Multiferroics

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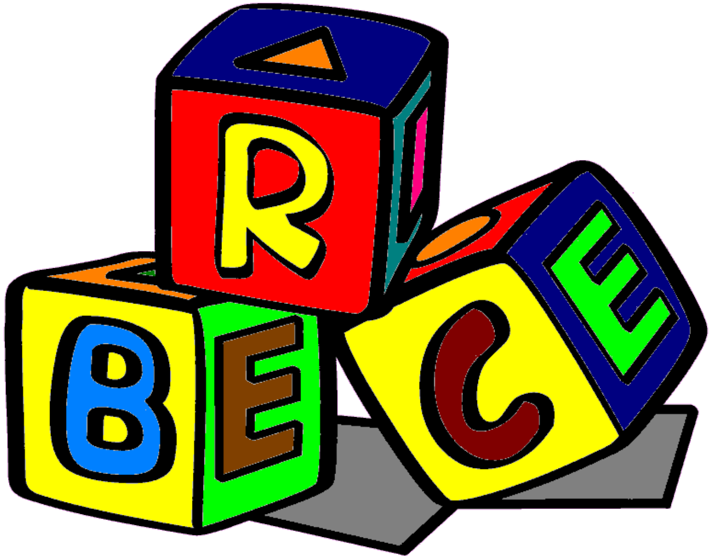
Outline

Introduction to Multiferroics
- Definitions
- Taxonomy
- $BiFeO_3$ & $TbMnO_3$

Concepts
- Symmetry
- Ferroelectric transitions
- Theoretical digressions

Optics
- Toolbox
- Phonons
- Electromagnons

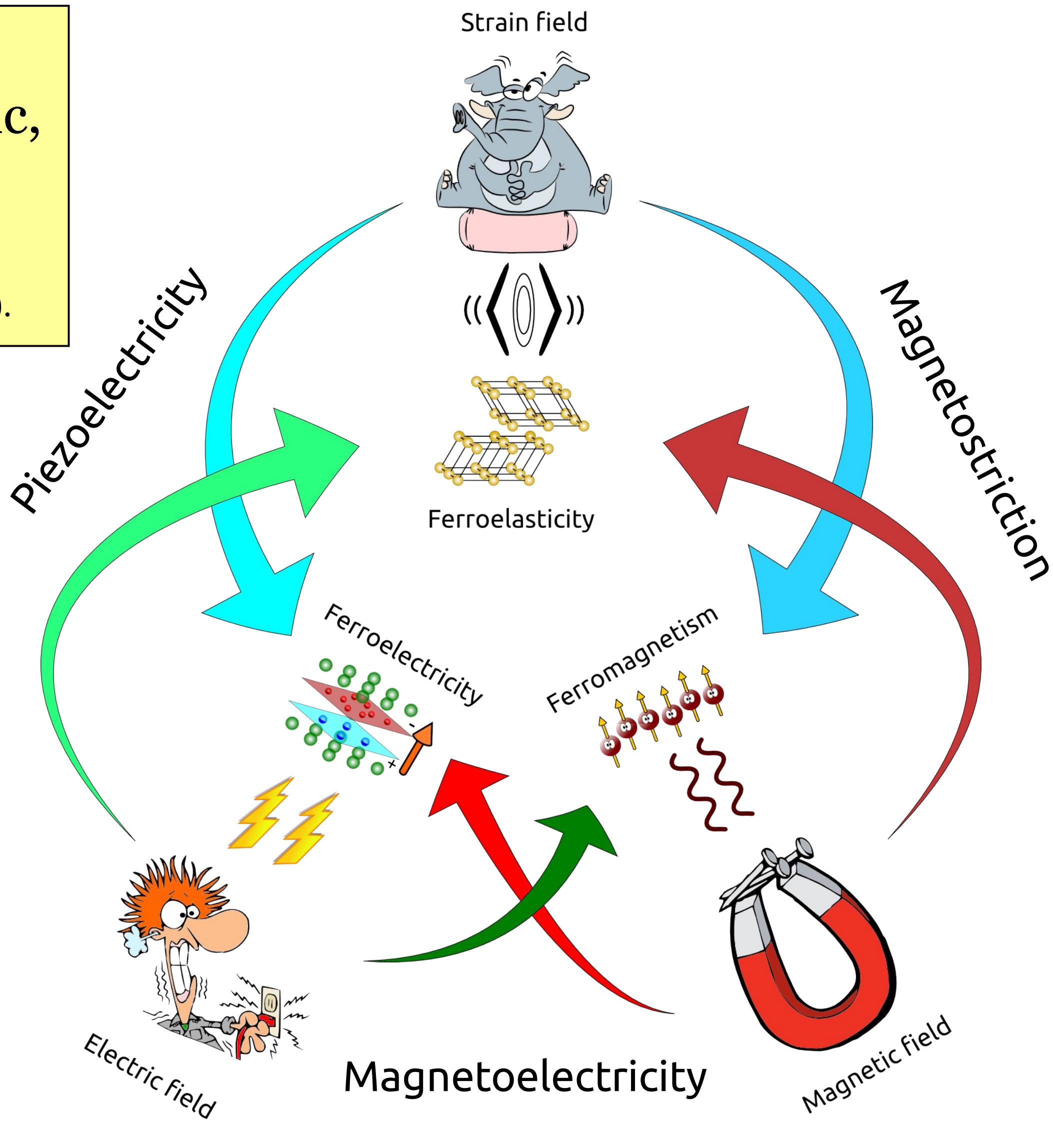
The Basic Concepts



The Multiferroic Totem

Coexistence of at least two ferroic orders [ferromagnetic, ferroelectric, ferroelastic, ferrotoroidal (??)]

Schmid, Ferroelectrics **162**, 317 (1994).



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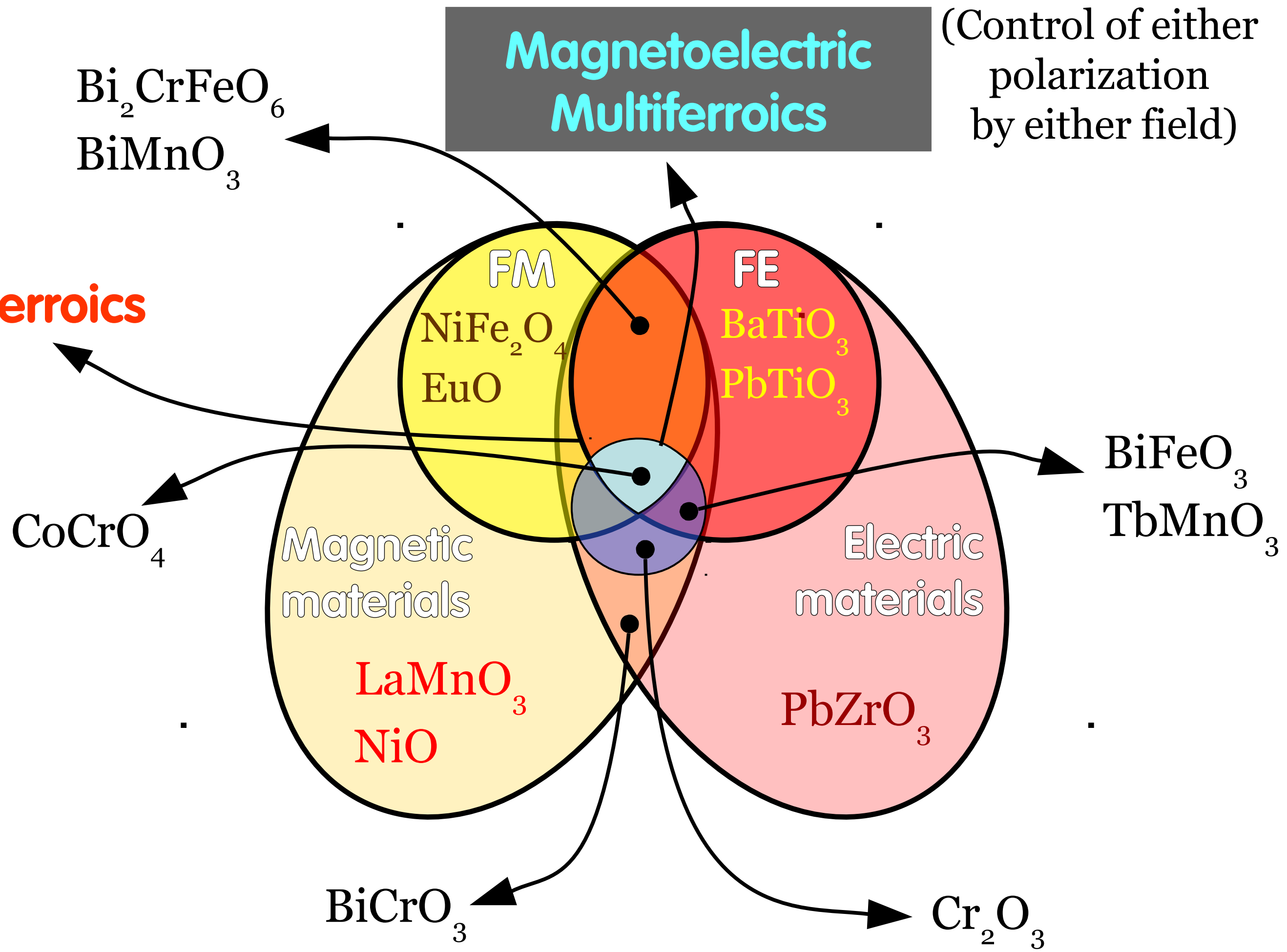
The Multiferroic Butterfly

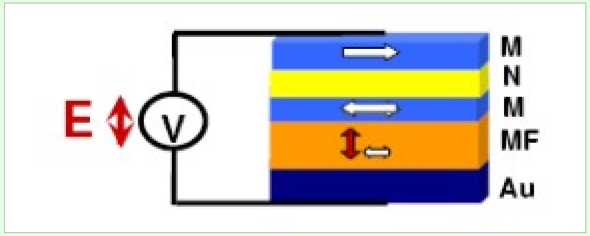


Eerenstein et al., Nature 442, 759 (2006).
Béa et al, J. Phys. Cond. Matter **20**, 434221 (2008)

Fundraising Excuses

Small coupling – 4 state memory

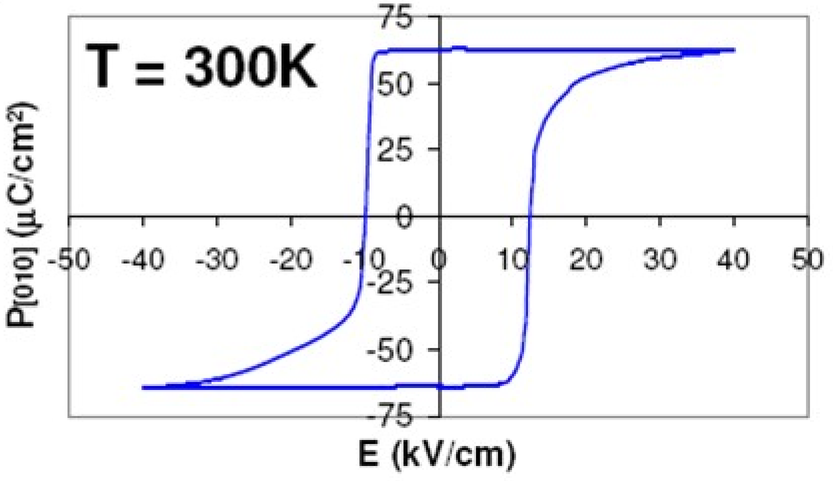
Large coupling – "E" write / "M" read



Taxonomy of Multiferroics

Ferroelectricity & Magnetism coexist

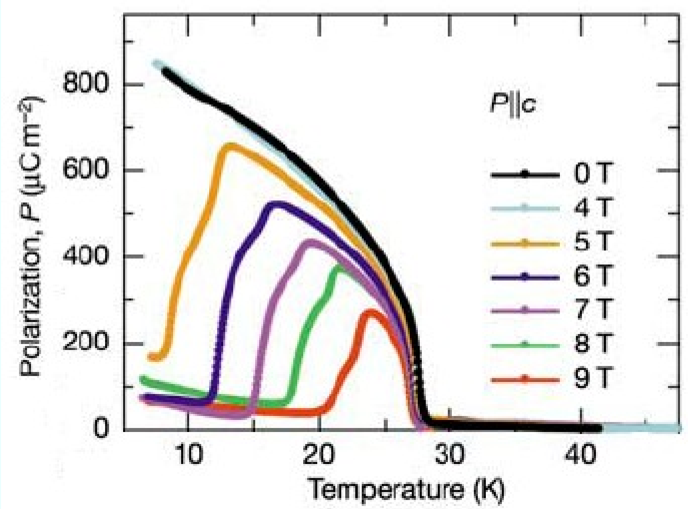
- ✓ $BiFeO_3$
- ✓ Large moments
- ✓ High temperature transitions
- ✓ Weak coupling



Lebeugle et al. APL 2007

Magnetism causes Ferroelectricity

- ✓ $TbMnO_3$
- ✓ Small moments
- ✓ Low temperatures
- ✓ Strong coupling



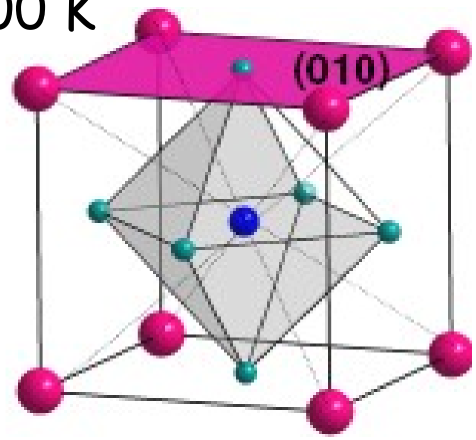
Kimura, Nature 2003

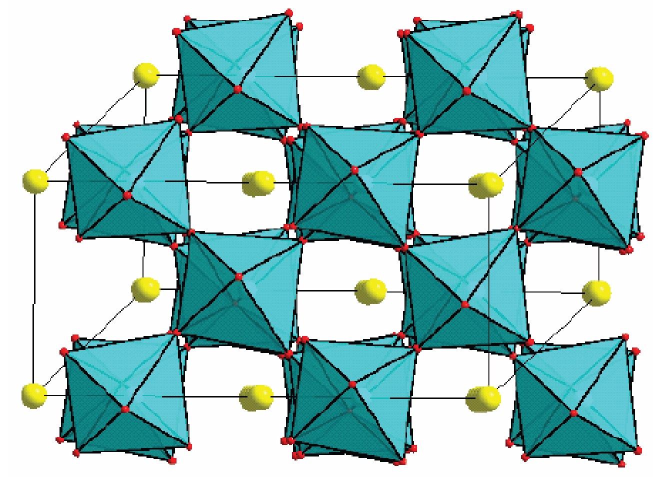
Orders of Magnitude

Composition	T_c (K)	P ($\mu C / cm^2$)	Obs.
$BaTiO_3$	400	15.	Displacive
$Pb(Zr,Ti)O_3$ (PZT)	~600	40.	Displacive
PDVF	(?) ~500	10.	No mag., melts at 450 K
KH_2PO_4 (KDP)	123	4.	Order-disorder
K_2SeO_4	93	0.06	Improper FE
$BiFeO_3$	~1100	100.	MF type I – Lone pairs
$TbMnO_3$	27	0.08	MF type II
$MnWO_4$	12	0.005	MF type II

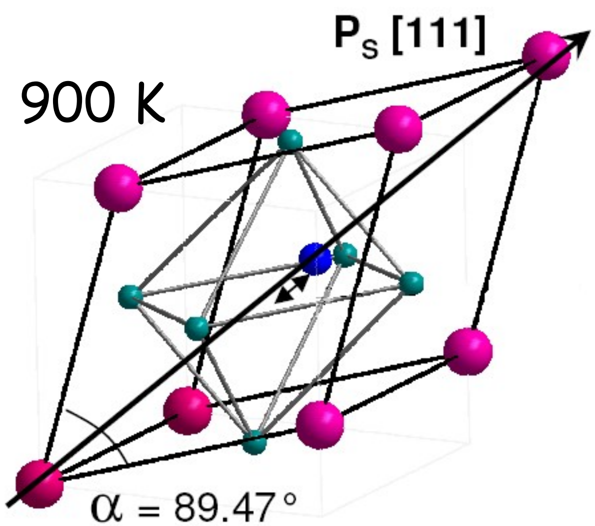
$BiFeO_3$ – Ferroelectric / Antiferromagnet

T > 1100 K

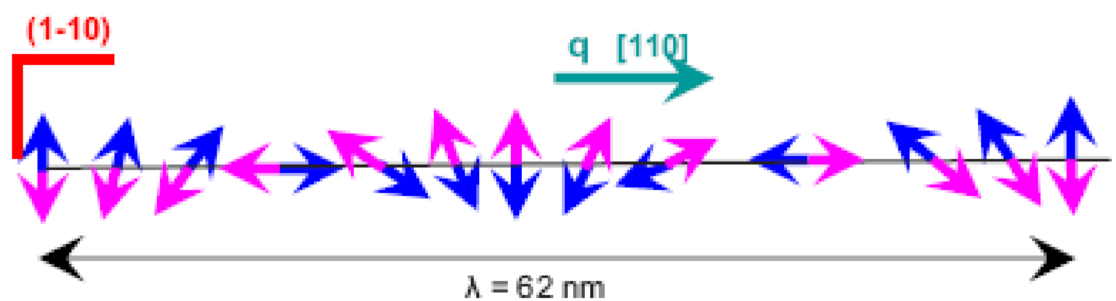




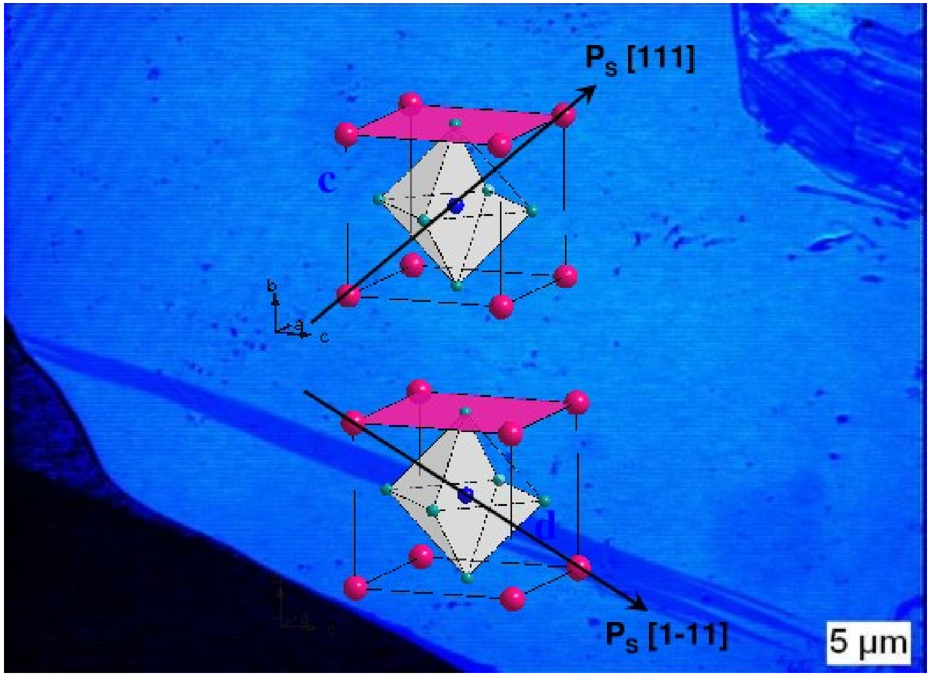
T < 900 K

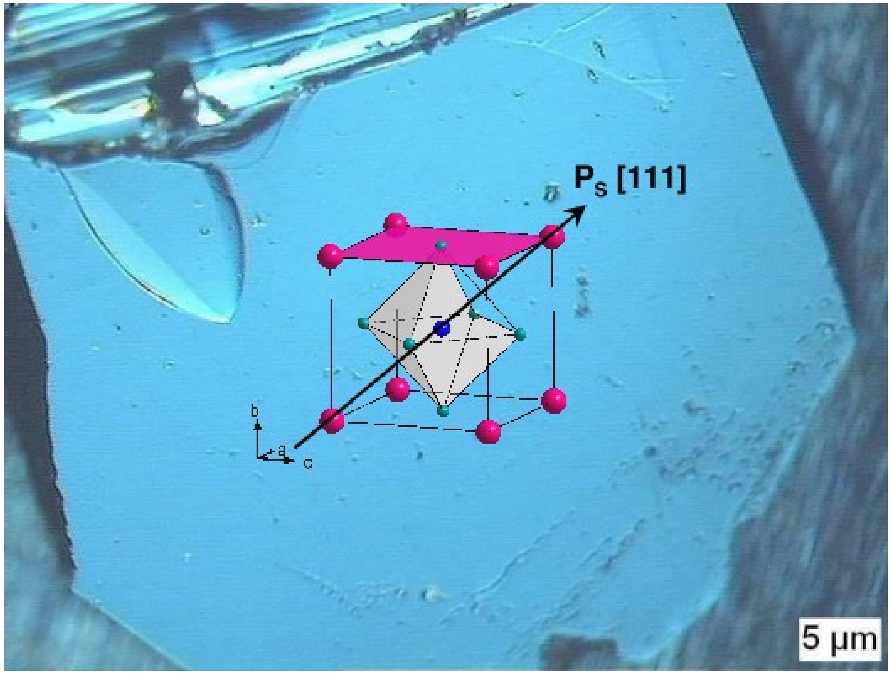


- ✓ Rhomboedral distortion of cubic perovskite
- ✓ Incommensurate AF spiral ordering
- ✓ T_C = 1100 K & T_N = 640 K



