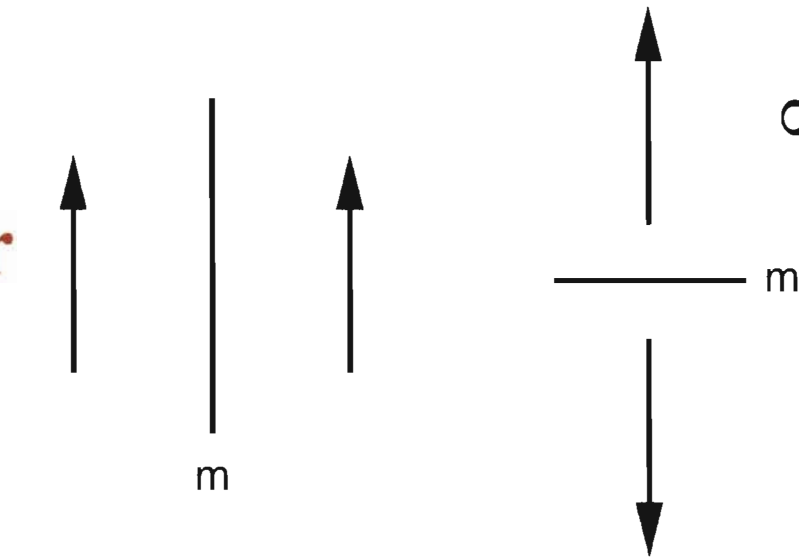
Seven Nonmagnetic Curie Groups



Symmetry of Ferroic Order Parameters

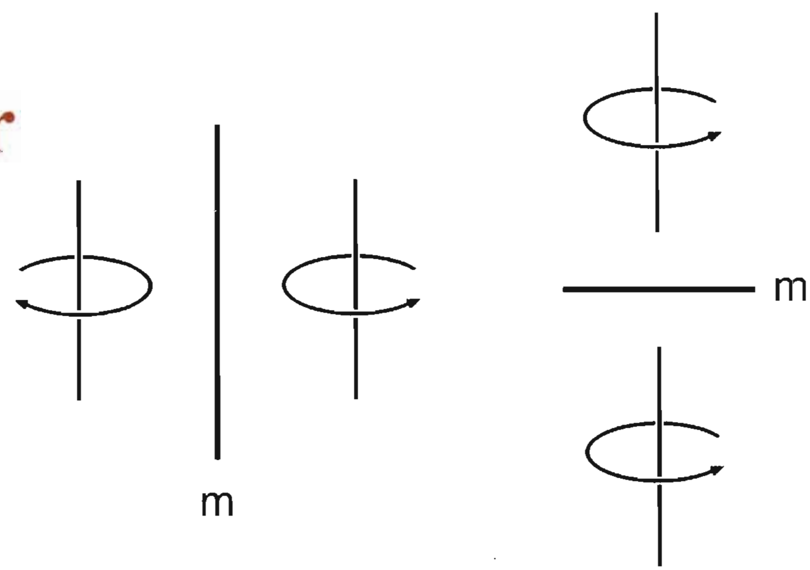


Polar Vector



$$\infty m \quad or \quad \frac{\infty}{m'}m$$

Axial Vector



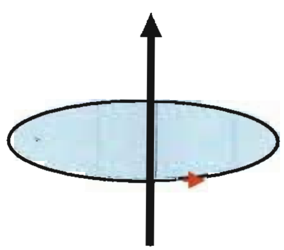
$$\frac{\infty}{m} \quad or \quad \frac{\infty}{m}m'$$

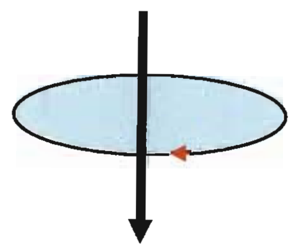
The use of the prime is to introduce black/white symmetry