$BiFeO_3$ Ferroelastic Domains

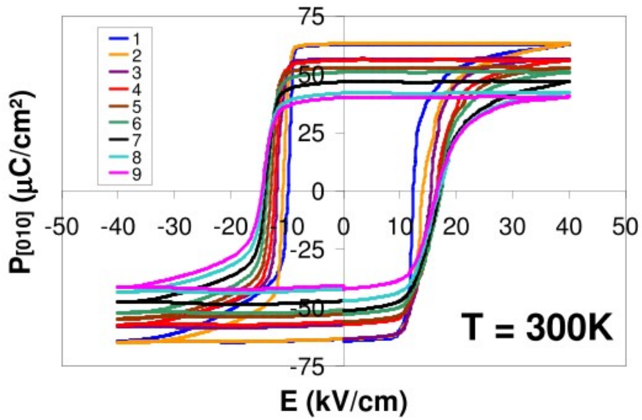




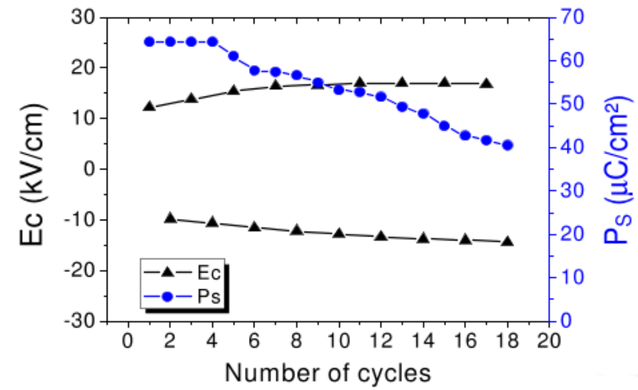
D. Lebeugle, PhD thesis

$BiFeO_3$ Properties

Large cyclable polarization

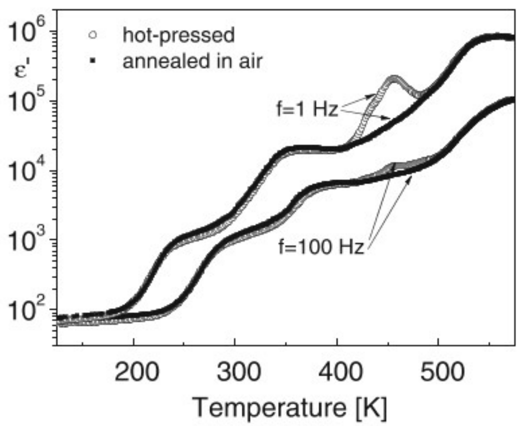


Electric fatigue



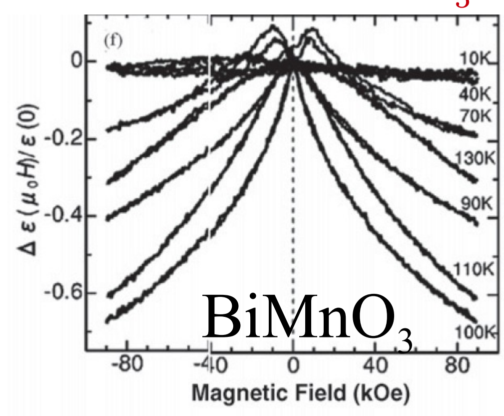
Lebeugle et al., APL **91**, 022907 (2007)

Large dielectric constant



Markiewiks, J. Electroceram **27**, 154 (2011)

Weak coupling ($BiMnO_3$)



T. Kimura PRB 67, 180401R (2003)

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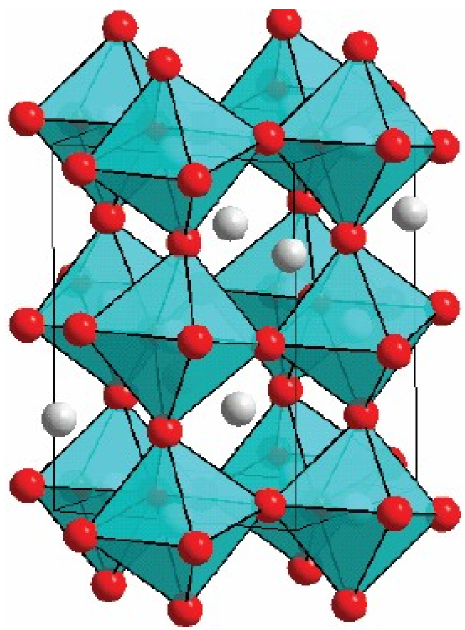
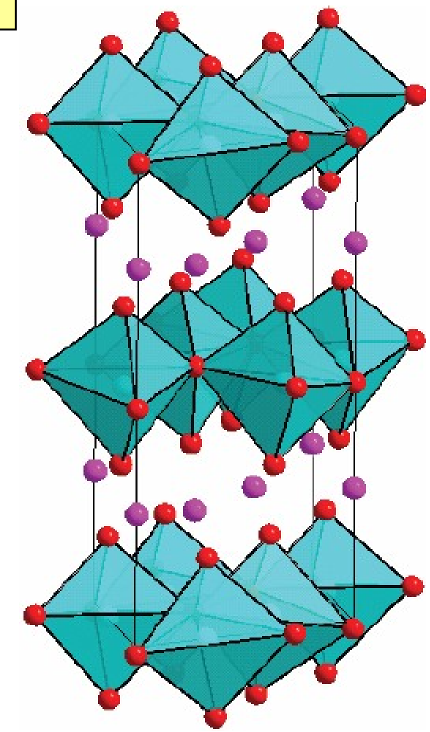
$RMnO_3$ structure

Perovskite

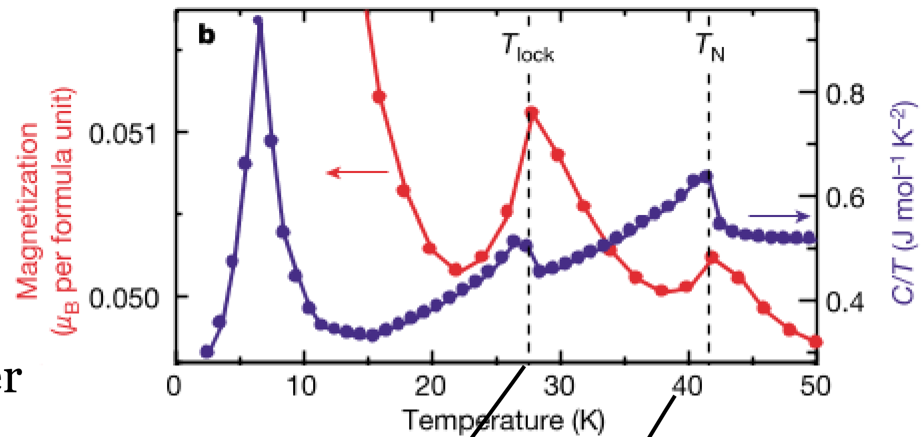
Hexagonal

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
										Y				

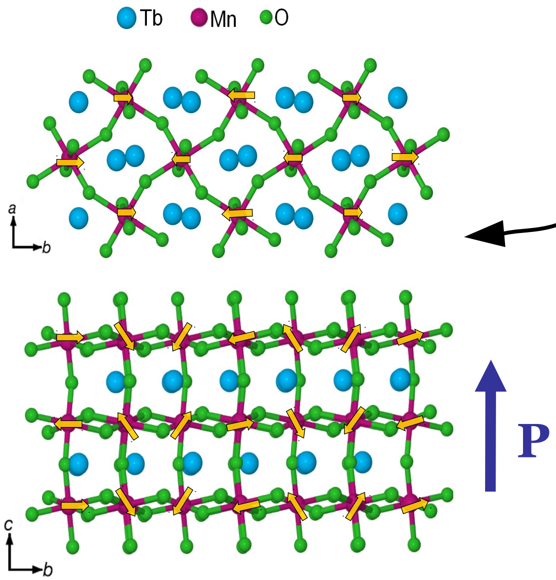




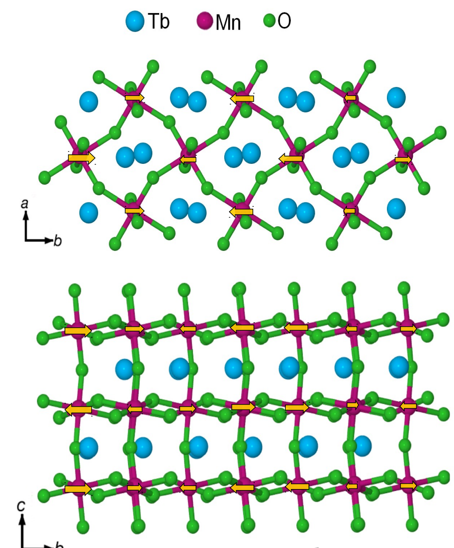
Multiferroicity in $TbMnO_3$



T < 27 K
Cycloidal spin order
Ferroelectric



T < 41 K
Sinusoidal spin order
Paraelectric



Kimura *et al*, Nature 426, 55 (2003).

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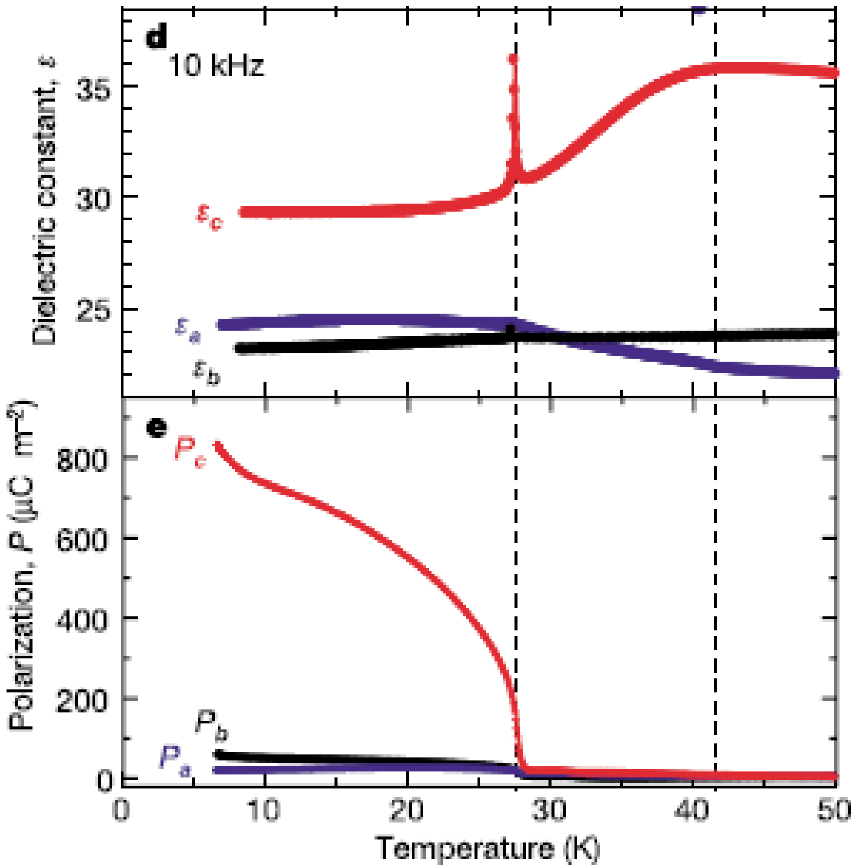
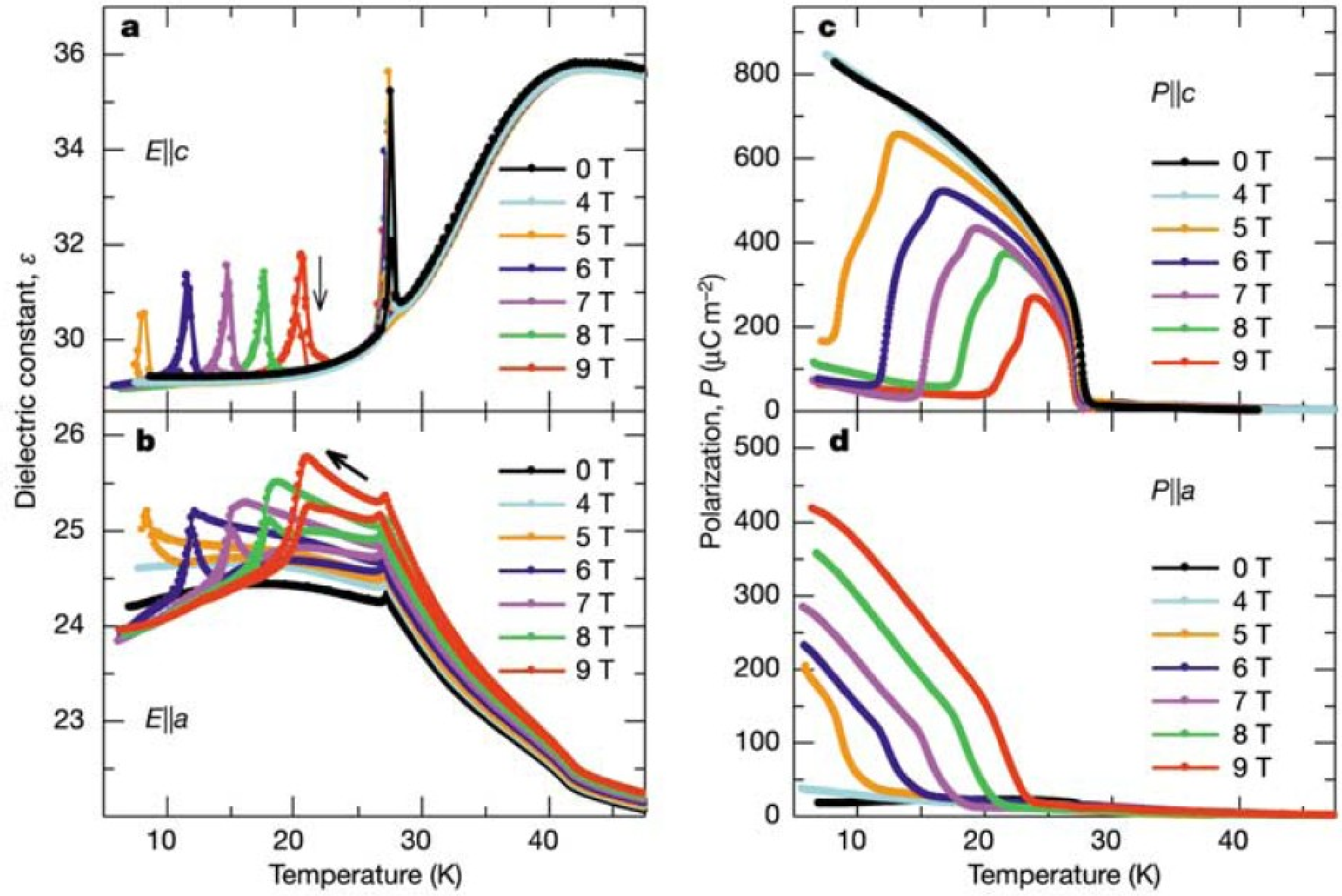
Ferroelectricity in $TbMnO_3$



- ✓Narrow divergence dielectric constant
- ✓Polarization of the order of that in improper ferroelectrics
- ✓Ferroelectricity induced by magnetic order

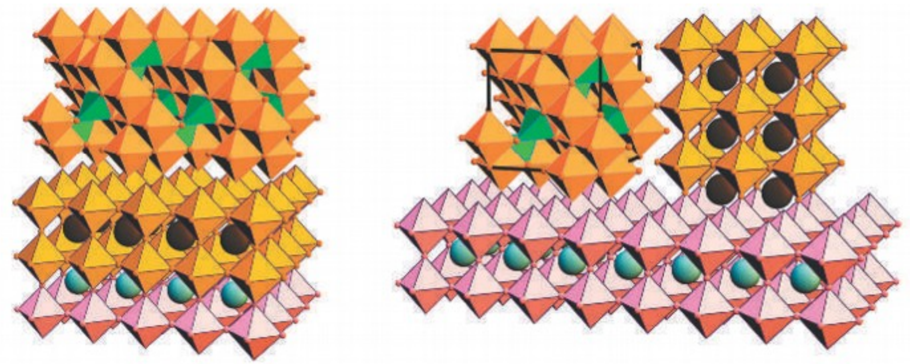
Kimura *et al*, Nature 426, 55 (2003).

Magneto-electric coupling in $TbMnO_3$



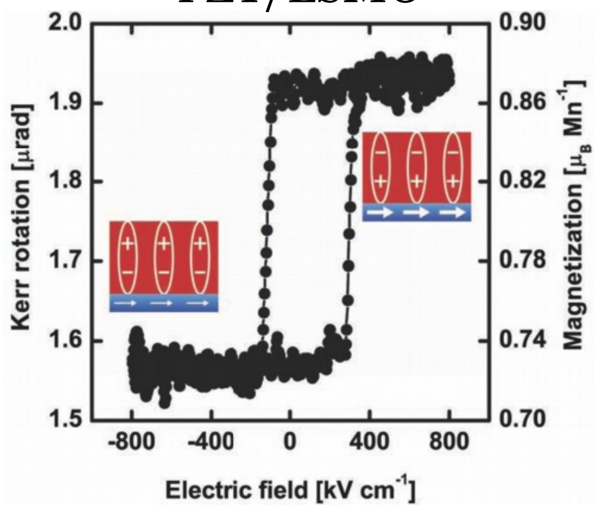
Kimura *et al*, Nature 426, 55 (2003).

Composite Materials



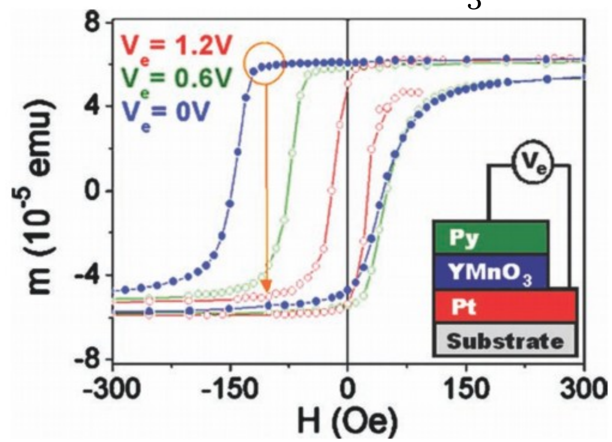
Alternation of piezoelectric and magnetostricitve materials

PZT/LSMO



Molegraaf *et al.*, Ad. Mat. **21**, 3470 (2009)

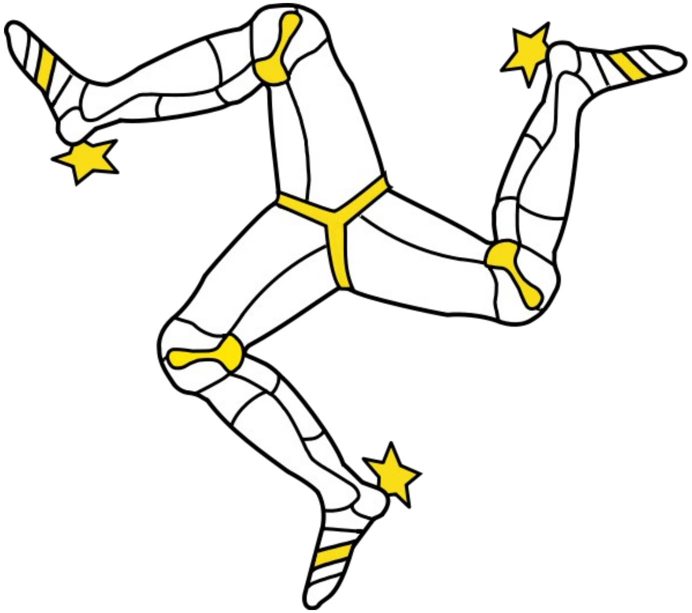
NiFe/YMnO$_3$



Laukin, PRL **97**, 227201 (2006)

Fiebig, J. Appl. Phys. D **38**, R123 (2005)
Ramesh and Spalding, Nat. Mat. **6**, 22 (2007)
Vaz et al. Ad. Mat. 22, 2900 (2010)

Symmetry Considerations



Vectors and Symmetry Operations

Polar

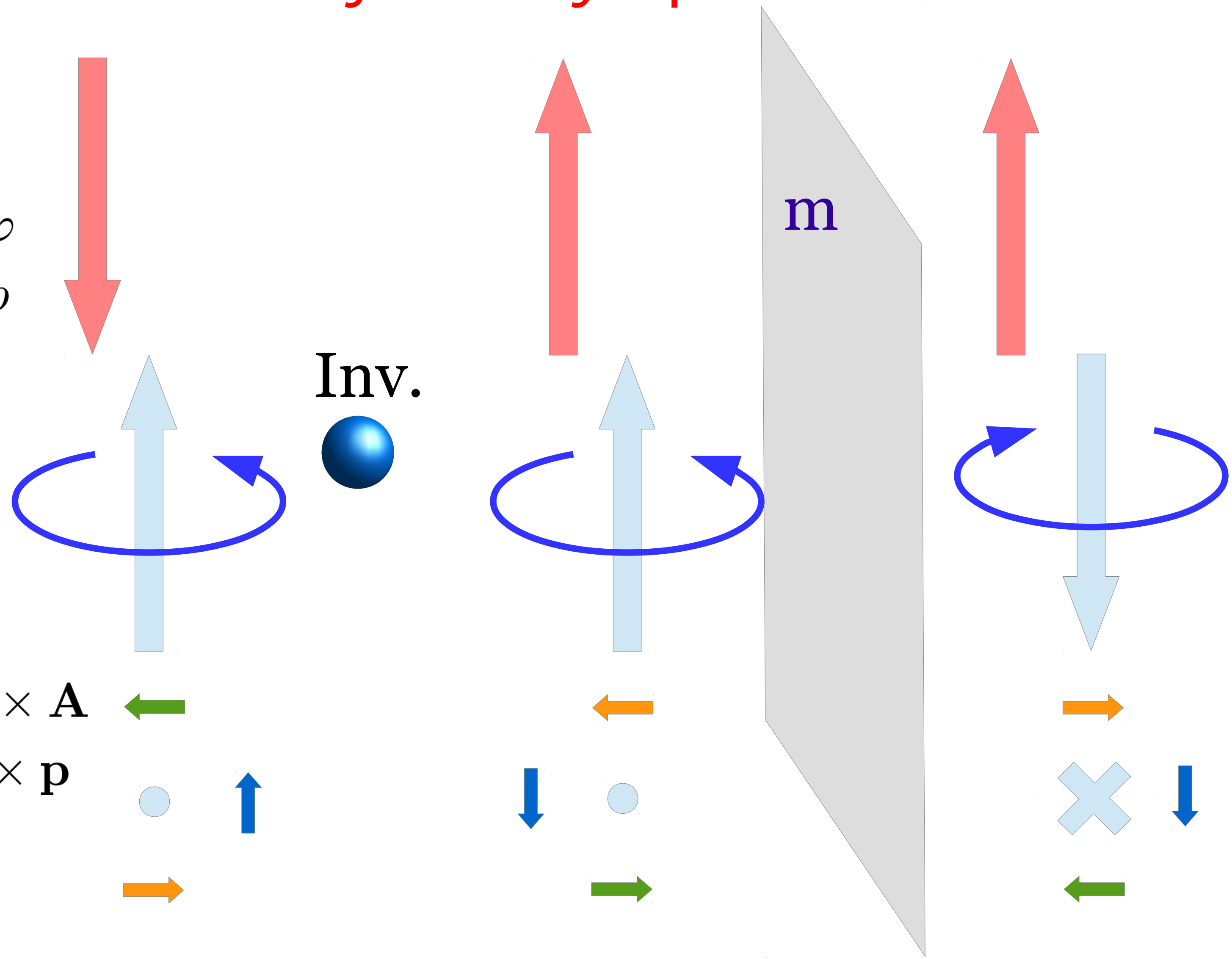
$$\mathbf{E} = -\nabla\varphi$$

$$\mathbf{P} = -\nabla\rho$$

Axial

$$\mathbf{H} = \nabla \times \mathbf{A}$$

$$\mathbf{M} = \mathbf{r} \times \mathbf{p}$$



The first ideas…

SUR LA SYMÉTRIE DANS LES PHÉNOMÈNES PHYSIQUES, SYMÉTRIE D'UN CHAMP ÉLECTRIQUE ET D'UN CHAMP MAGNÉTIQUE;

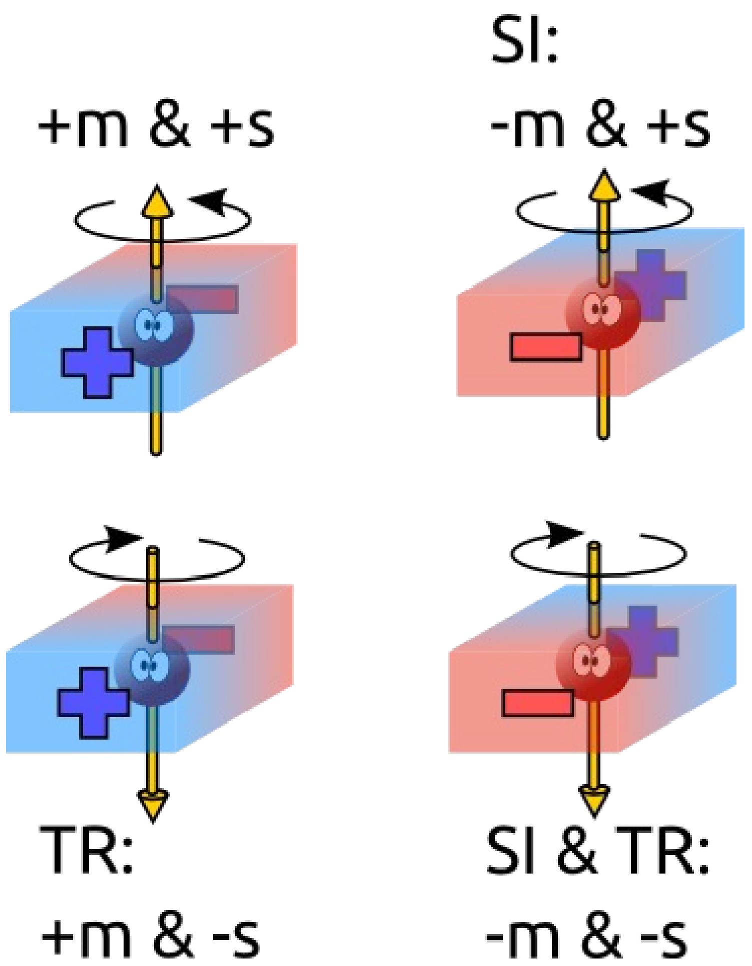
Par M. P. CURIE.

J. de Phys., 3ᵉ série, t. III. (Septembre 1894.)

Same year as Rochelle salt (Pockels)

Les phénomènes généraux de l'électricité et du magnétisme nous indiquent donc seulement une *liaison entre les symétries* du champ électrique et du champ magnétique, de telle sorte que, si l'on adopte (*c*) pour la symétrie de l'un, il faut admettre (*d*) pour la symétrie de l'autre, et réciproquement. Pour lever cette indétermination, il faut faire intervenir d'autres phénomènes, les phénomènes électrochimiques ou d'électricité de contact, les phénomènes pyro ou piézoélectriques, ou encore le phénomène de Hall, ou celui de la polarisation rotatoire magnétique.

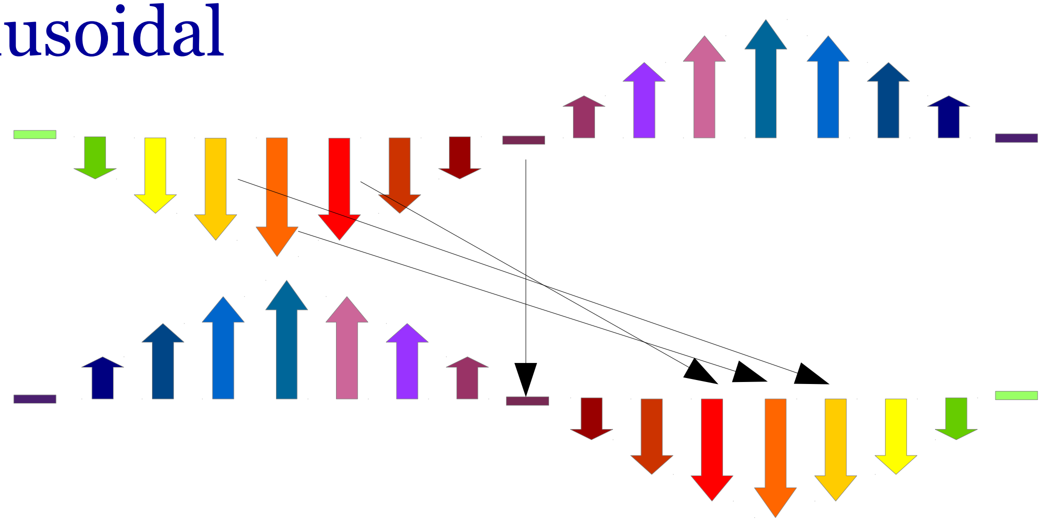
Symmetry Shattering



- Spatial Inversion (SI) symmetry breaking:
  Makes sure that the electrical polarization exists but has no effect on the magnetization
- Time Reversal (TR) symmetry breaking:
  Allows for spontaneous magnetic ordering but ignores polar vector quantities
- SI + TR breaking
  *Both, expontaneous **P** and **M** exist*

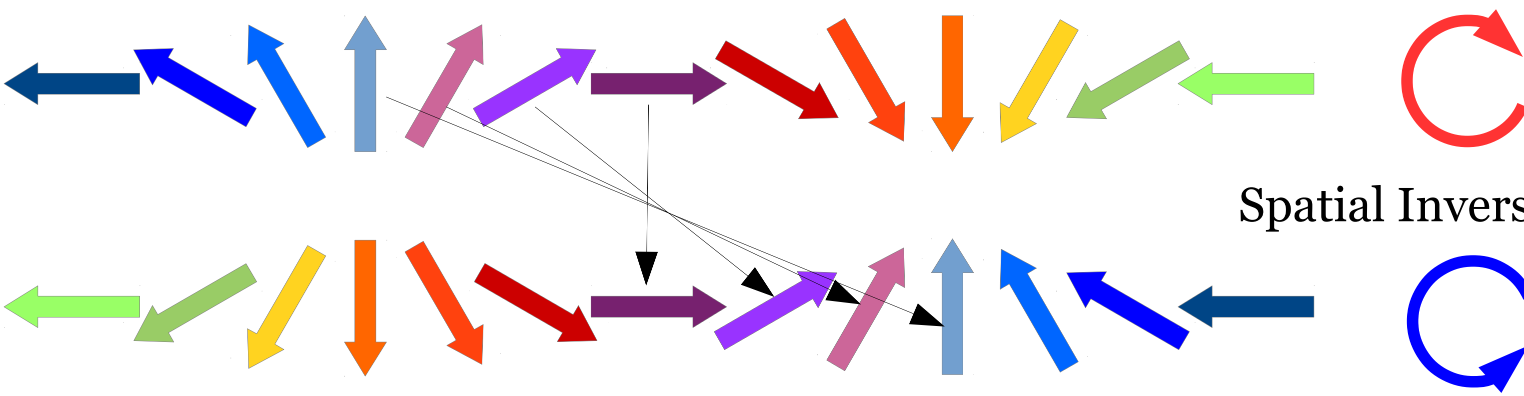
Spin Ordering

Sinusoidal



No Spatial Inversion breaking

Cycloidal



Spatial Inversion broken

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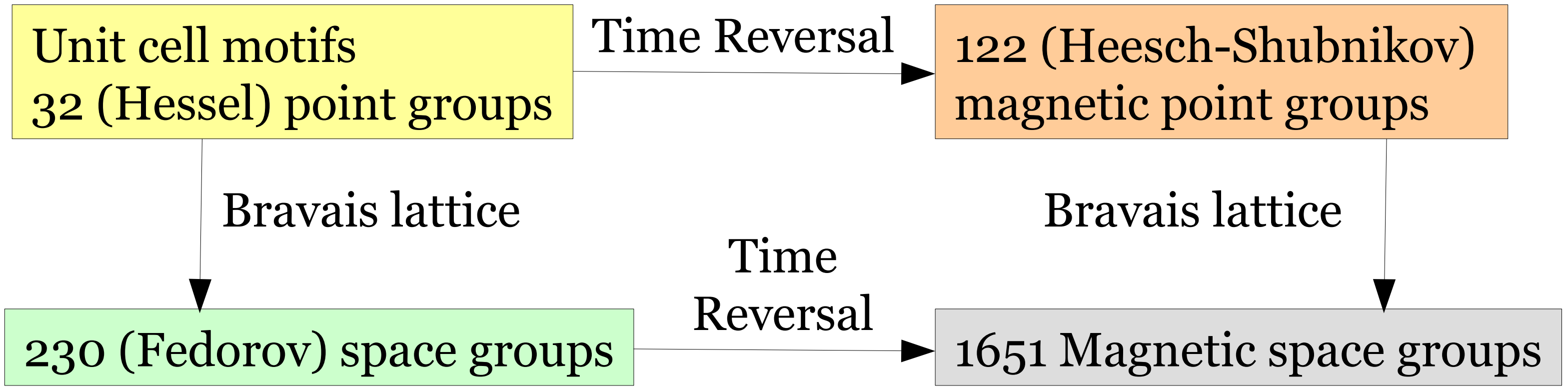
Symmetry groups



112 H-S groups
- 31 allow **P**
- 31 allow **M**
- 13 allow **P & M**

Magnetic point group	Required relations between P_s and M_s	Ferroelectrically induced spin canting
1	none	allowed
m'	$\hat{P} \parallel m'$, $\hat{M} \parallel m'$	allowed
m	$\hat{P} \parallel m$, $\hat{M} \perp m$	allowed
$2'$	$\hat{P} \perp \hat{M}$, $\hat{P} \parallel 2'$	allowed
$m'm2'$	$\hat{P} \parallel 2'$, $\hat{M} \perp m$	allowed
$2, m'm'2$	$\hat{P} \parallel 2 \parallel \hat{M}$	forbidden
$3, 3m', 4, 4m'm', 6, 6m'm'$	$\hat{P} \parallel \hat{M} \parallel$ principal axis	forbidden

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

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Magnetoelectric Effect

$$-g(\mathbf{E},\mathbf{H}) = \cdots + P_i E_i + M_i H_i$$
$$+ \tfrac{1}{2}\varepsilon_0 \varepsilon_{ik} E_i E_k + \tfrac{1}{2}\mu_o \mu_{ik} H_i H k$$
$$+ \alpha_{ik} E_i H_k$$

→ Linear coupling

$$+ \tfrac{1}{2}\beta_{ijk} E_i H_j H_k + \tfrac{1}{2}\gamma_{ijk} H_i E_j E_k$$
$$+ \tfrac{1}{6}\delta_{ijk} E_i E_j E_k + \tfrac{1}{6}\eta_{ijk} H_i H_j H_k + \cdots$$

} Bilinear coupling

$$\alpha_{ik} \sim 10^6 \beta_{ijk}$$

$$P_k(\mathbf{E},\mathbf{H}) = -\frac{\partial g}{\partial E_k} = \cdots + P_k + \varepsilon_0 \varepsilon_{ki} E_i + \alpha_{ki} H_i$$
$$+ \tfrac{1}{2}\beta_{kij} H_i H_j + \gamma_{ijk} H_i E_j + \cdots$$

$$M_k(\mathbf{E},\mathbf{H}) = -\frac{\partial g}{\partial H_k} = \cdots + M_k + \mu_0 \mu_{ki} H_i + \alpha_{ik} E_i$$
$$+ \beta_{ijk} E_i H_j + \tfrac{1}{2}\gamma_{kij} E_i E_j + \cdots$$

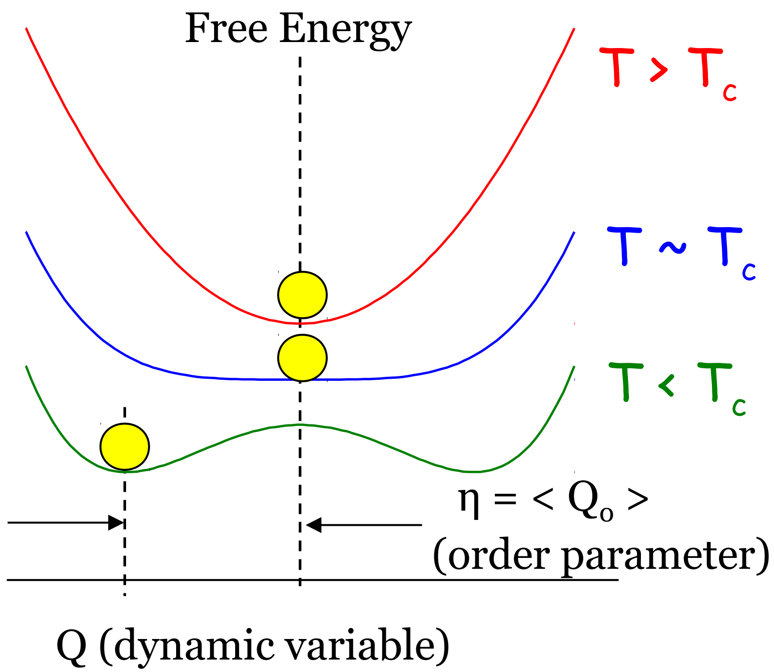
Rivera, Eur. Phys. J. B **71**, 299 (2009)

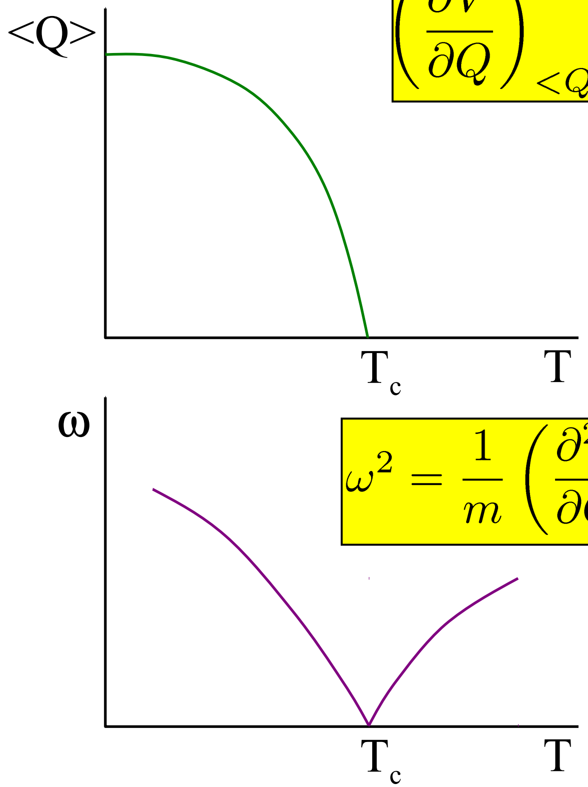
Strong Ferroelectric Phase Transitions

Soft Mode & Phase Transitions

Q is a dynamic variable of the system

Order parameter $\eta = \langle Q \rangle \begin{cases} = 0, & T > T_c \\ \neq 0, & T < T_c \end{cases}$



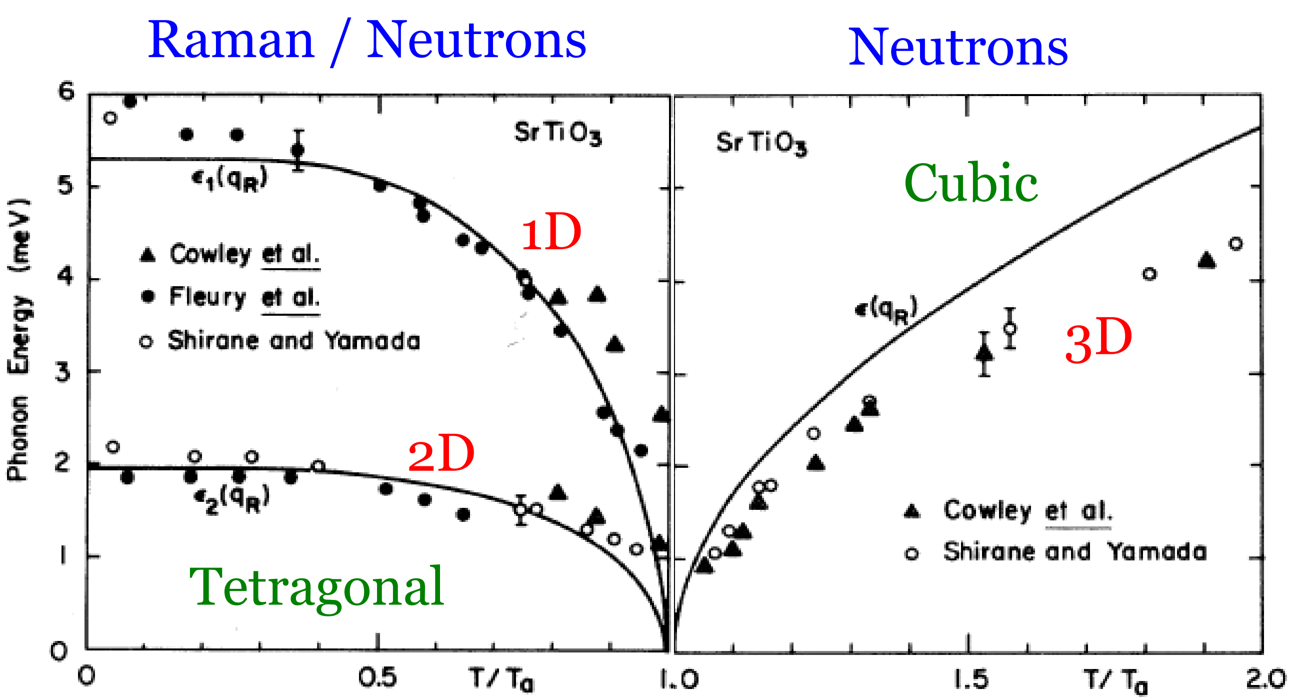


$$\left(\frac{\partial V}{\partial Q}\right)_{<Q>} = 0$$

$$\omega^2 = \frac{1}{m}\left(\frac{\partial^2 V}{\partial Q^2}\right)_{<Q>}$$

Is this soft mode mambo-jambo real?