Time reversal

$$i = \frac{dq}{dt}$$

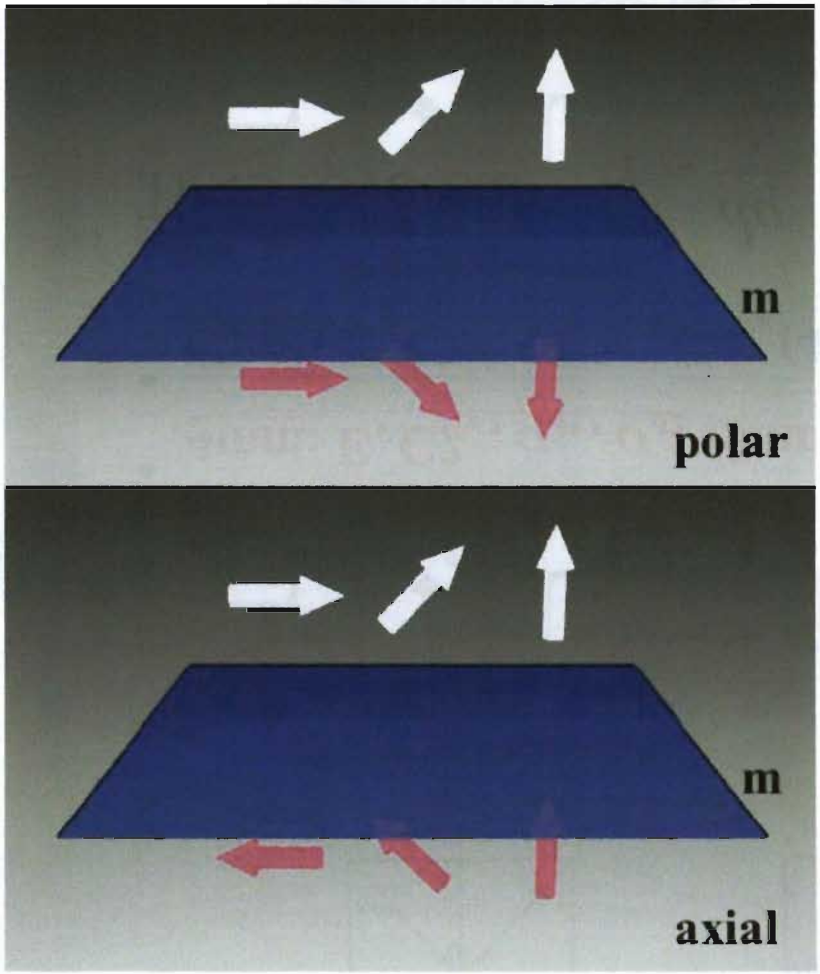
$$-i = \frac{dq}{d(-t)}$$



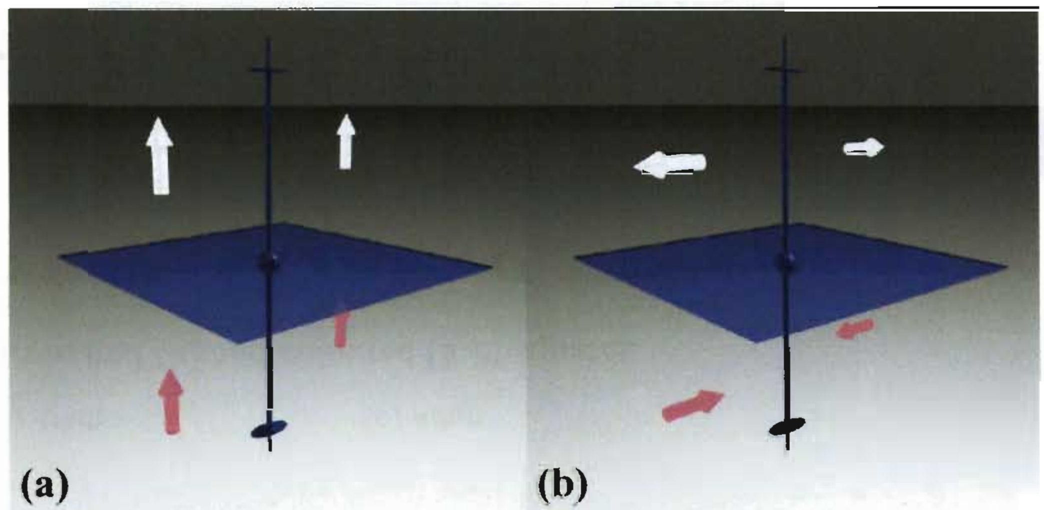


MAGNETIC SYMMETRY

MIRROR PLANE



POINT GROUP: 2/m



M. De Graef, 2009

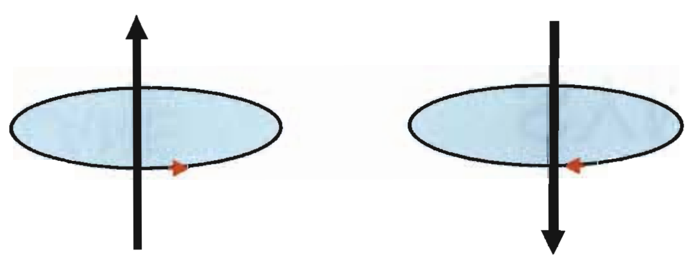
MAGNETIC POINT GROUPS

(a) 4mm (b) $\underline{4}m\underline{m}$ (c) $4\underline{mm}$

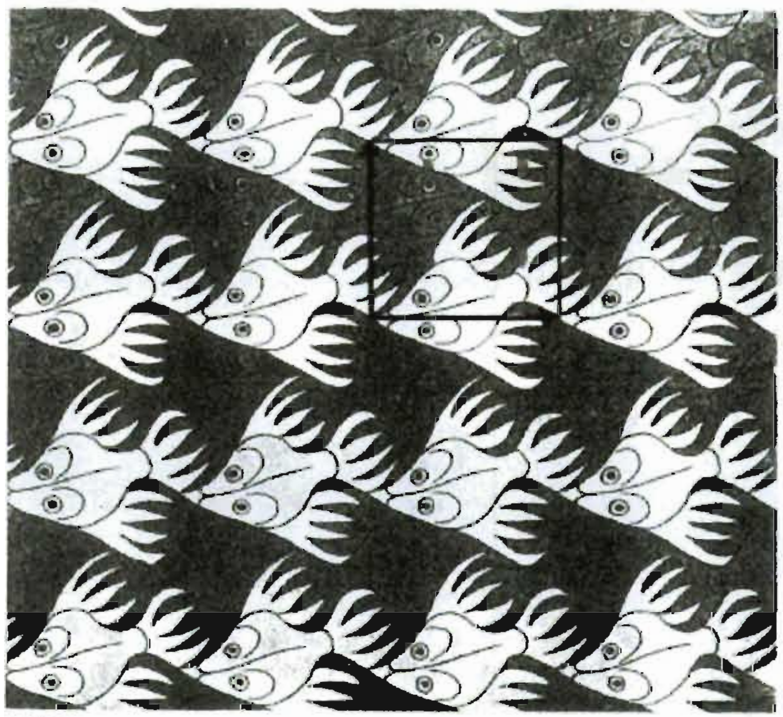
Figure: Point-group symmetry of uncoloured (*a*) and coloured (*b*, *c*) squares.

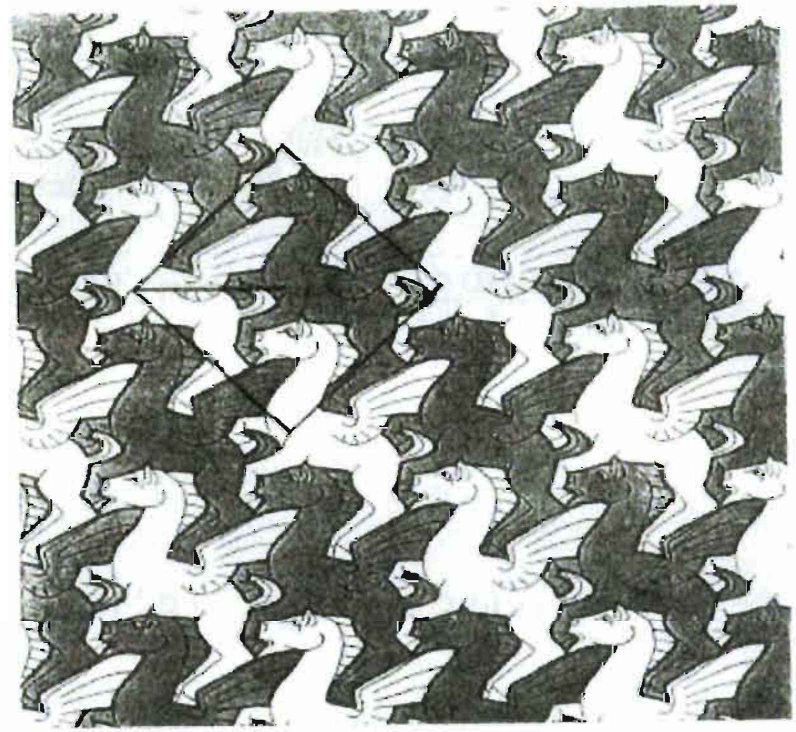
- **4mm: E, $C4^{+}_{z}$, $C2_{z}$, $C4^{-}_{z}$;** $\sigma_{d1}, \sigma_{d2}, \sigma_{vx}, \sigma_{vy}$
- **$\underline{4}m\underline{m}$: E, $C2_{z}$, σ_{d1}, σ_{d2} (2mm);** $RC4^{+}_{z}, RC4^{-}_{z}, R\sigma_{vx}, R\sigma_{vy}$
- **$4\underline{mm}$: E, $C4^{+}_{z}$, $C2_{z}$, $C4^{-}_{z}$ (4);** $R\sigma_{d1}, R\sigma_{d2}, R\sigma_{vx}, R\sigma_{vy}$

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



Examples of black-white symmetry





Drawings by M.C. Escher, reproduced in Macgillavry (1965)

2D Magnetic (Shubnikov) Point Groups

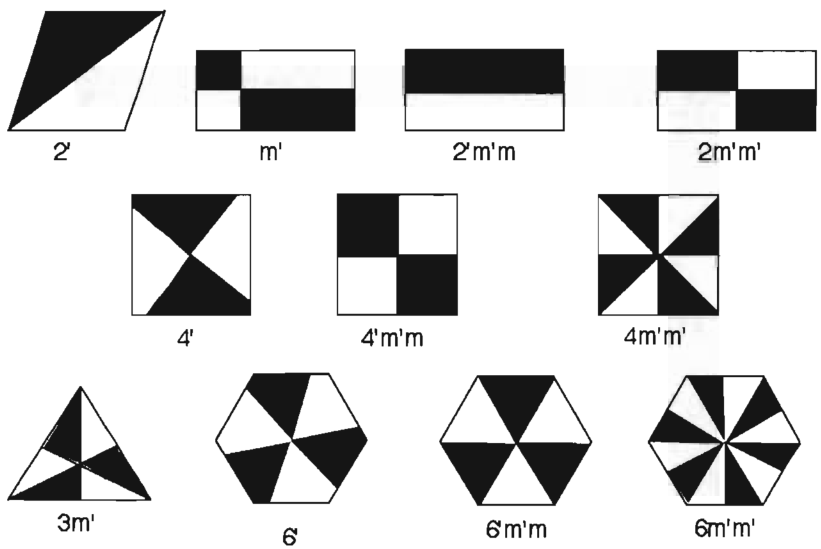
I. (White, Polar, Fedovov) Go: 1, 2, m, 2mm, 4, 4mm, 3, 3m, 6, 6mm

II. (Neutral, Gray): G = Go + 1' Go

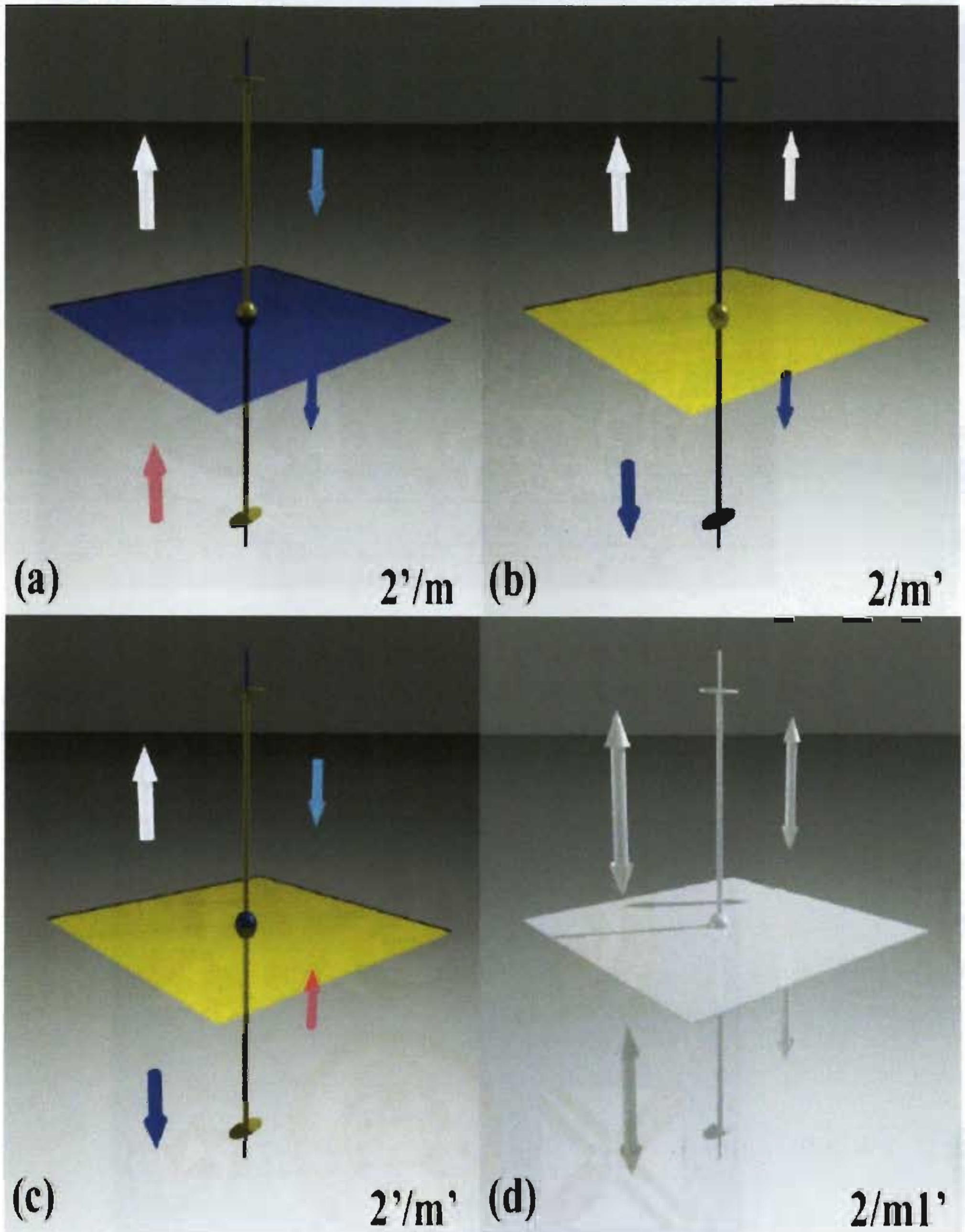
1', 21' m1', 2mm1', 41', 4mm1', 31', 3m1', 61', 6mm1'

III. (Black-White, mixed polarity): G = G1 + 1' G2

2', m', 2'm'm, 2m'm', 4', 4'm'm, 4m'm', 3m', 6', 6'm'm, 6m'm'



MAGNETIC POINT GROUPS DERIVED FROM: 2/m



Ferromagnetic state

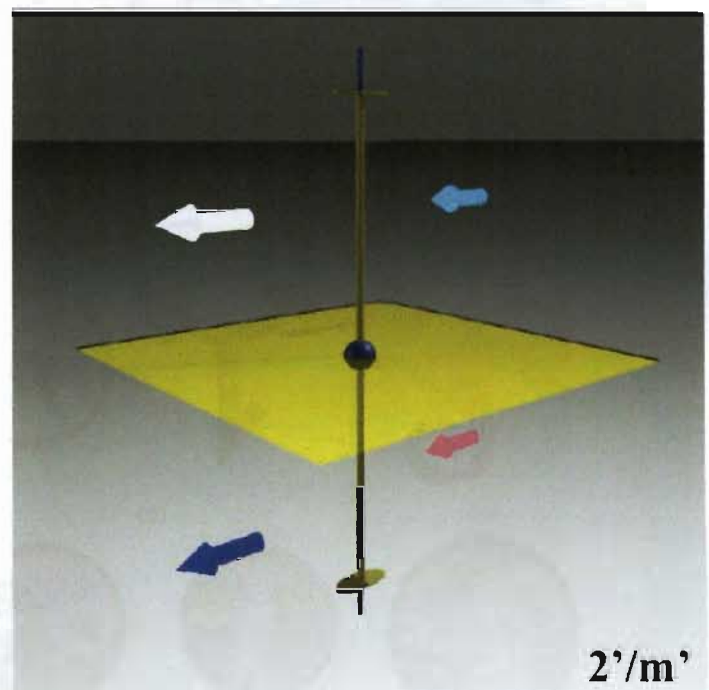


Figure 2.27
Antisymmetry rosettes in Neolithic ornamental art: (a) D_4/D_2, Danilo, Yugoslavia, about 3500 B.C.; (b) D_6/D_3, Near East; (c) D_4/D_2, Near East; (d) D_4/C_4, Middle East; (e) C_8/C_4, Middle East; (f) C_4/C_2, Dimini, Greece.