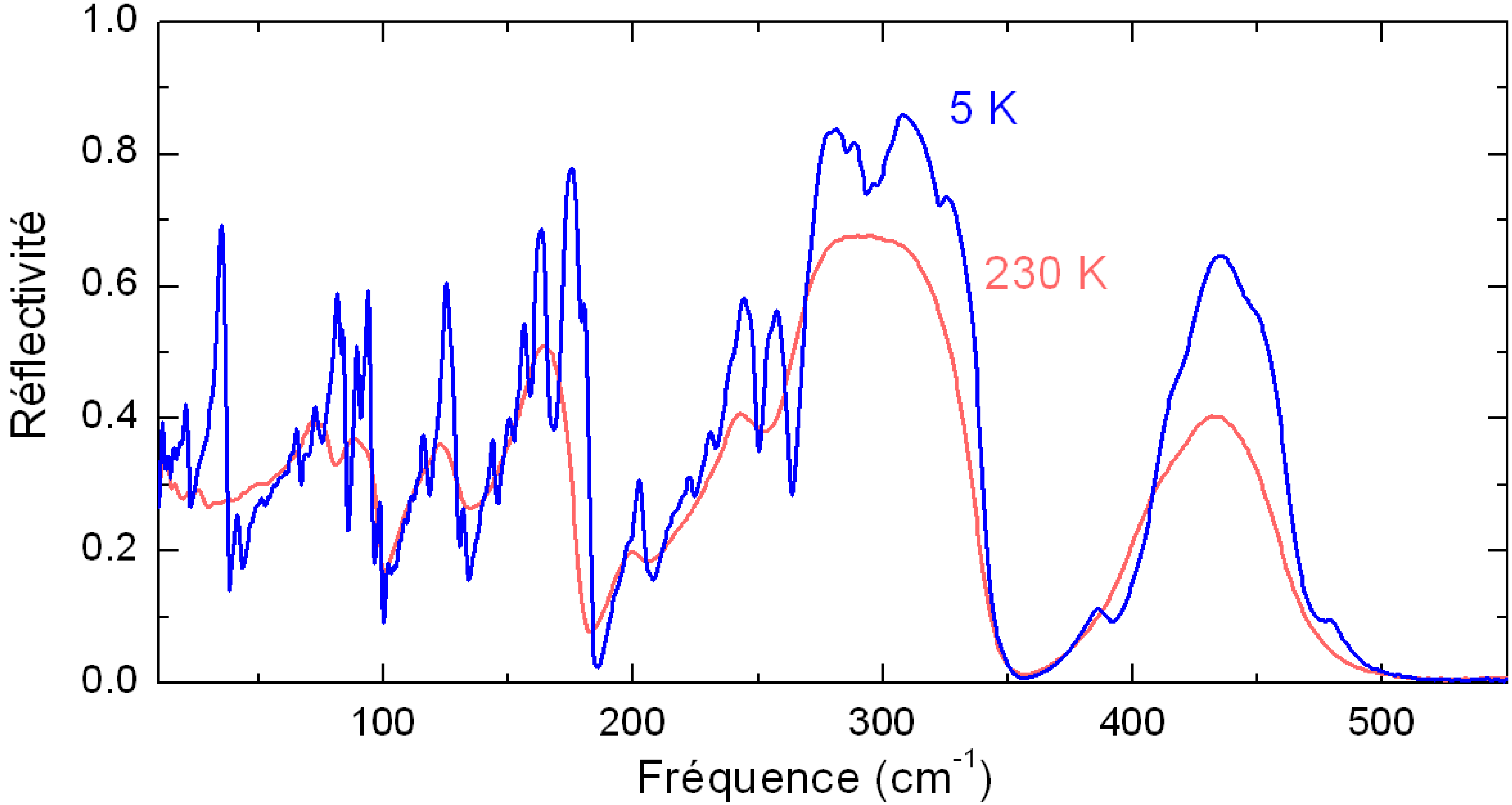
$SrTiO_3$: Cubic → Tetragonal transition at T_c = 110 K



Soft mode = Phonon → Displacive transition

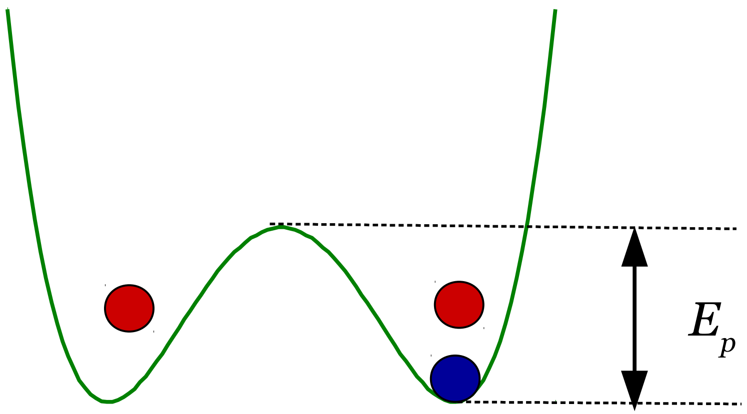
Feder & Pytte, PRB **1**, 4803 (1970)

Orthorhombic-triclinic(?) transition in $BaMnF_4$



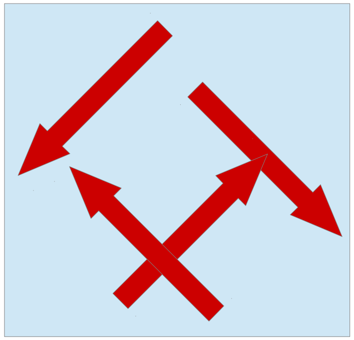
Schleck et al. 2012.

Order-Disorder transitions



$k_B T > E_p$

Random polarization orientation

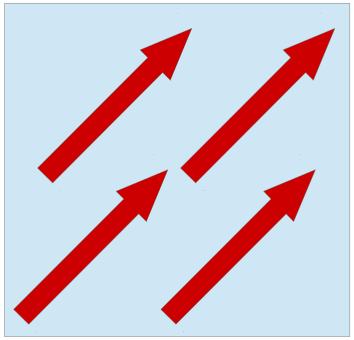


$k_B T_c \sim E_p$

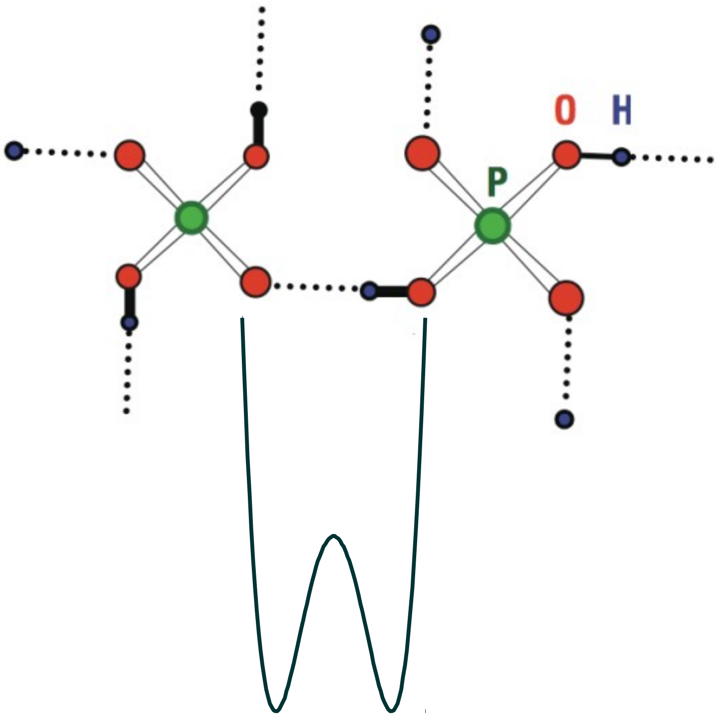
- Same potential for paraelectric and ferroelectric phases
- "Soft-mode" with a relaxation character

$k_B T < E_p$

One polarization direction freezes

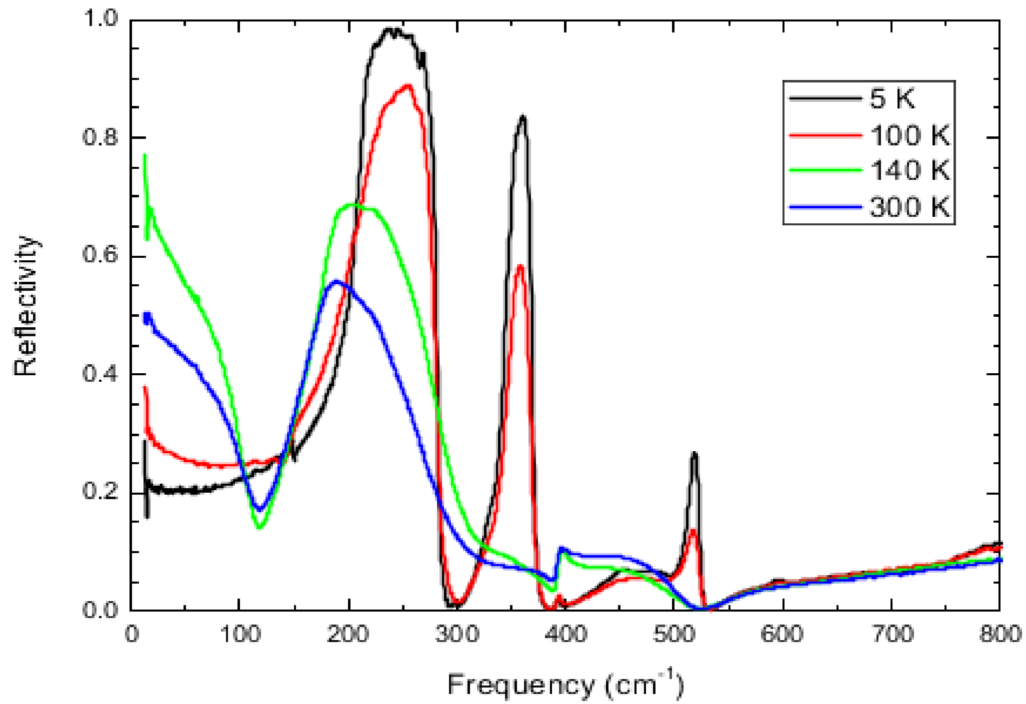


Ferroelectricity in KH_2PO_4 (KDP)



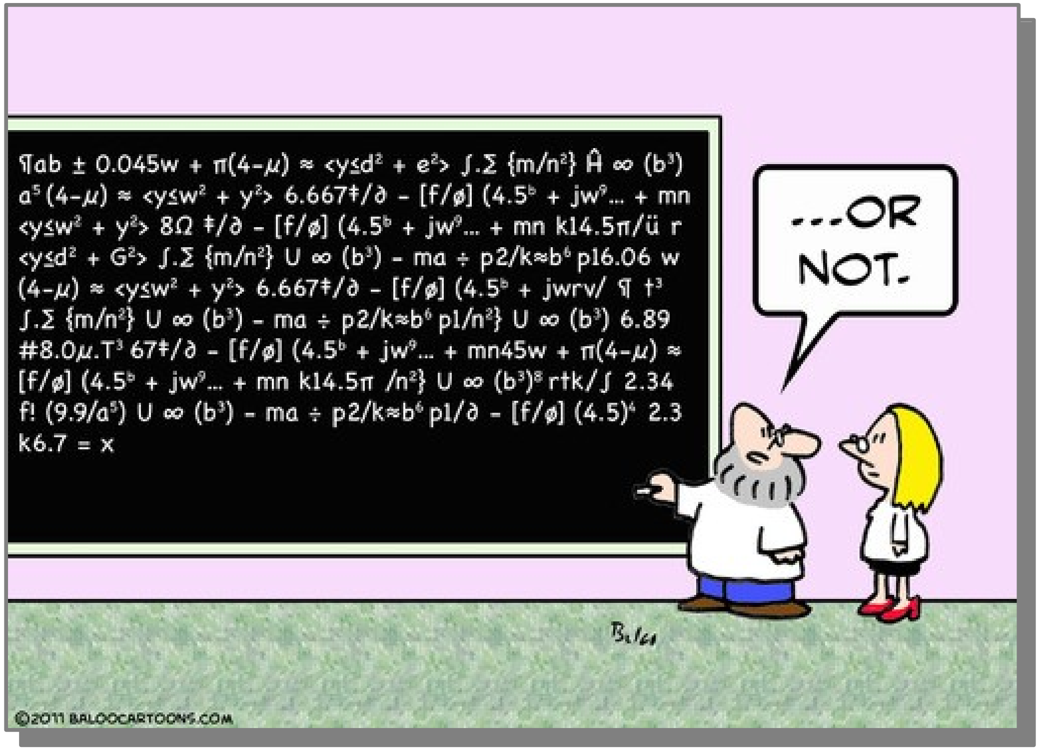
Double well potention
on O-H bonds

A4 axis (polarization)



Akrap et al, unpublished

Tentative Theoretical Aspects



Multiferroicness

6694 *J. Phys. Chem. B* **2000**, *104*, 6694–6709

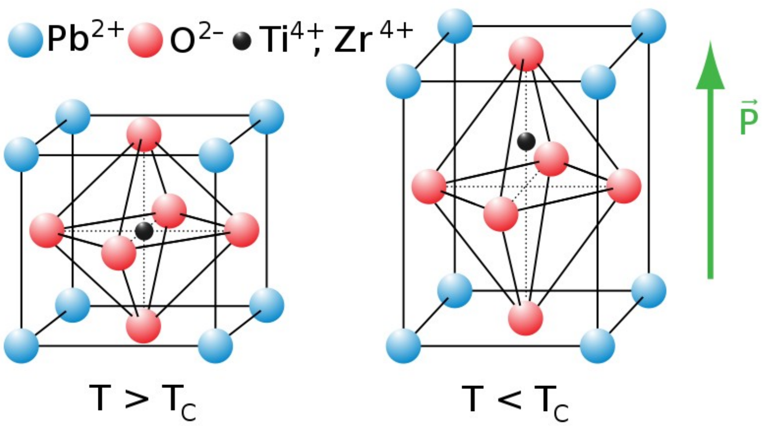
FEATURE ARTICLE

Why Are There so Few Magnetic Ferroelectrics?

Nicola A. Hill
Materials Department, University of California, Santa Barbara, California 93106-5050

- ✓ Symmetry: 13 (out of 122) point groups allow spontaneous P and M to coexist
- ✓ Ferromagnetic materials like to be metallic (so AFM is welcome to the club)
- ✓ d^0-ness

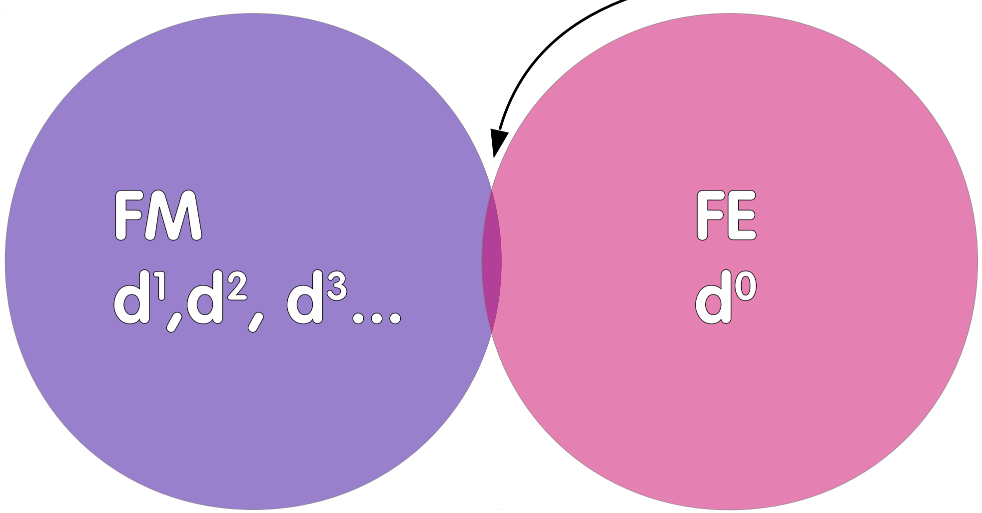
d^0-ness and Ferroelectricity



Ti: [Ar] $3d^2\ 4s^2 \rightarrow Ti^{4+}$: [Ar] $3d^0\ 4s^0$

Zr: [Kr] $5s^2\ 4d^2 \rightarrow Ti^{4+}$: [Ar] $5s^0\ 4d^0$

Ferroelectric distortions in perovskites like d^0 electronic configurations



Multiferroics

Ab initio and observation shows that filling *d* orbitals inhibits FE distortions in perovskites

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

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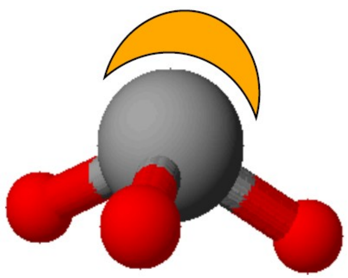
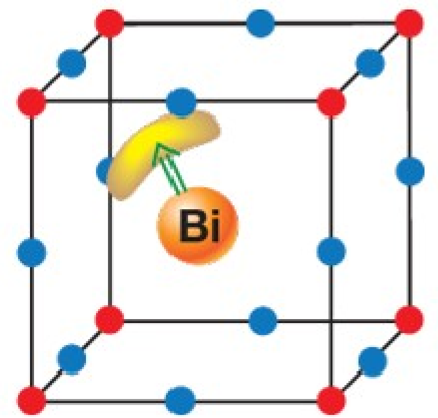
Lone Pairs Ferroelectricity

Pb: [Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^2$
Bi: [Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^3$

s^2 → "Dangling bonds"



p orbitals handle the chemical bonding



- High polarizability of s^2 electrons
- Local dipoles
- Main mechanism in $BiFeO_3$
- Enhances ferroelectricity in PZT

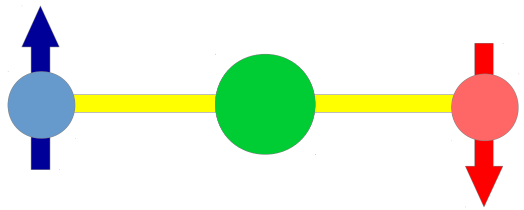
$BiFeO_3$ beats d^0-ness:

Ferroelectricity in A site (Bi)
Antiferromagnetist in B site (Fe)

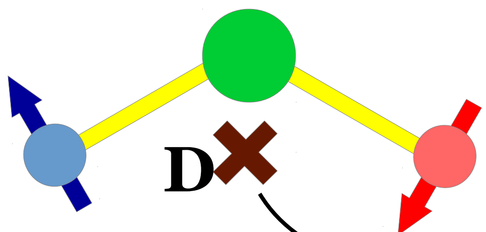
(Inverse) Dzyaloshinskii-Moriya

Dzyaloshinskii:

Why weak ferromagnetism in AFM materials?

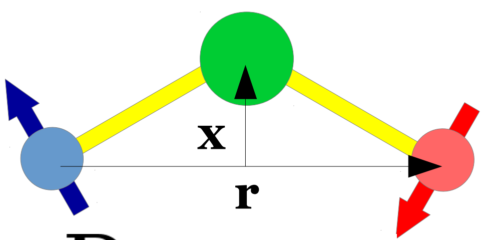


$\mathbf{D} \cdot (\mathbf{S}_1 \times \mathbf{S}_2)$ into free energy



Spin canting and FM component...
...but no information about **D**

Moriya:

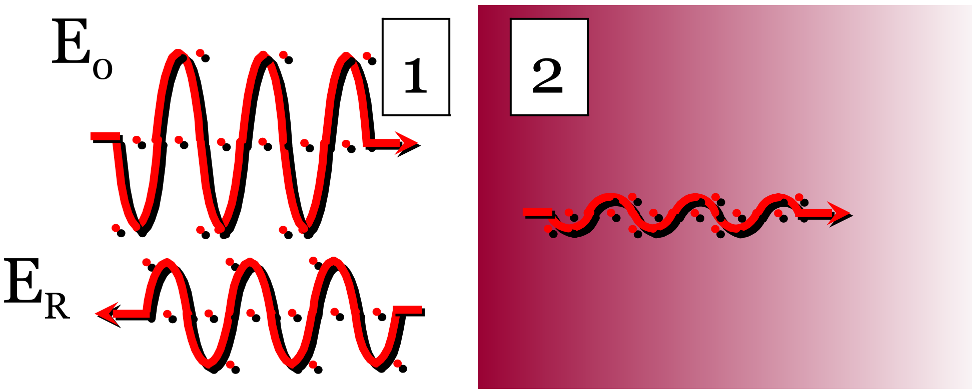


$$\mathbf{D} \propto \mathbf{r} \times \mathbf{x}$$

Inverse DM: If the spins are already canted...

Spectroscopical Toolbox

Infrared



$\Delta\vec{k} \approx 0$ Momentum averaged

$\omega = \omega'$ Elastic scattering

$\omega \in [0, \infty]$ Broadband spectroscopy

$\chi_{Elec} \gg \chi_{Mag}$ Electric field dominates

$$R = \left|\frac{E_R}{E_0}\right|^2 = \left|\frac{1-\sqrt{\varepsilon}}{1+\sqrt{\varepsilon}}\right|^2 = \left|\frac{1-n}{1+n}\right|^2$$

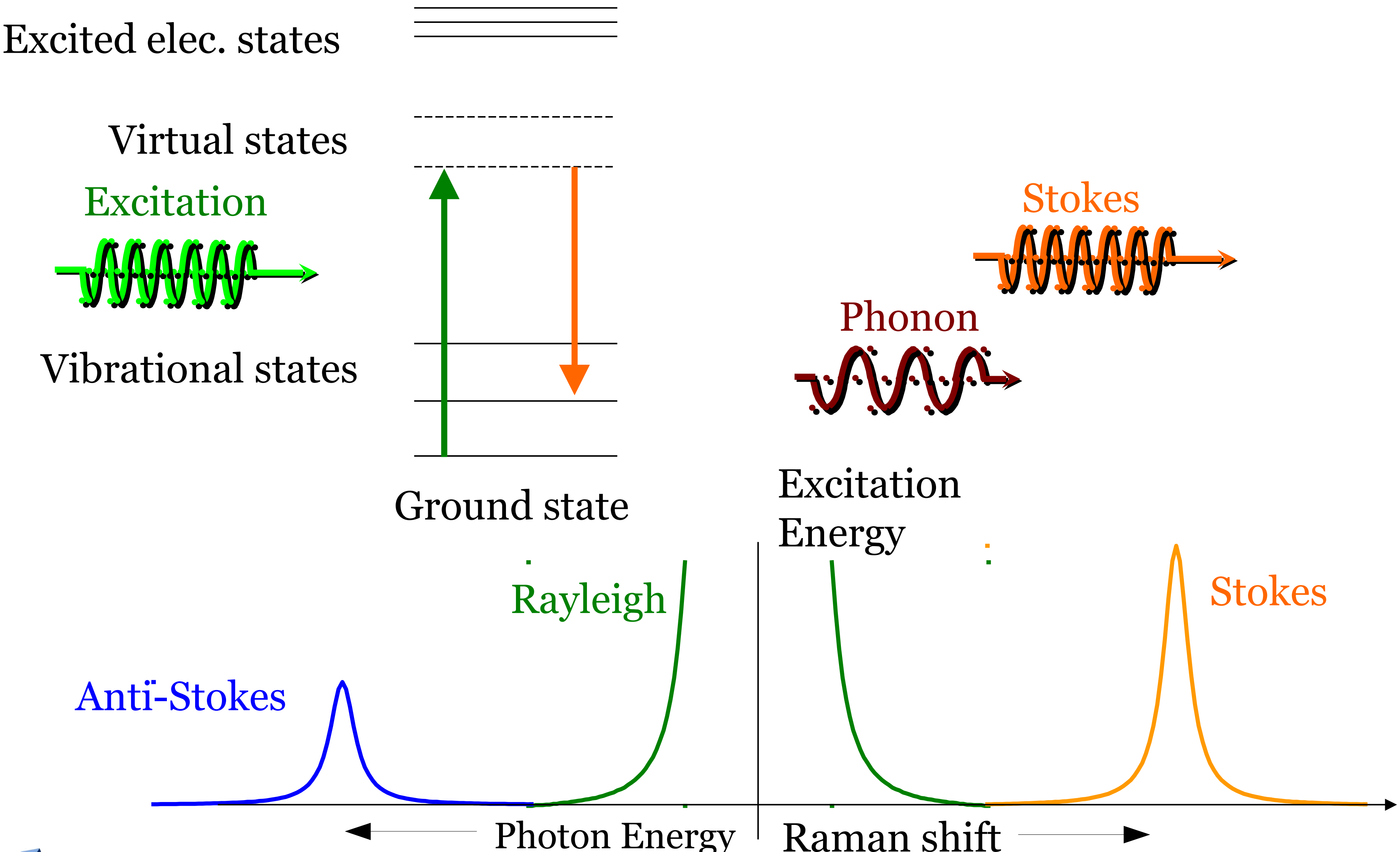
Reflected Power (Real)

Do something...

Complex Optical Function

$$\sigma = \sigma_1 + i\sigma_2$$
$$= i\varepsilon_0\omega(1-\varepsilon)$$

Raman explained by Infrared people



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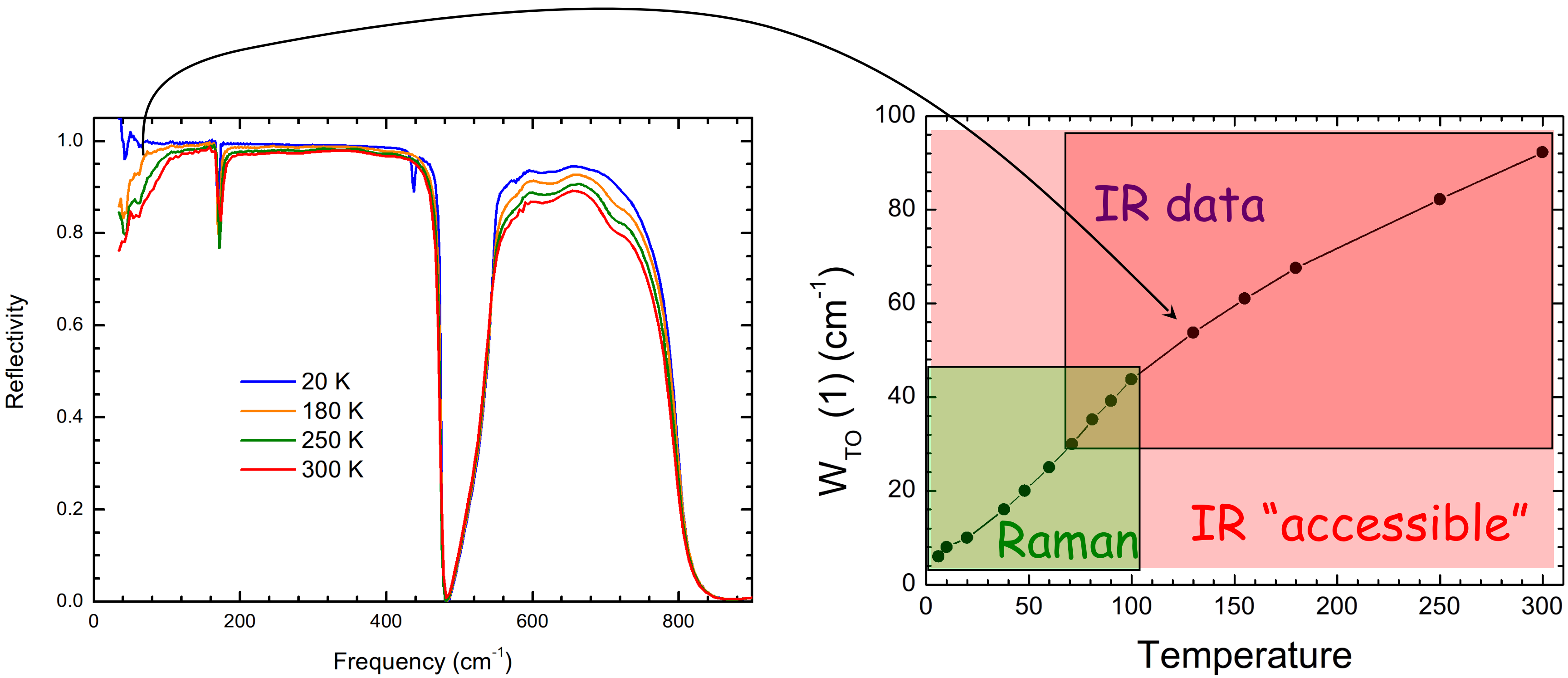
Infrared vs. Raman

$$\mu = \alpha E$$

μ – Dipole moment → Infrared
α – Polarizability (2nd order tensor) → Raman

32 Point Groups	Classes	IR vs. Raman
C_1, C_2, C_s, C_3, C_{3v}	5 polars (= pyro)	Raman = IR
C_{2v}, C_4, C_{4v}, C_6, C_{6v}	5 polars (= pyro)	Raman $\supset$ IR
D_2, S_4, D_{2d}, T, T_d	5 piezo, non pyro	Raman $\supset$ IR
D_4, D_3, C_{3h}, D_6, D_{3h}	5 piezo, non pyro	E in Raman & IR; A in IR; Other in Raman
C_{2h}, D_{2h}, C_{4h}, D_{4h}, S_6, D_{3d}, C_{6h}, D_{6h}, T_h, O_h, O	11 inversion symmetry and O	Raman $\cap$ IR = $\varnothing$

$SrTiO_3$ – IR / Raman working together

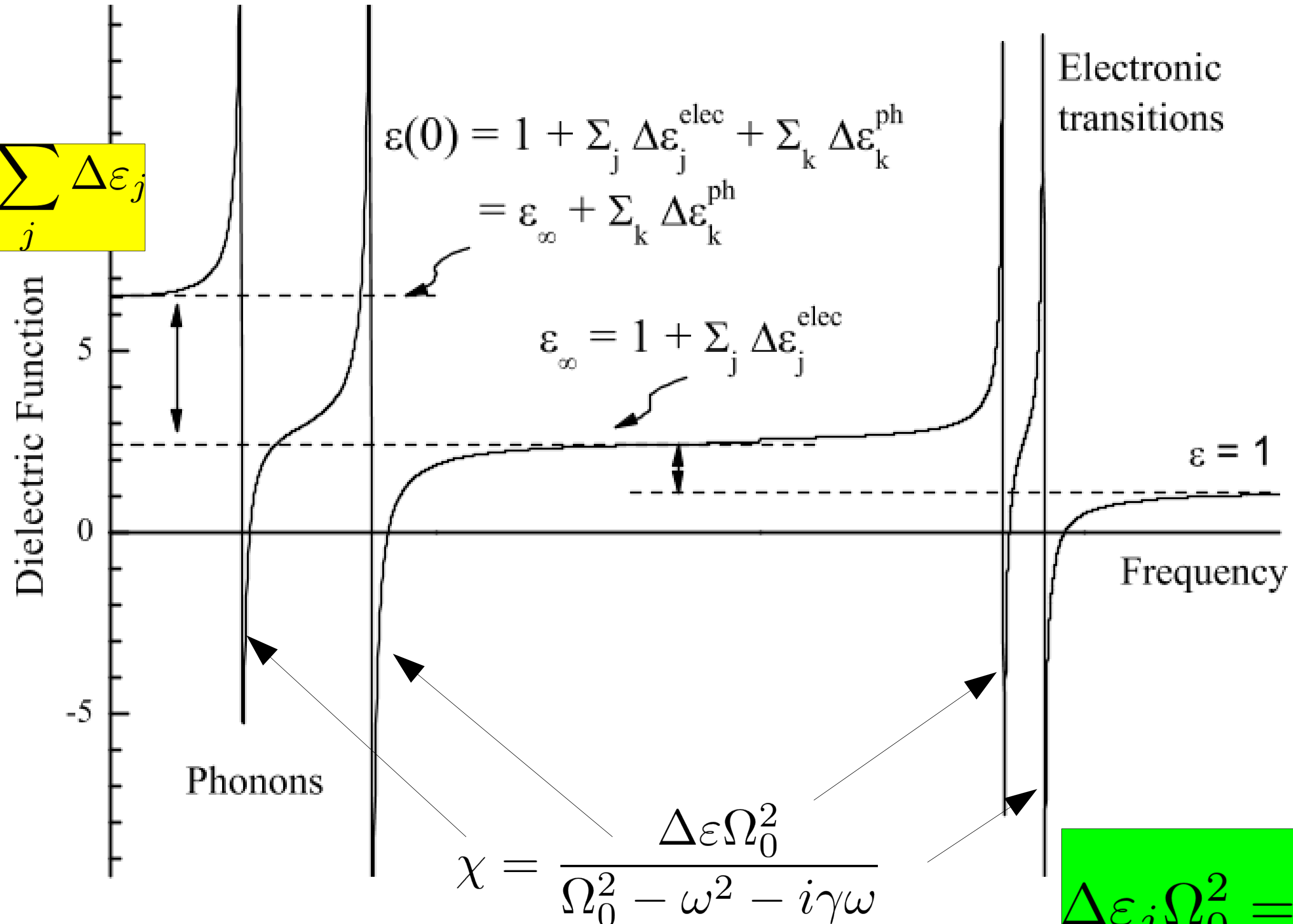


Bad: Long wavelengths (low energies) in IR hit diffraction (technical only) problems.

Good: IR access the polar phonons in high T and low T symmetries

Building the Dielectric Constant

$$\varepsilon(0) = 1 + \sum_j \Delta\varepsilon_j$$



$$\Delta\varepsilon_j \Omega_0^2 = \frac{n_j q_j^2}{m_j}$$

The f-sum rule

(Pour les voyageurs dans le temps, voir cours de Vihn samedi et revenir...)

The f-sum rule (particle conservation):

$$\int_0^\infty \sigma_1(\omega)\, d\omega \sim \int_0^\infty \omega\varepsilon''(\omega)\, d\omega \sim \frac{n}{m}$$

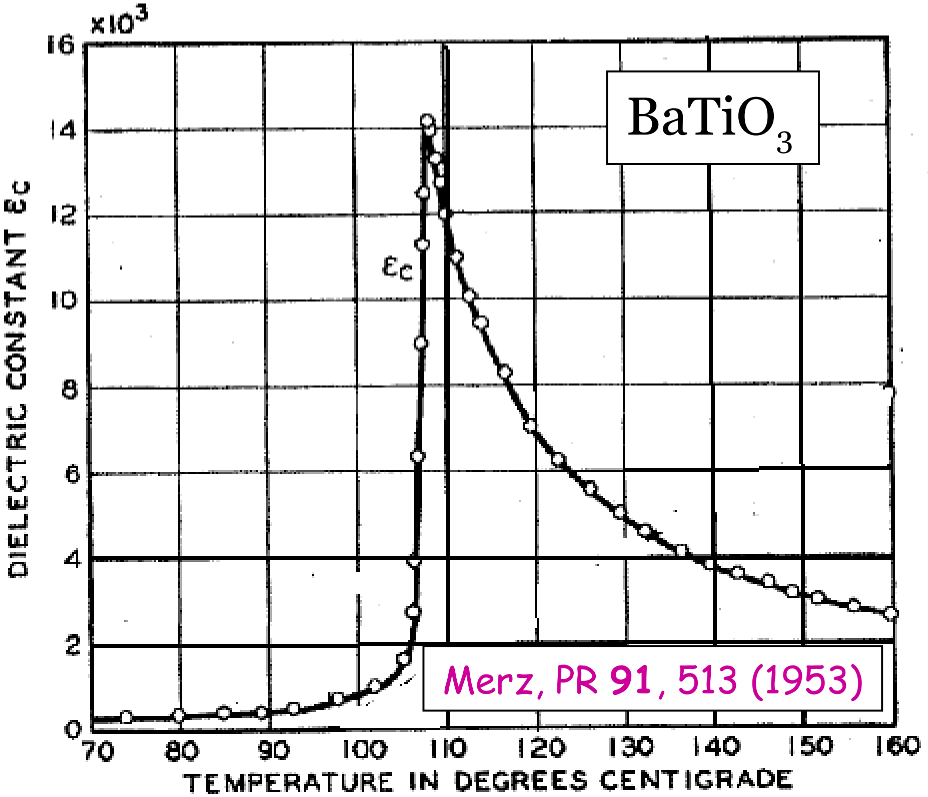
The f-sum rule for phonons:

$$\sum_j \Delta\varepsilon_j \Omega_{0j}^2 = \sum_j \frac{n_j q_j^2}{m_j} = const$$

The f-sum rule for decoupled phonons:

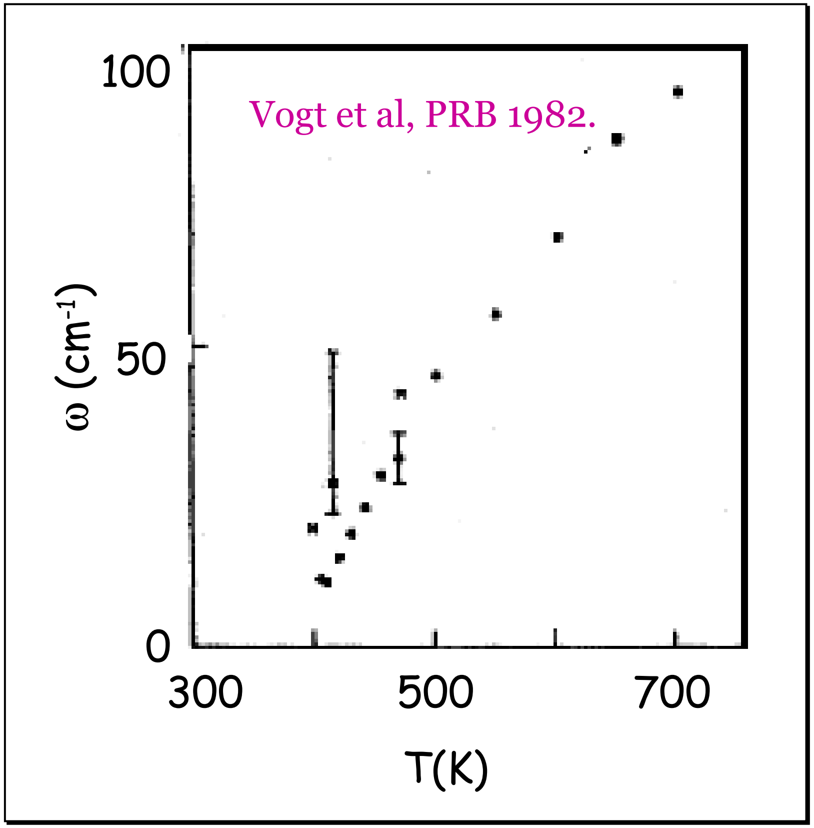
$$\Delta\varepsilon_j \Omega_{0j}^2 = \frac{n_j q_j^2}{m_j} = const$$