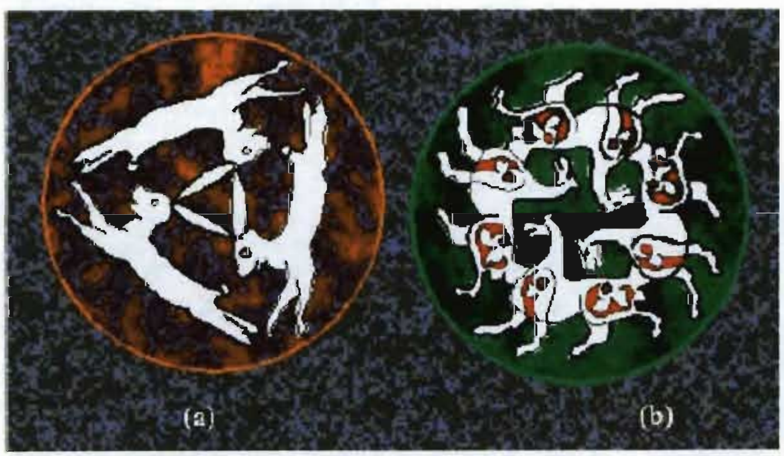


Figure 2.25
Examples of rosettes with the symmetry group (a) C_4 (4), 15th century; (b) C_3 (3), with the dominant decorative component.

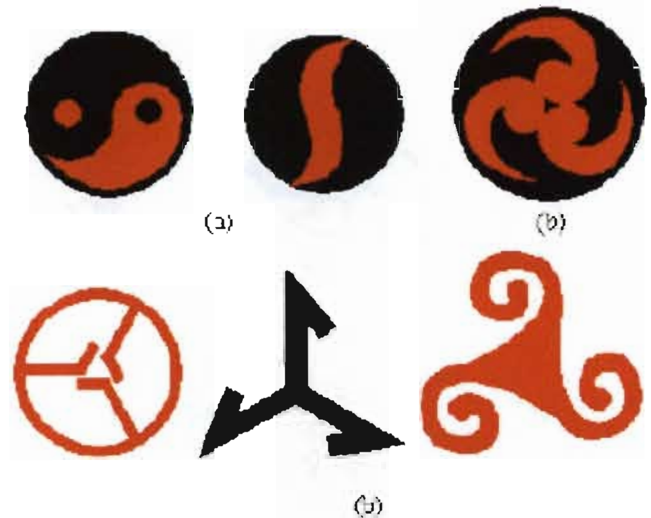


Figure 2.22
Variations of the (a) Chinese symbol "yang-yin" with the symmetry group C_2 (2) and (b) the triquetra motif with the symmetry group C_3 (3).

Magnetic Groups & Color Symmetry

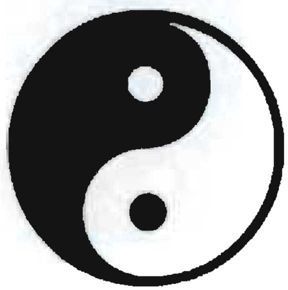
Black & white (or Shubnikov) groups.

- 3D point groups: 32+32+58=**122**
- 3D space groups: 230+230+1191=**1651**

  (14 $\longrightarrow$ 22 Bravais lattices)

- 2D point groups: 10+10+11=**31**
- 2D space groups: 17+17+46=**80**
- (5 Bravais lattices)

- 1D point groups: 1+1+1=**3**
- 1D space groups: 2+2+3=**7**



Melodic verses: Antisymmetry

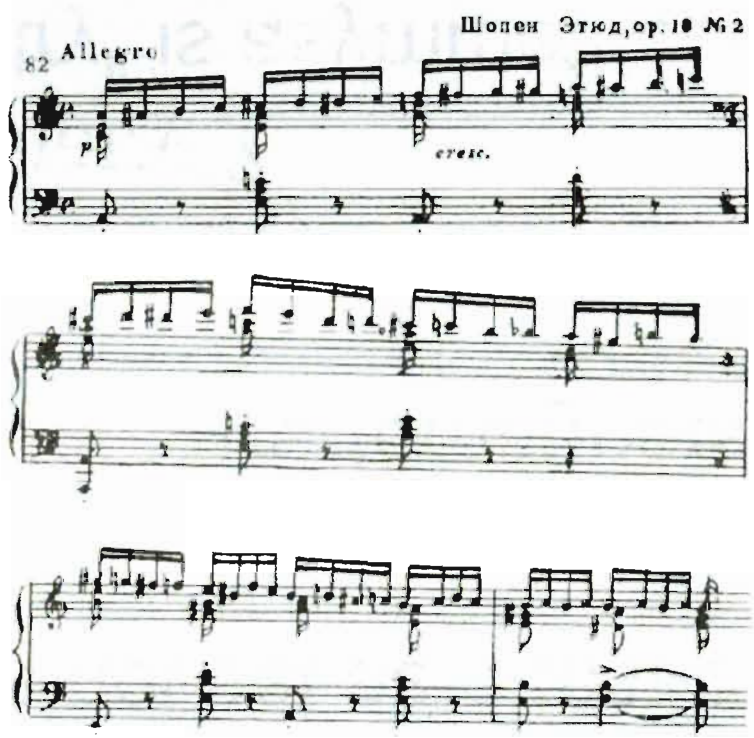



Figure 1.

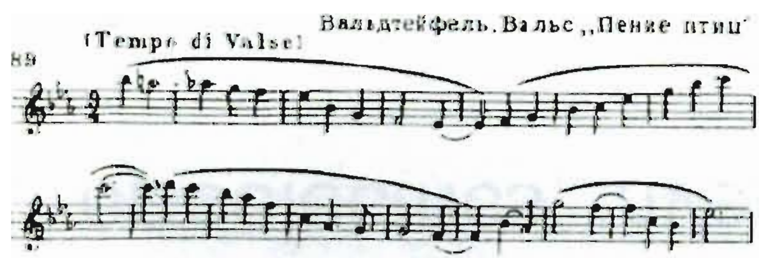



Figure 2.

Palindromes: (Ferroelectrics; inversion symmetry)

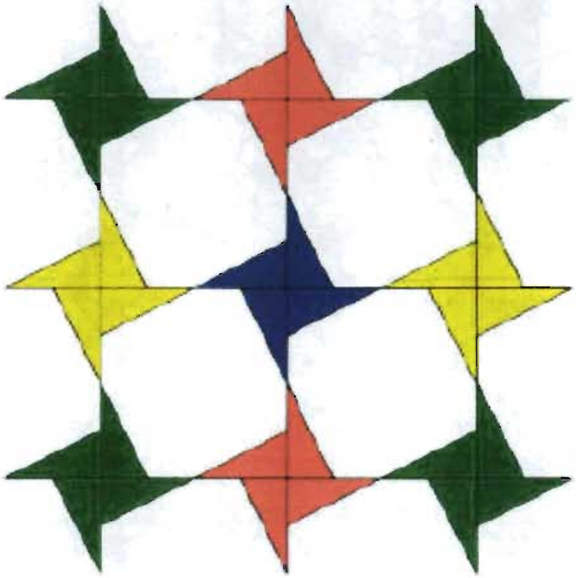
Niagara O! Roar again.
A man, a plan, a canal: Panama.
Sums are not set as a test on Erasmus.

-1

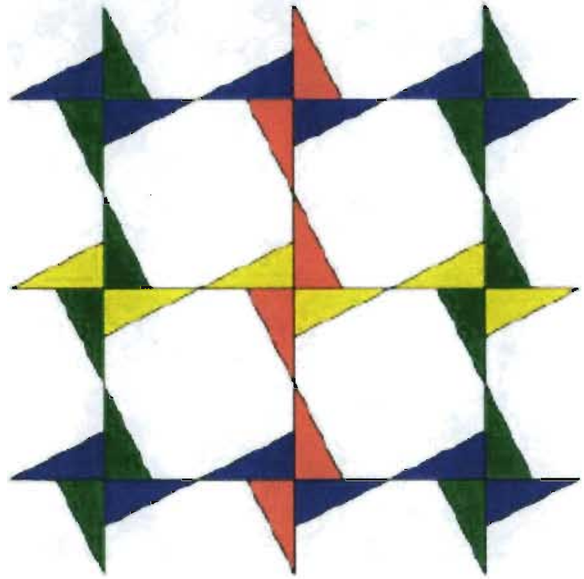
Anacyclic verses: (Ferromagnets; time reversal)

Is it odd how asymmetrical
Is "Symmetry"?
"Symmetry" is asymmetrical.
How odd It is!

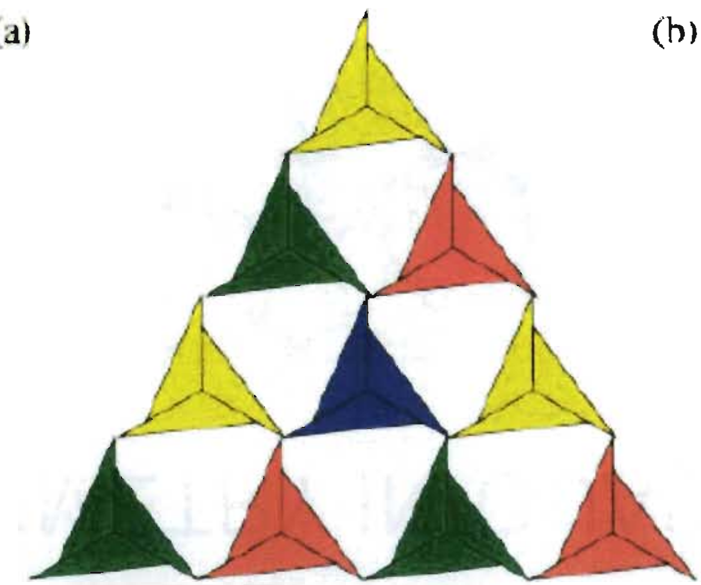
-1'



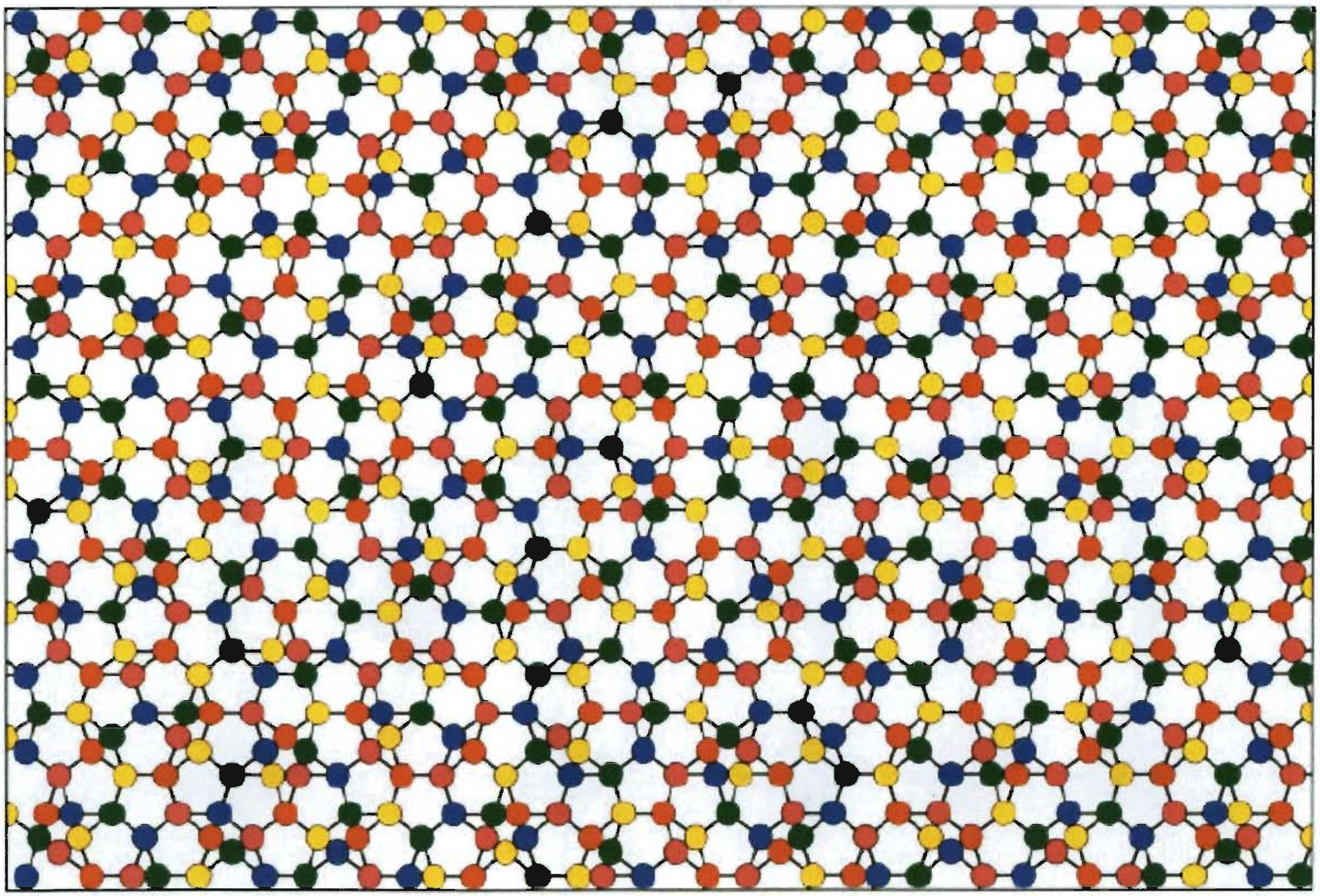
(a)



(b)



COLOR SYMMETRY IN QUASI-CRYSTALS



MAGNETIC PHASE TRANSITIONS

Symmetry Breaking

- Spontaneous P (no inversion symmetry): 31 magn. point groups
- Spontaneous M (no time reversal symmetry): 31 magn. point groups
- Both P, M: 13 magnetoelectric point groups
- 1, 2, 2', m,m', 3, 3m', 4, 4m'm', m'm2', m'm'2, 6, 6m'm'
- Quasi-1D, quasi-2D magnetoelectric point groups: Tables.