Soft mode and Ferroelectrics

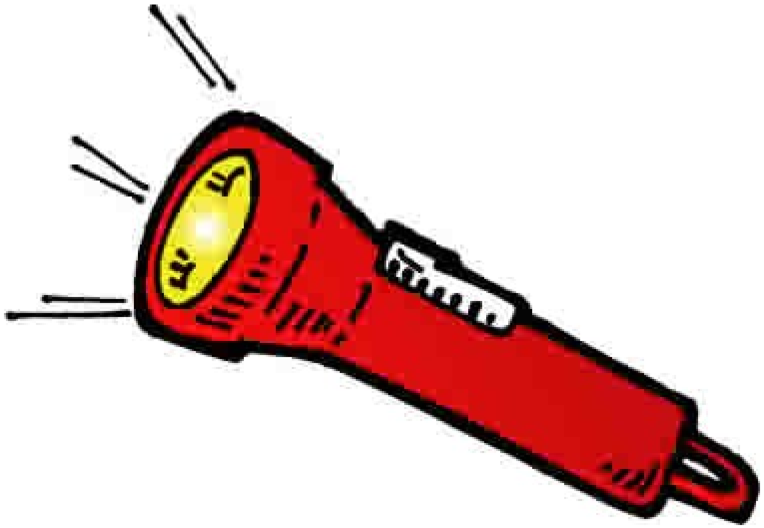


$$\varepsilon(0) = 1 + \sum_j \Delta\varepsilon_j$$

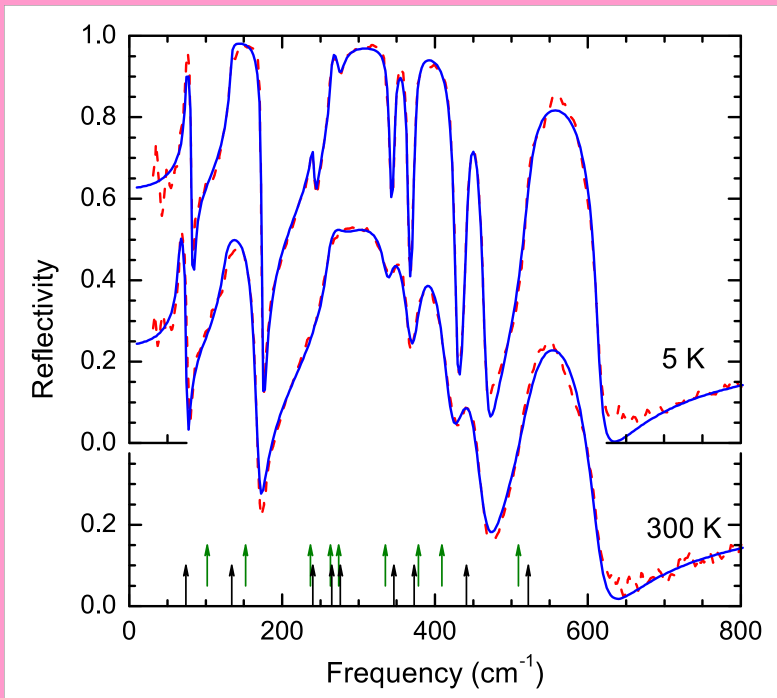
$$\Delta\varepsilon_j \Omega_{0j}^2 = \frac{n_j q_j^2}{m_j} = const$$



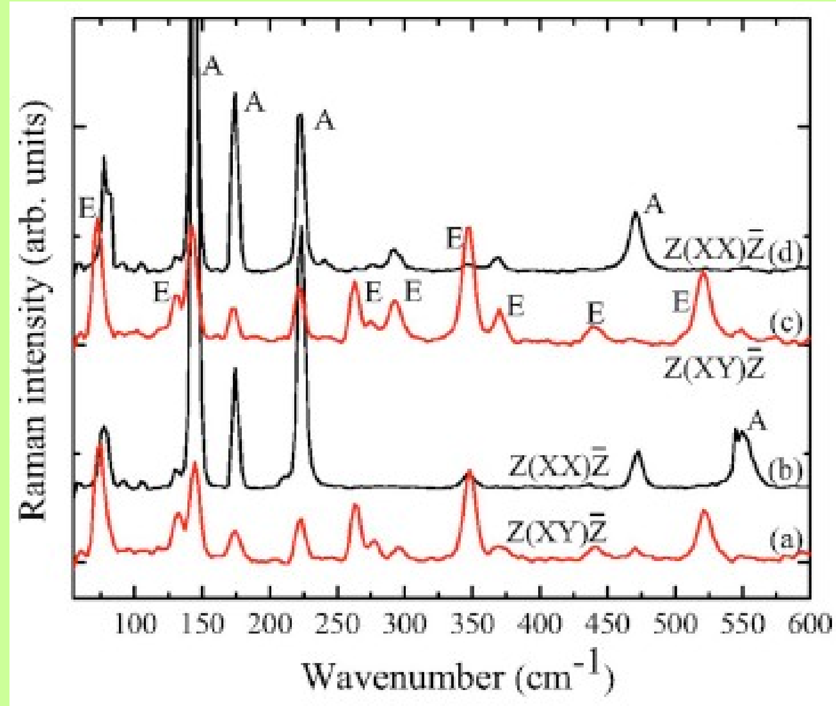
Spectroscopy of Multiferroics



Raman & IR on $BiFeO_3$



Lobo et al. PRB **76**, 172105 (2007)



Cazayous et al. APL **91**, 071910 (2007)

- ✓ Number of modes as predicted by group theory
- ✓ Good correlation with ab initio

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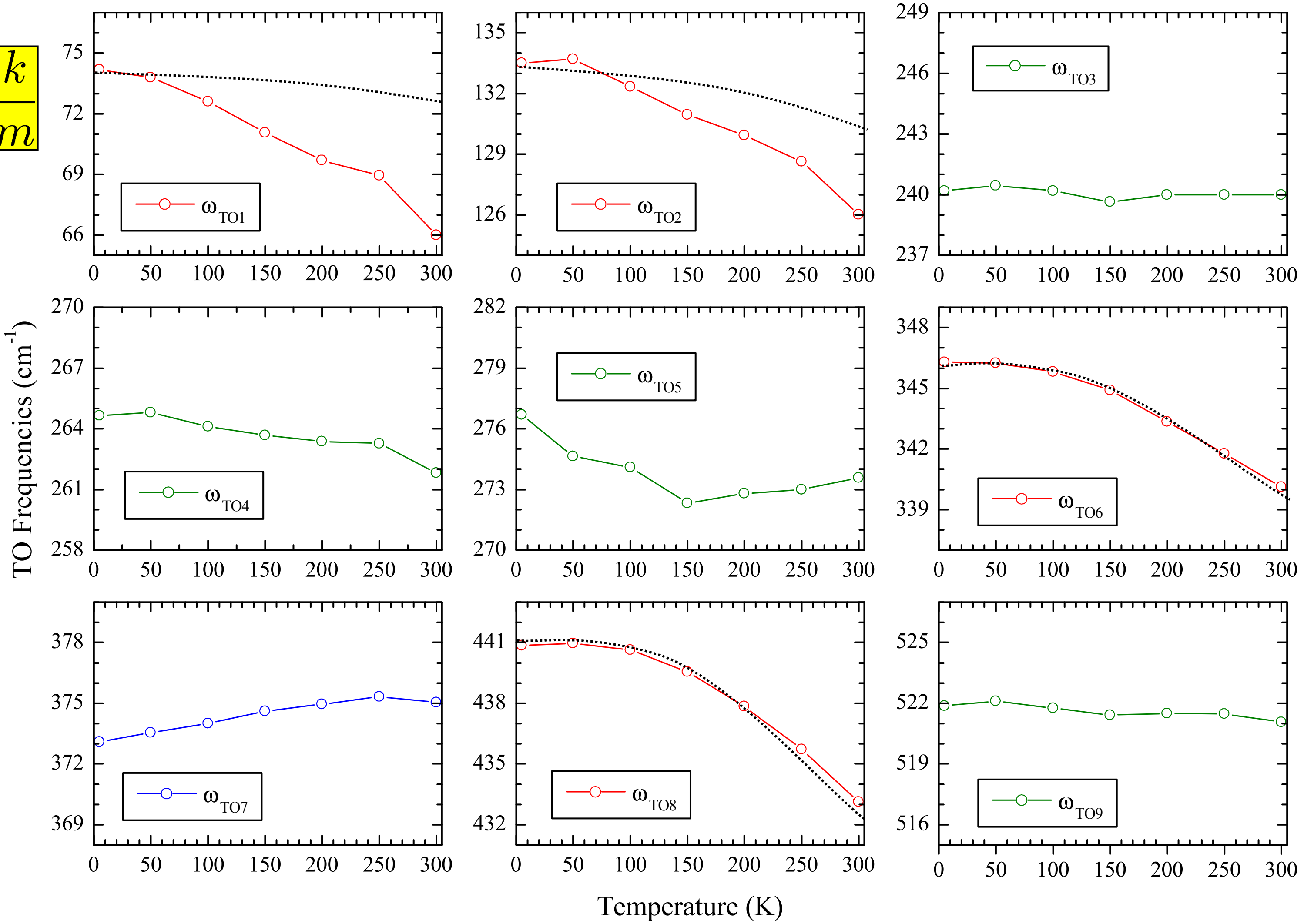
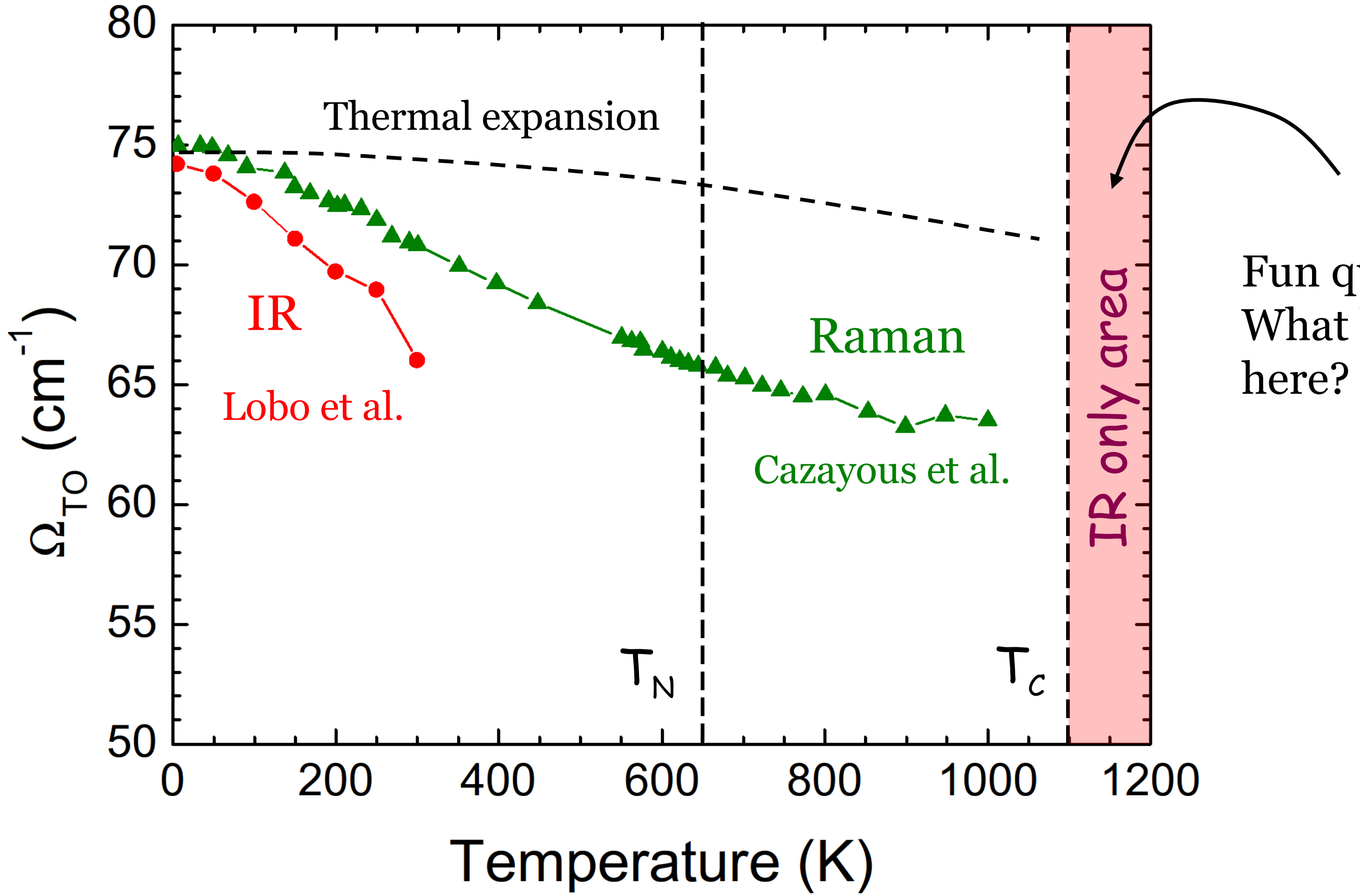
Transverse in-plane optical modes

$$\Omega_0^2 \sim \frac{k}{m}$$

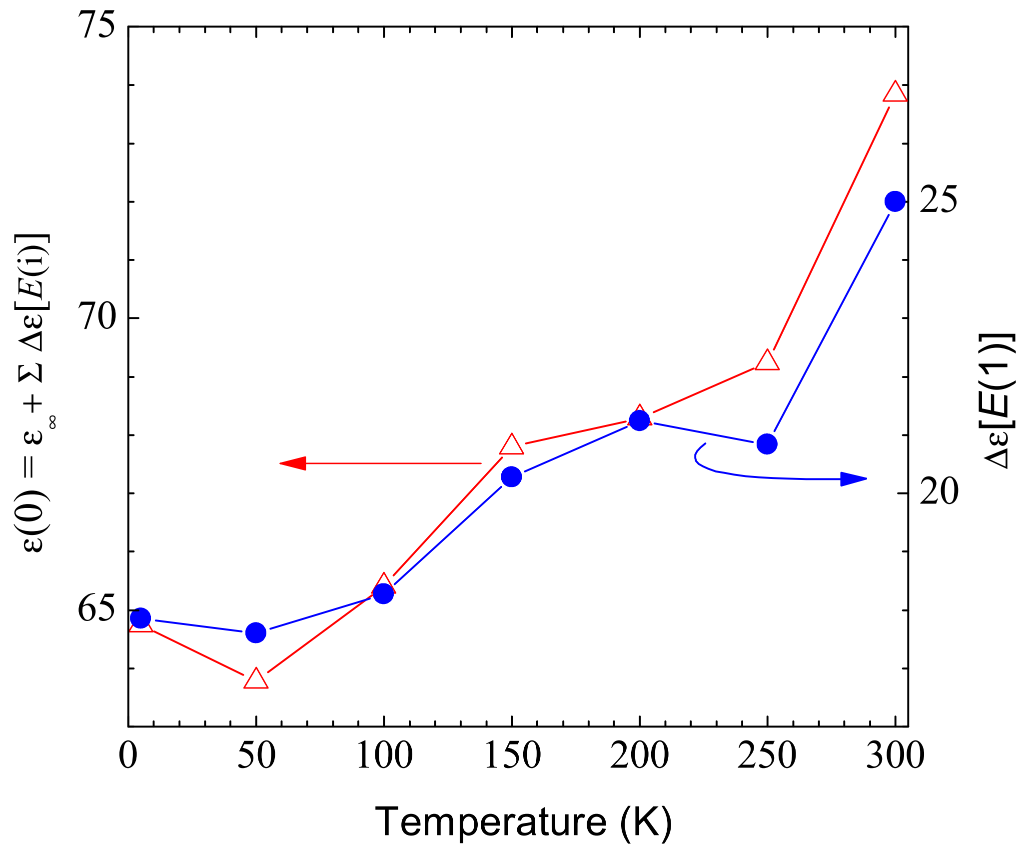


Hunting the Soft Mode



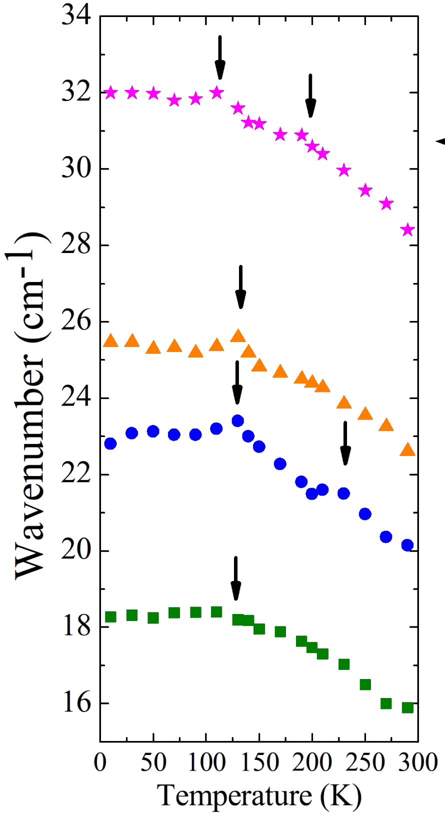
Fun question:
What happens
here?

The Soft Mode Controls the Dielectric Constant

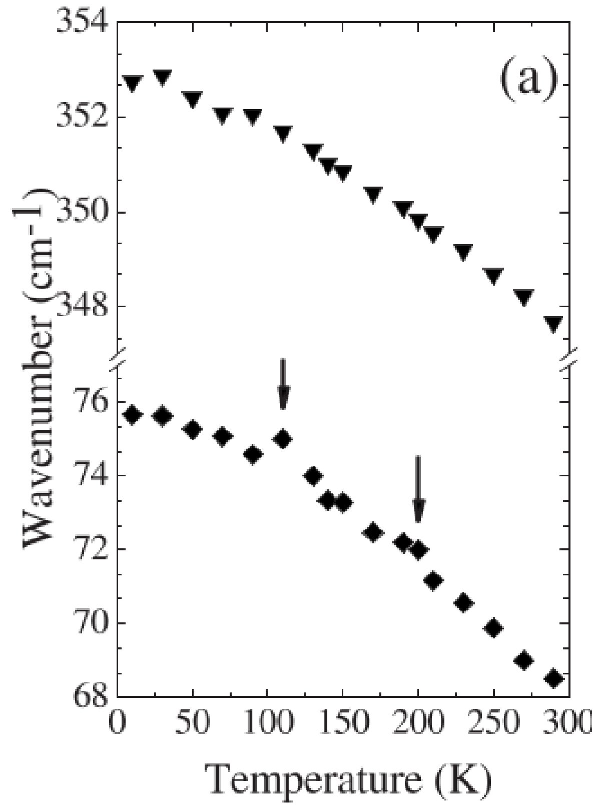


The temperature dependence of the static dielectric constant comes fully from the lowest *E* symmetry phonon.

Dielectric (phono) Magnetic (magnon) Interaction

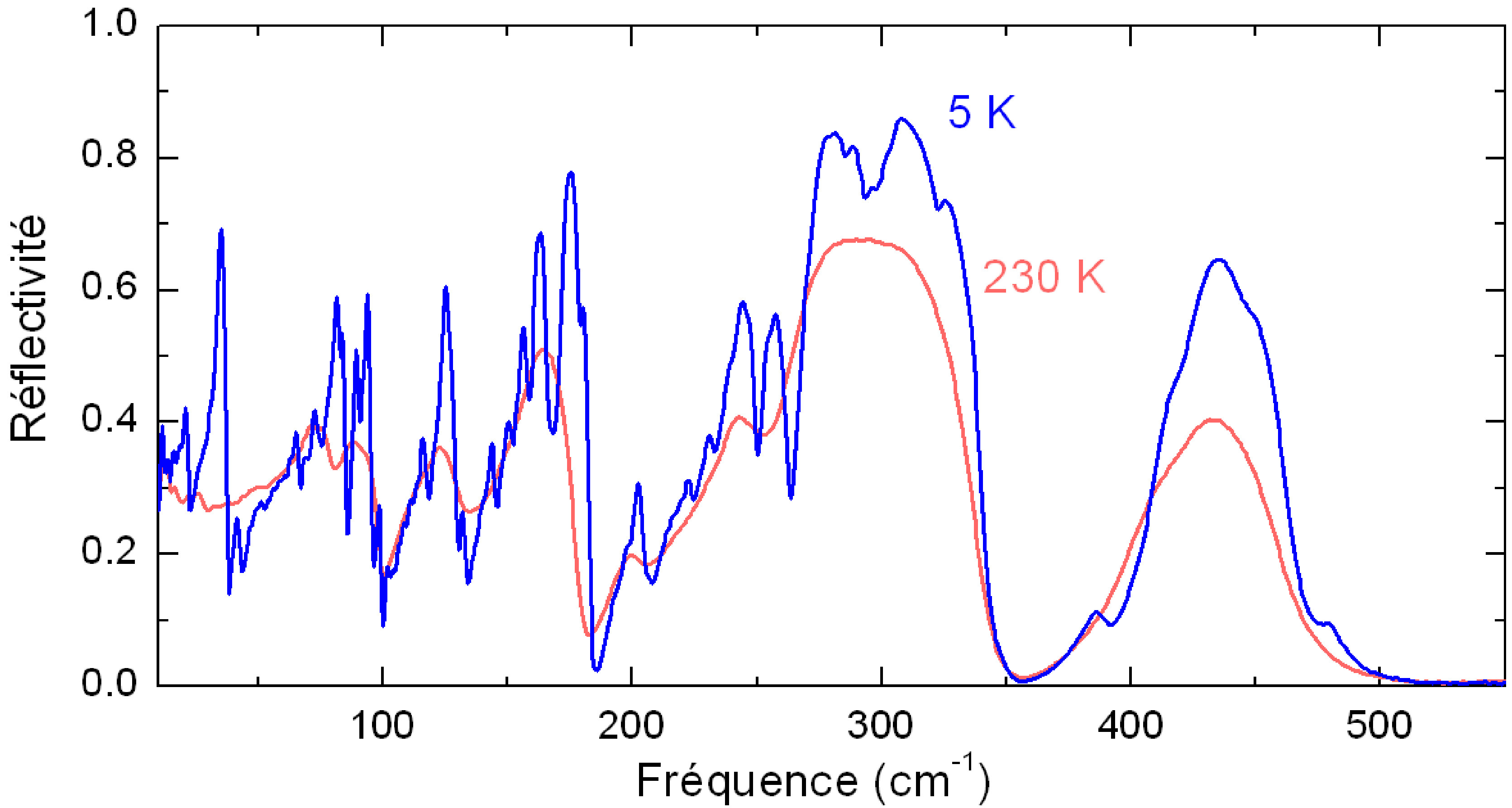


Magnons and Phonons
react to spin reorientations



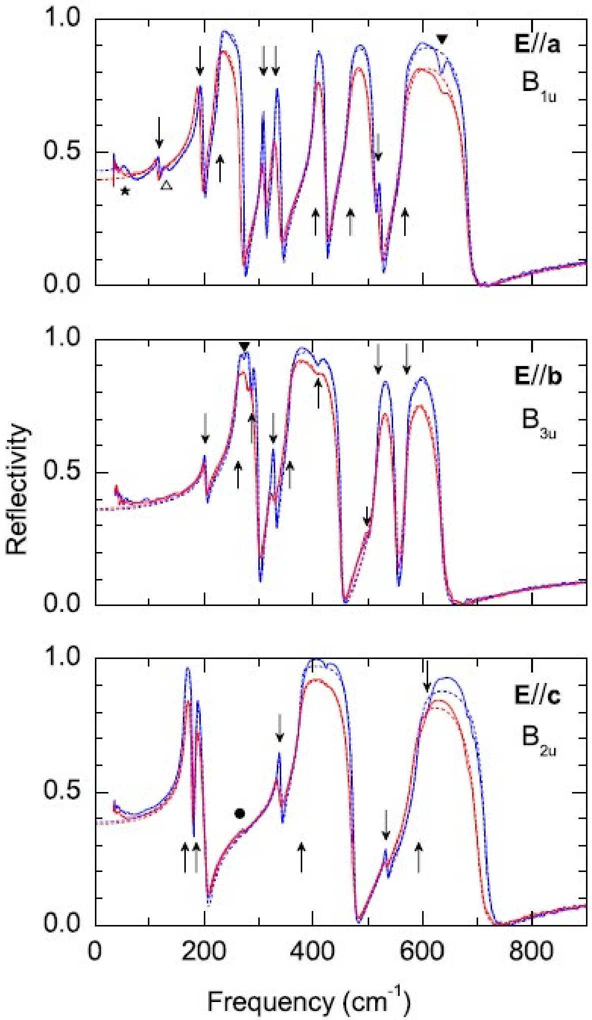
Rovillain et al., PRB **79**, 180411 (2009)

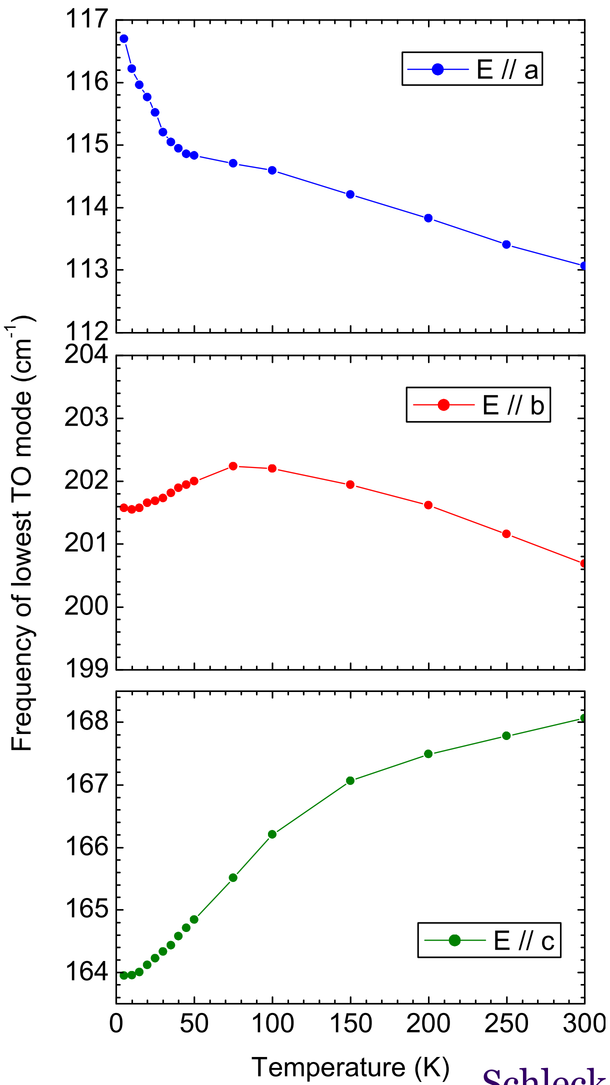
Before looking into $TbMnO_3$, remind $BaMnF_4$



Schleck et al. 2012.

Infrared response of $TbMnO_3$





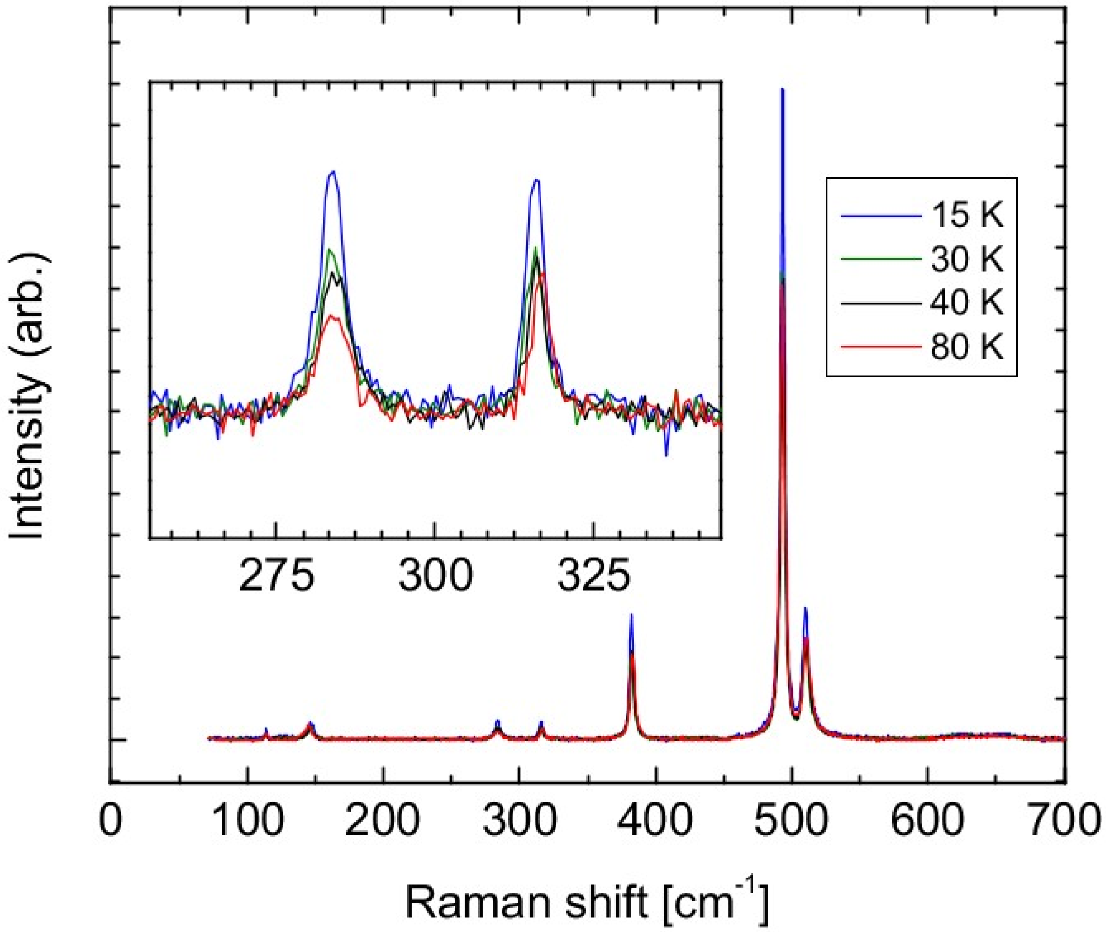
No sign of inversion symmetry breaking

No phonon spectra reconstruction

No soft mode

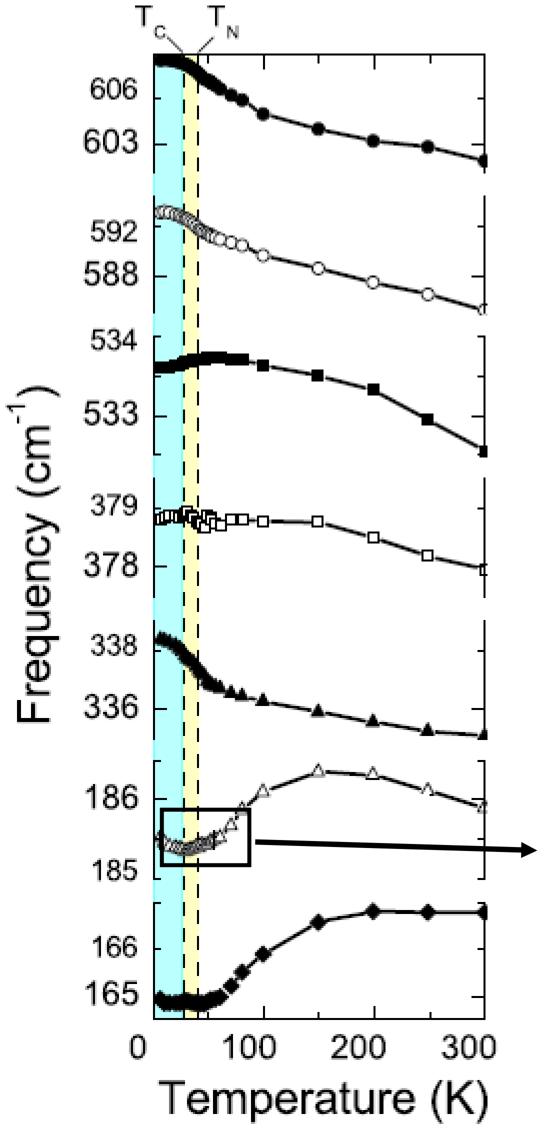
Schleck et al., PRB **82**, 144309 (2010)

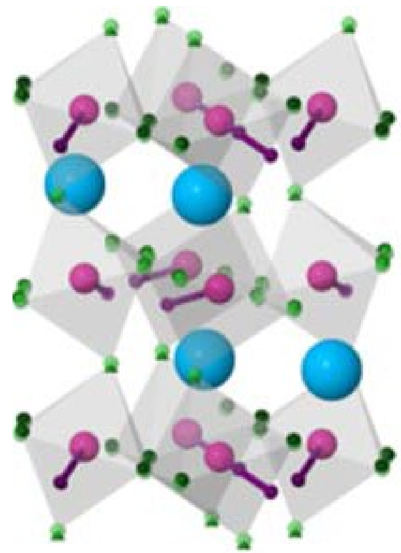
Raman in $TbMnO_3$ ain't any better

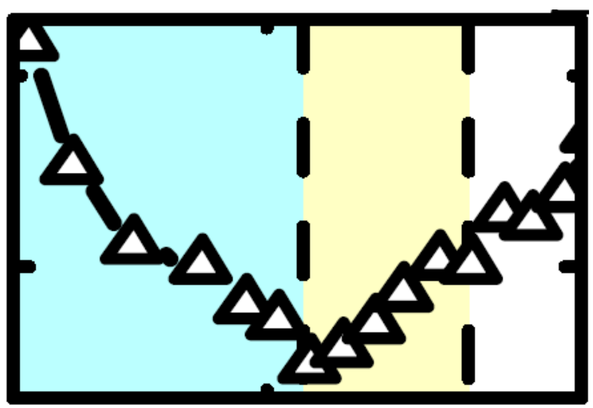


Rovillain, Cazayous, unpublished

Looking real close at $TbMnO_3$ phonons



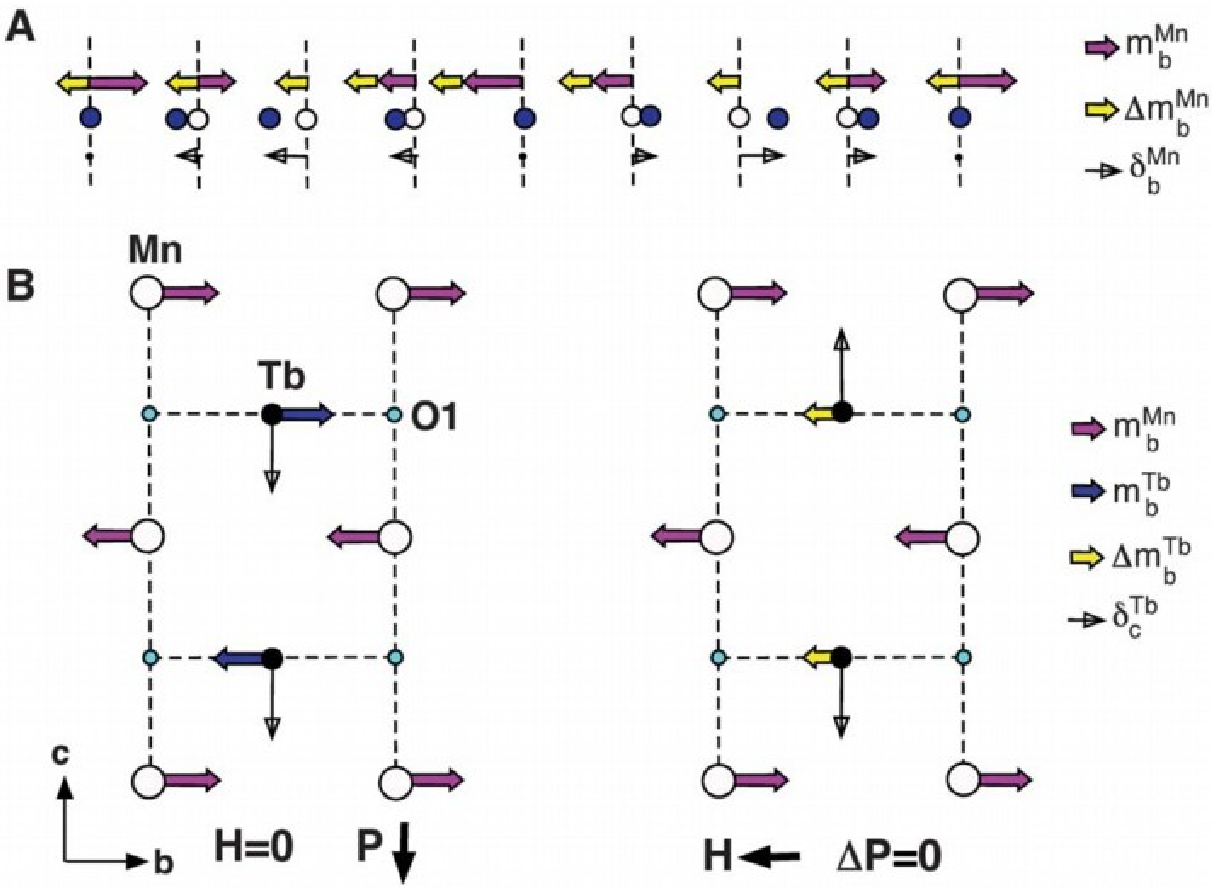




- ✓ Phonons are slightly renormalized at the AF transition
- ✓ The only phonon that has (a very tiny) modification at the ferroelectric transition is dominated by Mn atomic motions.

Schleck et al., PRB **82**, 144309 (2010)

Is there an atomic displacement



H= 0

δTb = 21 fm

P_{calc} = 176 µC / m2

P_{meas} = 800 µC / m2

H. C. Walker et al. Science **333**, 1273 (2011)

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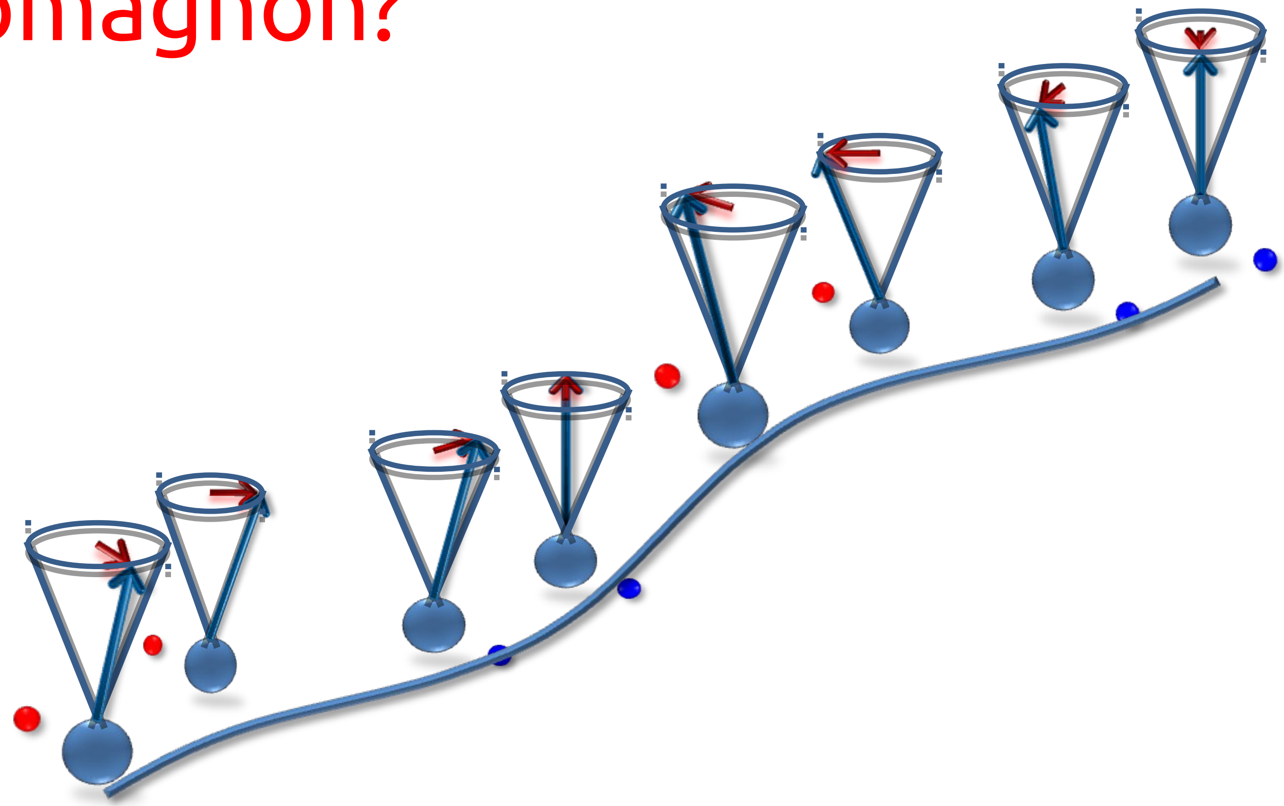
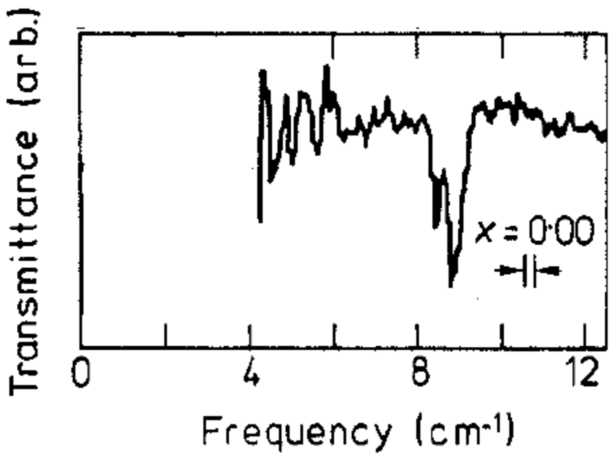
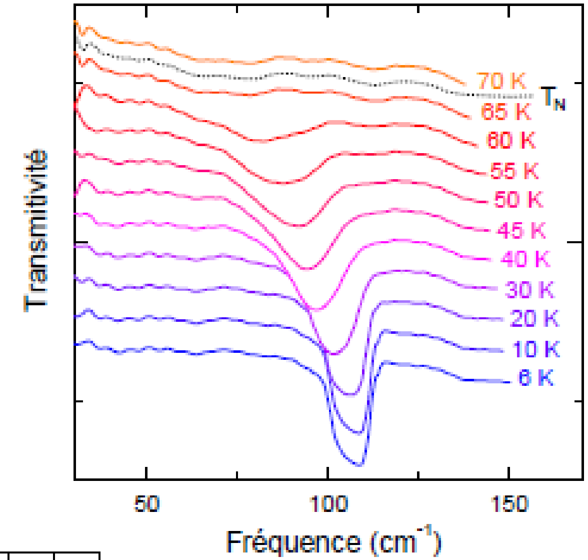
What is an Electromagnon?