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

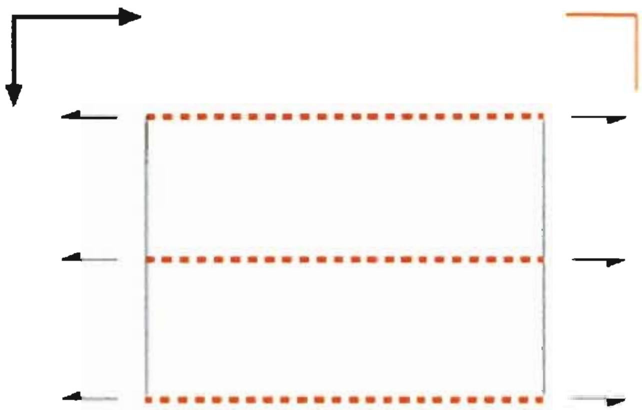
AFE/Chiral

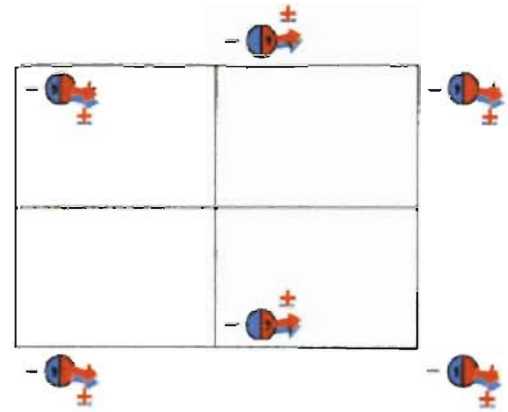
AFM/Chiral

AFM/Chiral

$pb'2_1m'$ $m'2m'$ Orthorhombic/Rectangular

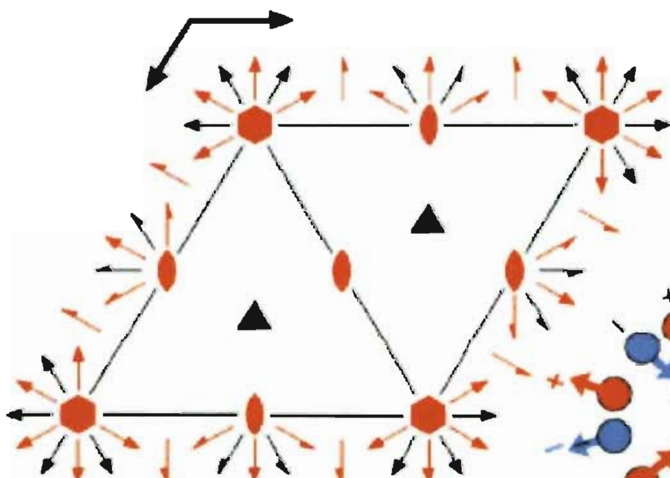
No. 29.3.176 $pb'2_1m'$

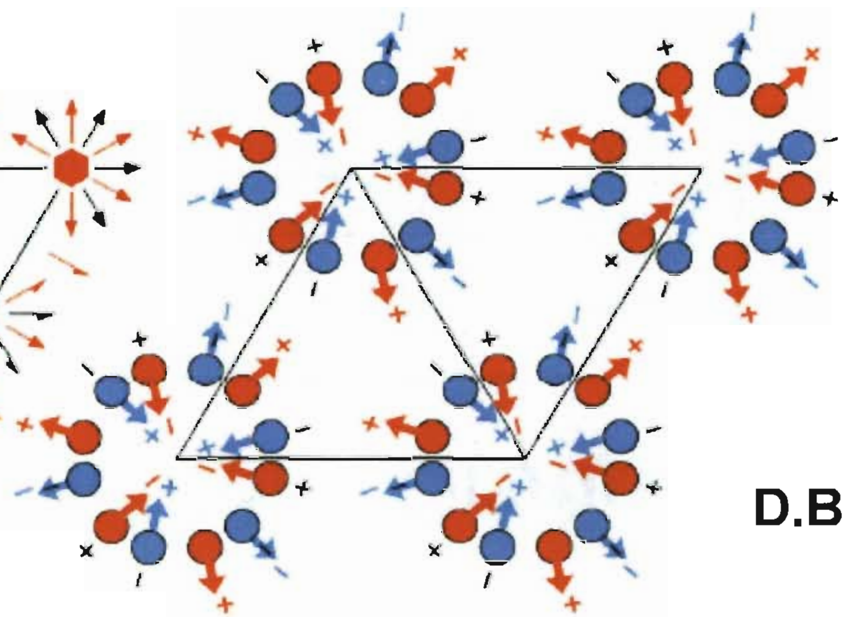




$p6'22'$ $6'22'$ Hexagonal/Hexagonal

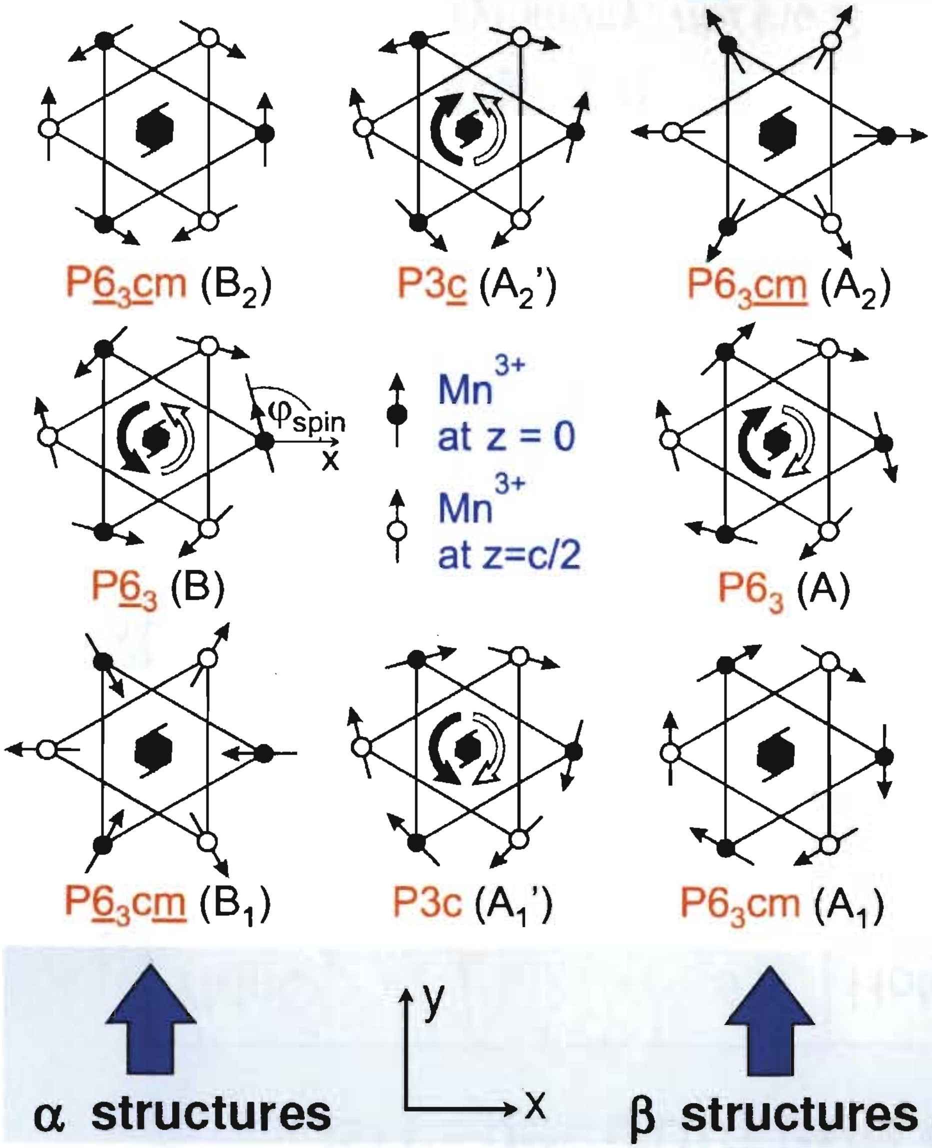
No. 76.4.503 $p6'22'$





D.B. Litvin

Magnetic Structure and SHG Selection Rules



At least 8 different triangular in-plane spin structures with different magnetic symmetries and different selection rules for SHG

α structures: SHG for k||z allowed

α_x ($\varphi = 0°$): $\chi_{xxx} = 0$, $\chi_{yyy} \neq 0$

α_y ($\varphi = 90°$): $\chi_{xxx} \neq 0$, $\chi_{yyy} = 0$

α_ρ ($\varphi = 0\text{-}90°$): $\chi_{xxx} \propto \sin\varphi$, $\chi_{yyy} \propto \cos\varphi$

β structures: SHG for k||z not allowed

β_x, β_y, β_ρ: $\chi_{xxx} = 0$, $\chi_{yyy} = 0$

Determine β structure from α-β transition

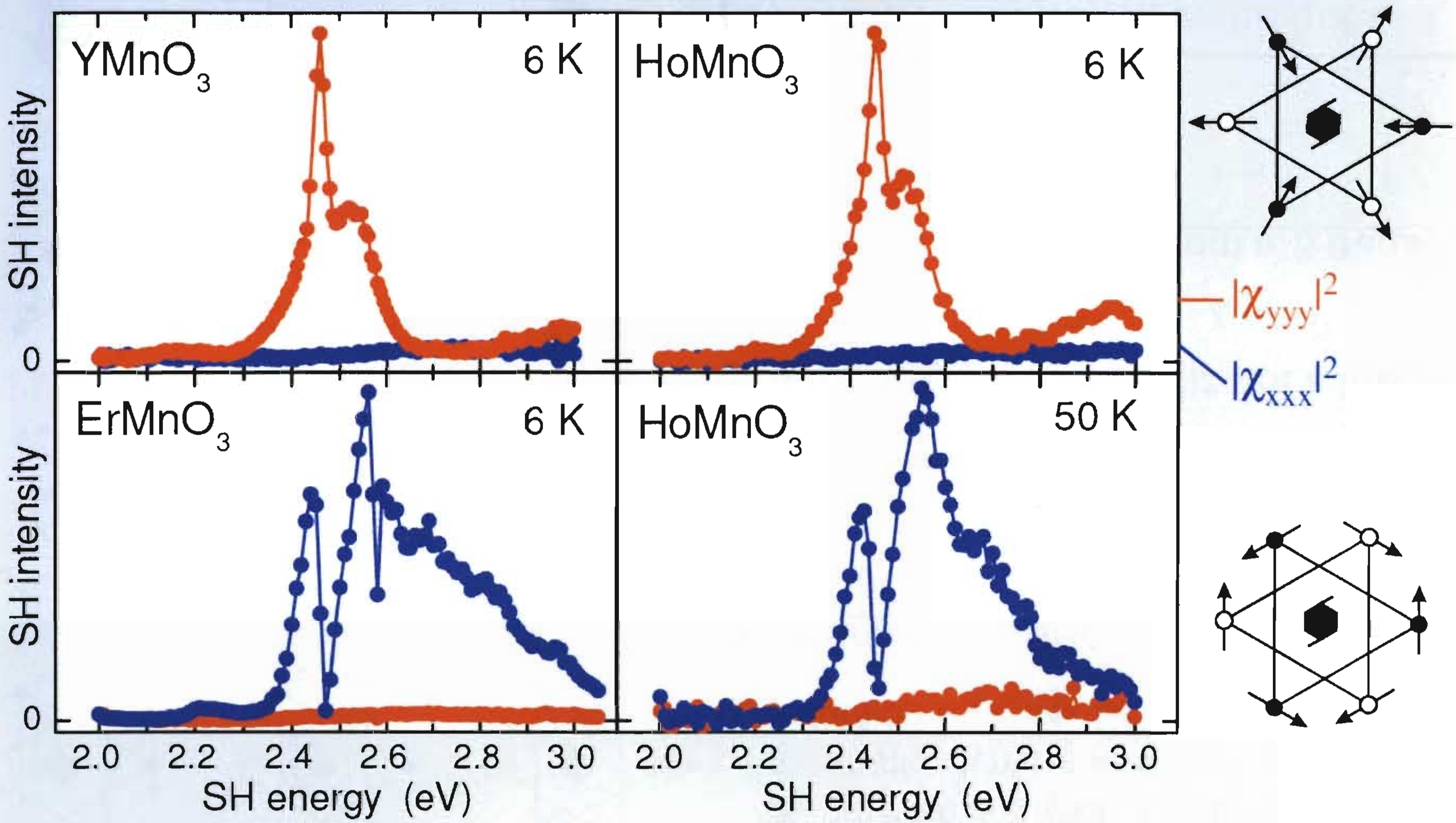
$\alpha_x \rightarrow \beta_y$: $\chi_{xxx} = 0$, $\chi_{yyy} \propto \cos\varphi$

$\alpha_y \rightarrow \beta_x$: $\chi_{xxx} \propto \sin\varphi$, $\chi_{yyy} = 0$

Contrary to diffraction techniques:
α and β models clearly distinguishable!

T. Lottermoser and M. Fiebig (2004)

SH spectrum and Magnetic Symmetry



The magnetic symmetry, ***not*** the R ion, determines the SH spectrum of $RMnO_3$

Free Energy for a 2D Multiferroic Transition

$$F(M,P,e) =$$

$$a_1(M_1^2+M_2^2)+b_1(M_1^2+M_2^2)^2+c_1(M_1^4+M_2^4)$$
$$+a_2(P_1^2+P_2^2)+b_2(P_1^2+P_2^2)^2+c_2(P_1^4+P_2^4)$$
$$+a_3(e_2^2+e_3^2)+b_3(e_2^3-3e_2e_3^2)+c_3(e_2^2+e_3^2)^2$$

$$+A[e_2(P_1^2-P_2^2)+e_3P_1P_2]$$
$$+B[e_2(M_1^2-M_2^2)+e_3M_1M_2]$$
$$+C[(P_1^2+P_2^2)(M_1^2+M_2^2)]$$

+ gradient terms

Gradient couplings: domains & vortices

$$F_G = M^2(\nabla\cdot P) + M\cdot[(M\cdot\nabla)P]$$

$$+ P\cdot[M(\nabla\cdot M) + P\cdot[M\times(\nabla\times M)]$$

$$+ \varepsilon(\nabla\cdot M)^2 + \varepsilon(\nabla\times M)^2$$

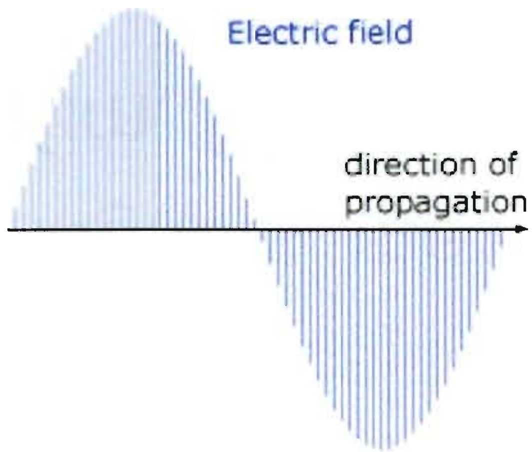
$$+ \varepsilon(\nabla\cdot P) + P\cdot(\nabla\varepsilon) + \varepsilon(\nabla\times P)^2$$

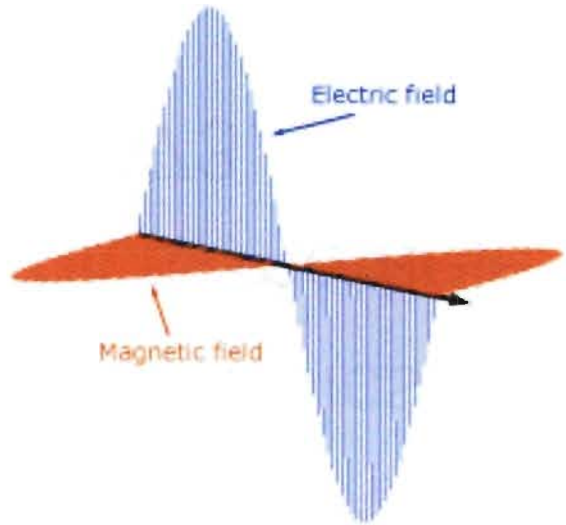
Microstructure simulations underway

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).

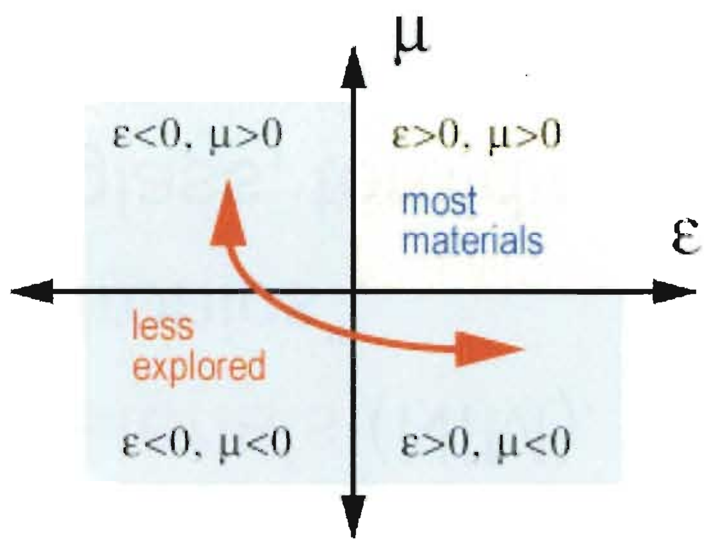
METAMATERIALS and MULTIFERROICS



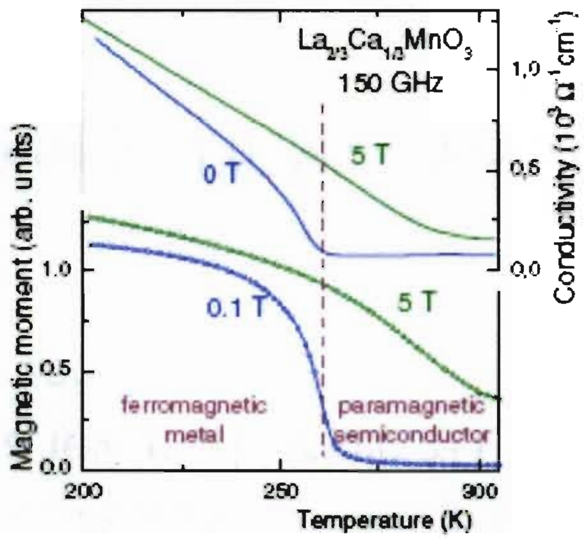


$$\nabla \times \mathbf{E} = -\mu \frac{\partial \mathbf{H}}{\partial t}$$

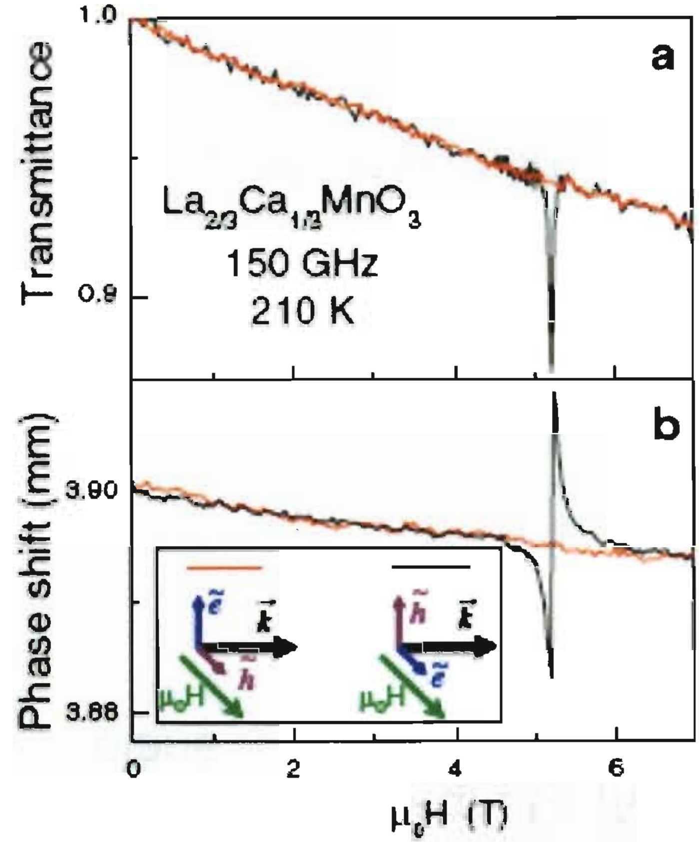
$$\nabla \times \mathbf{H} = \varepsilon \frac{\partial \mathbf{E}}{\partial t}$$



Negative Refraction in a CMR Material



A. Pimenov et al., PRL 98, 197401 (2007)



Conclusions

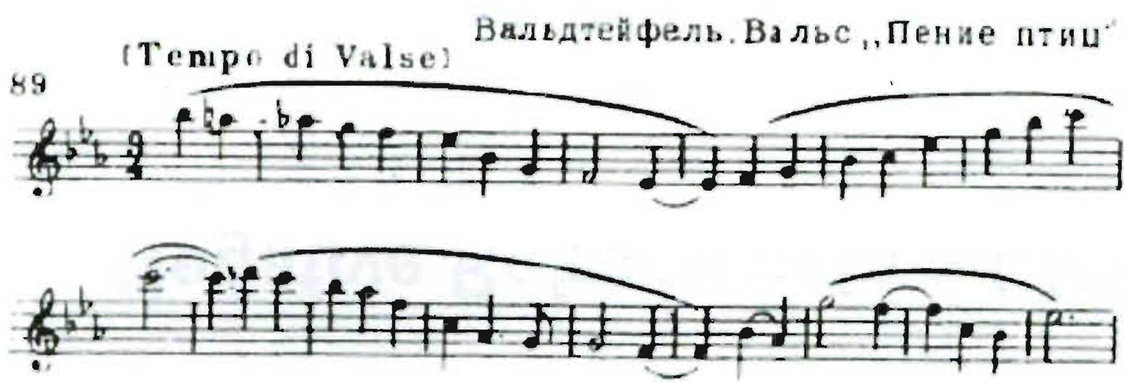
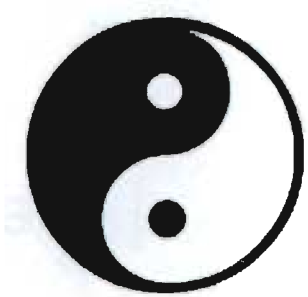
- Quasi-1D, quasi-2D Multiferroics: simultaneously ferromagnetic (M), ferroelectric (P), ferroelastic (e) in a chain, plane.
- Intrinsic inhomogeneity.
- Magnetoelectric versus structural tweed.
- Magnetoelectric chains/planes: coexisting P,M.
- Only a few multiferroic 1D, 2D point groups.
- Synthesis of new materials.
- Notion of color symmetry.
- Phase transitions to these subgroups.
- Free energy: F(P,M,e), domain walls, microstructure simulation.



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