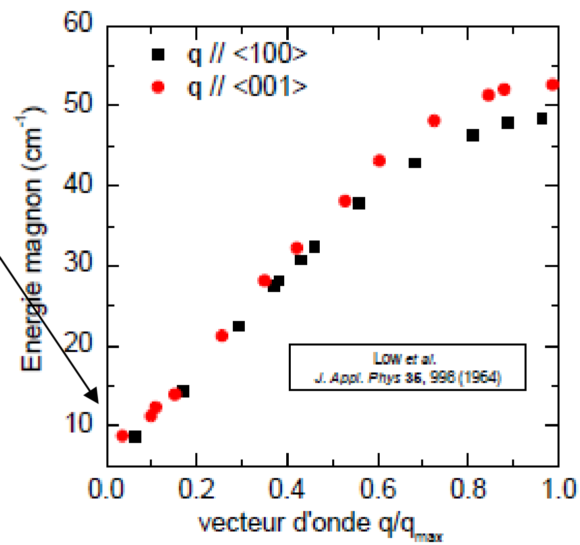
Infrared Magnetic Excitations in MnF_2



Allen et al., PRL 16, 463 (1966)

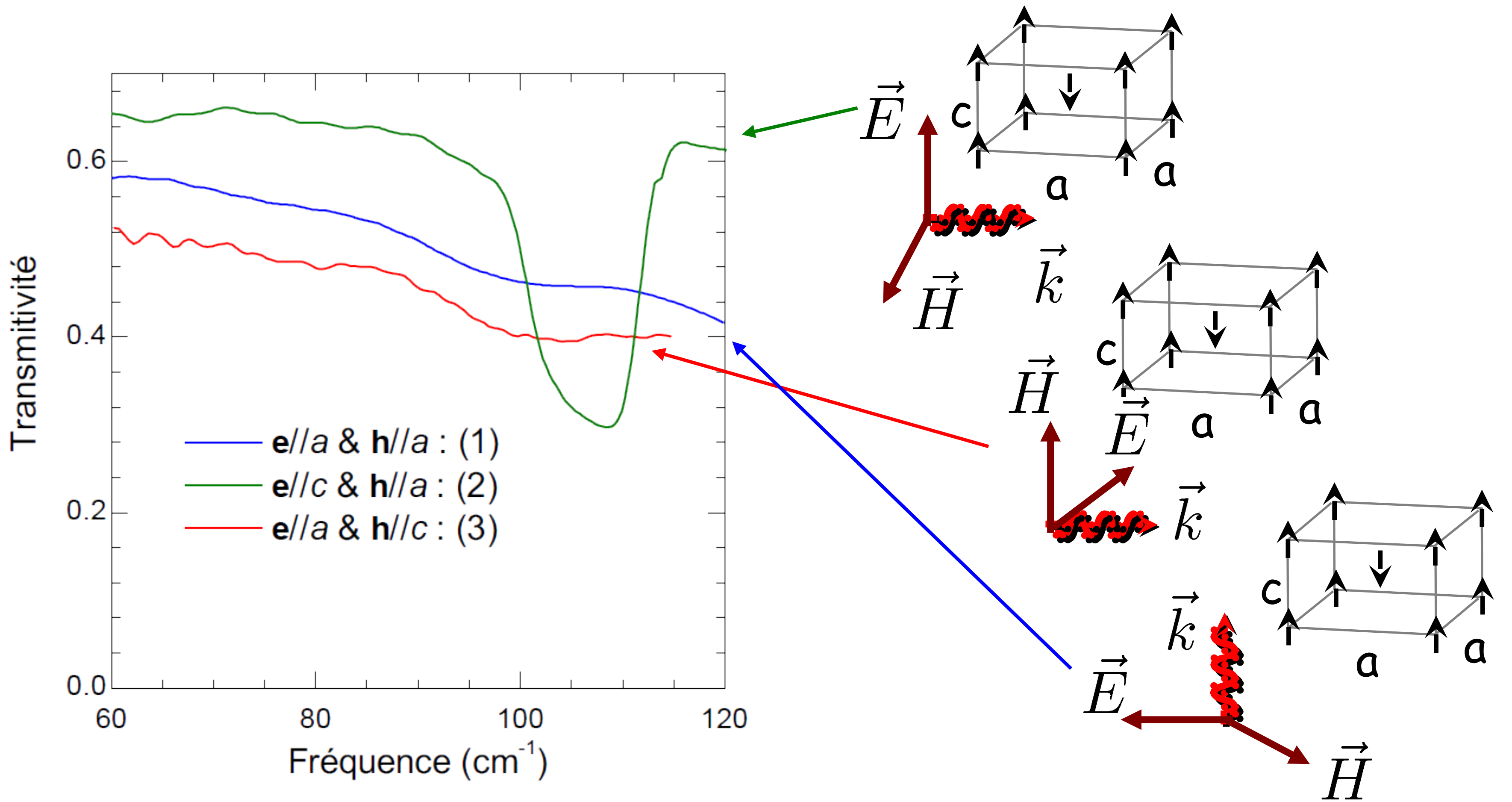


AFM resonance



Zone edge
bi- magnon

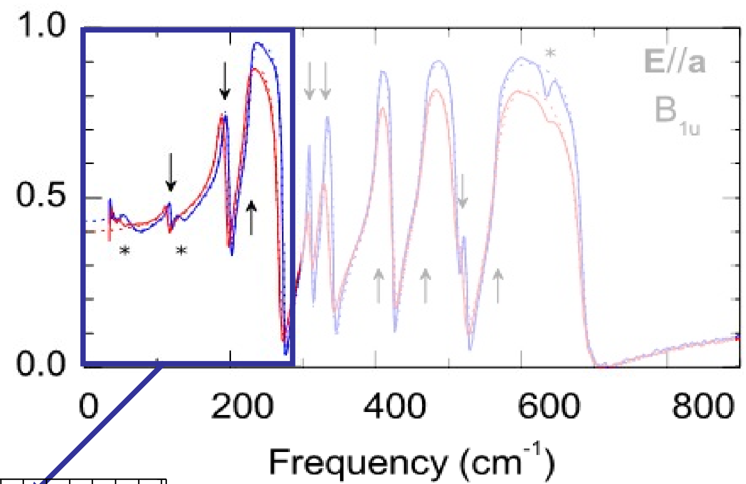
How to determine if an excitation is electric

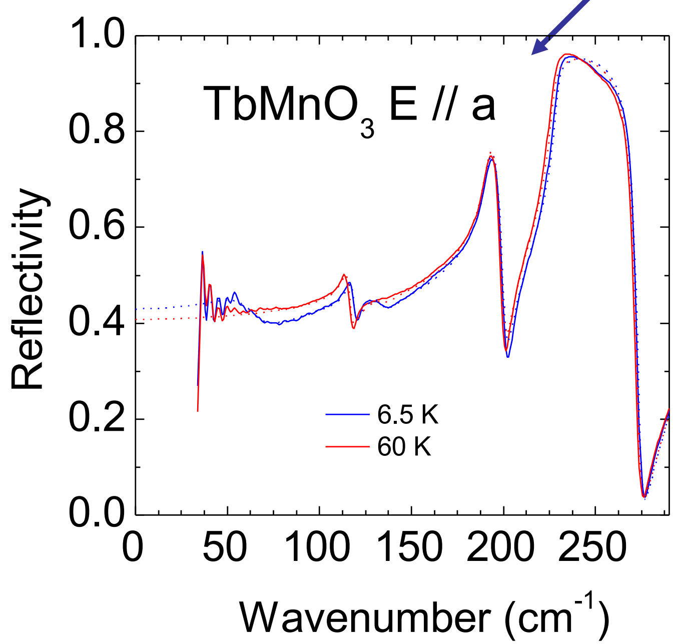


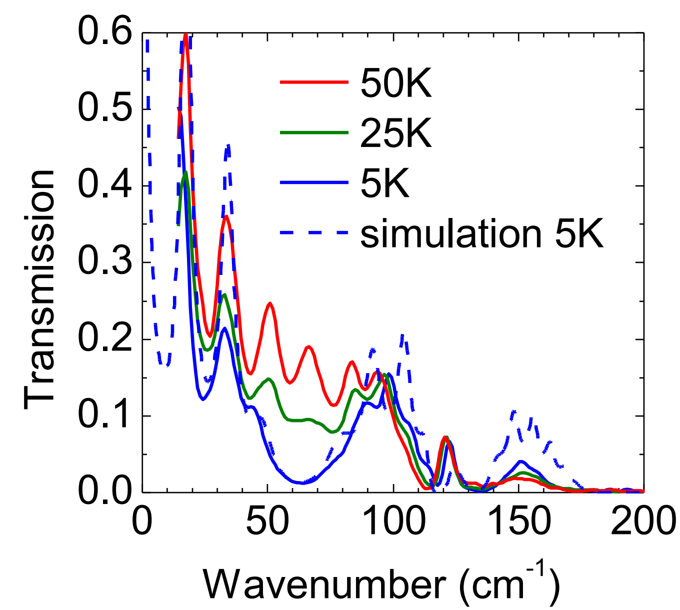
The bi-magnon in MnF_2 is activated by the electric field of light.

Not its magnetic field.

Taking a closer look at $TbMnO_3$







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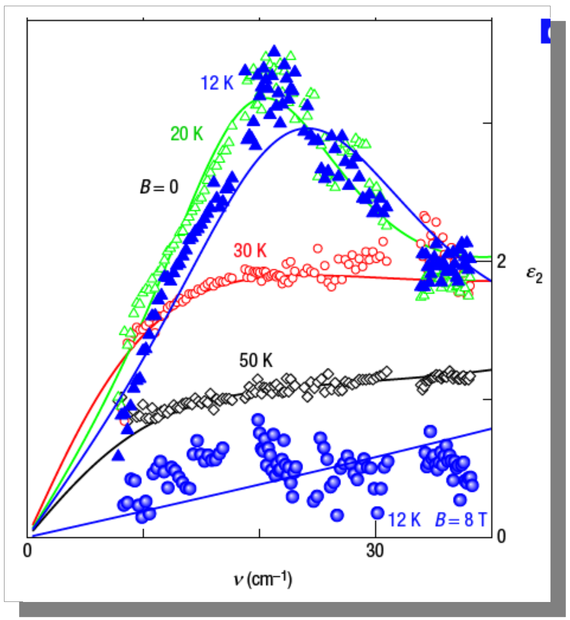
Rough definition of the Electromagnon

Possible evidence for electromagnons in multiferroic manganites

Nat. Phys, 2006.

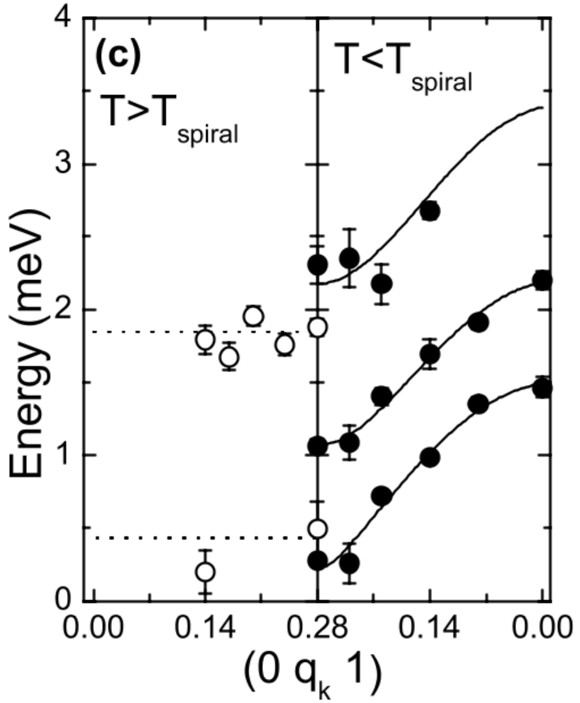
A. PIMENOV[1]*, A. A. MUKHIN[1,2], V. YU. IVANOV[2], V. D. TRAVKIN[2], A. M. BALBASHOV[3] AND A. LOIDL[1]

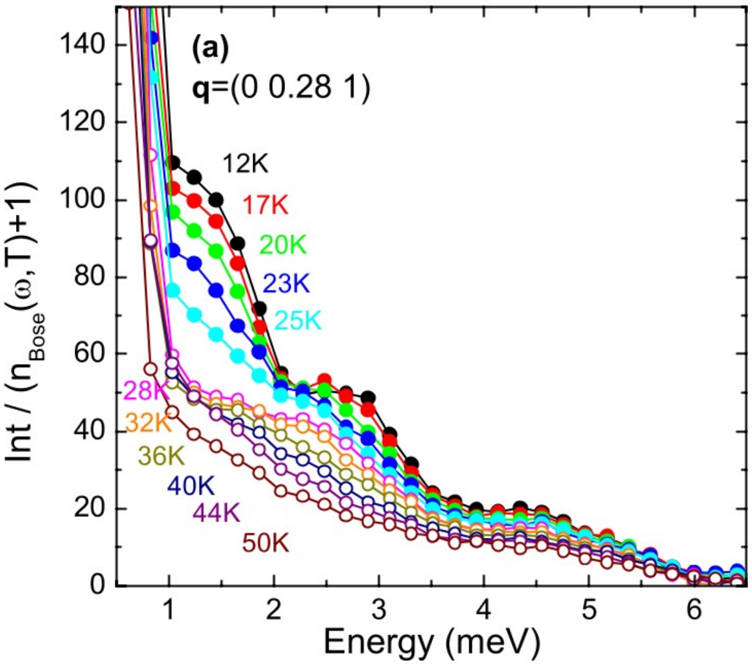
and polar order. Among other multiferroics, $TbMnO_3$ and $GdMnO_3$ reveal a strong magneto–dielectric coupling and as a consequence fundamentally different spin excitations exist: electro-active magnons (or electromagnons), spin waves that can be excited by a.c. electric fields. Here we provide evidence that



- ✓ Spin wave activated by electric field of light
- ✓ Is the electromagnon a new fundamental excitation?
- ✓ What is the relationship between the electromagnon and the magneto-electric coupling?
- ✓ Is the electromagnon a necessary excitation for ME coupling?
- ✓ Is the electromagnon restricted to multiferroics?

The Electromagnon is also a Magnon

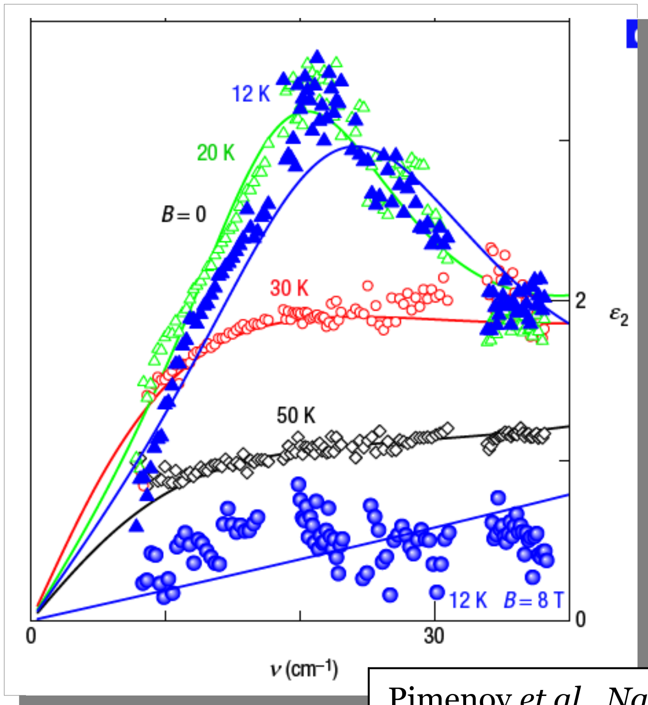




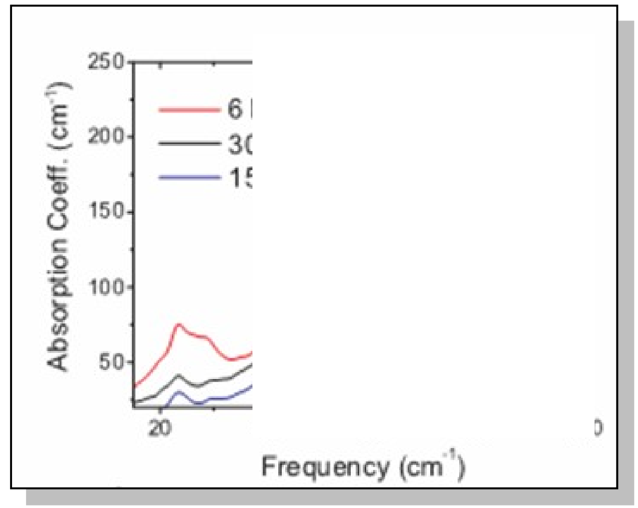
- Same energy of IR electromagnon
- Stronger below T_C
- Persists up to T_N

Senff et al., PRL **98**, 137206 (2007)

Not just one e-magnon in $TbMnO_3$



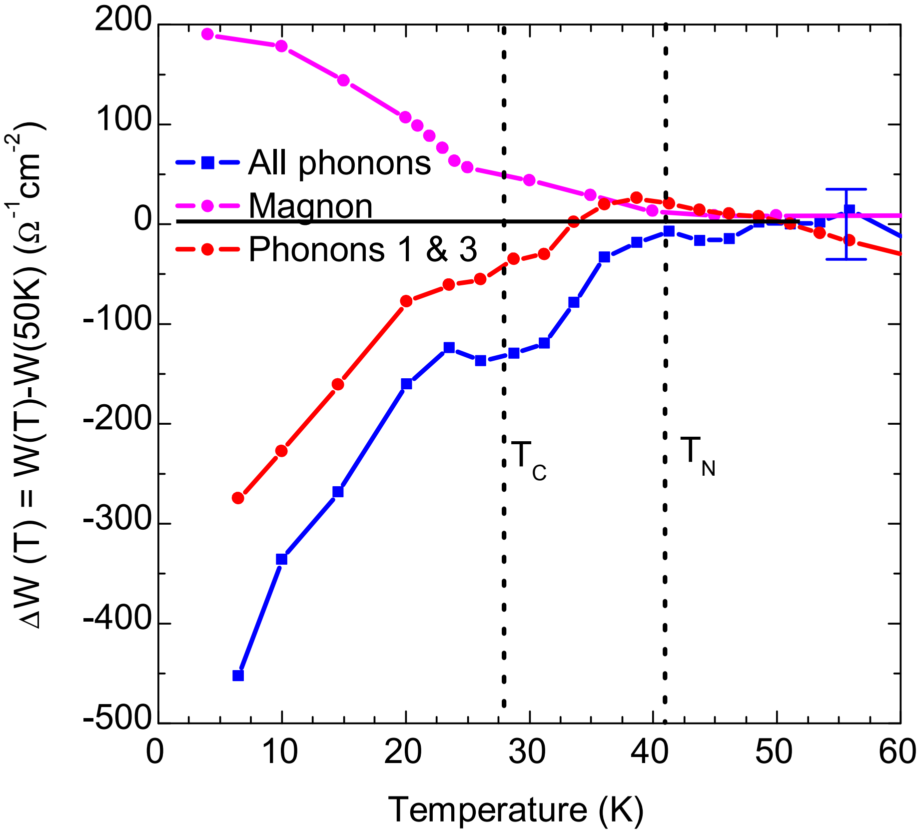
Pimenov *et al.*, *Nat. Phys*, 2006.



Valdés Aguilar *et al.*, *PRL*, 2009.

Most of the e-magnon spectral weight is at higher frequencies

The electromagnon (E//a) is built from two phonons

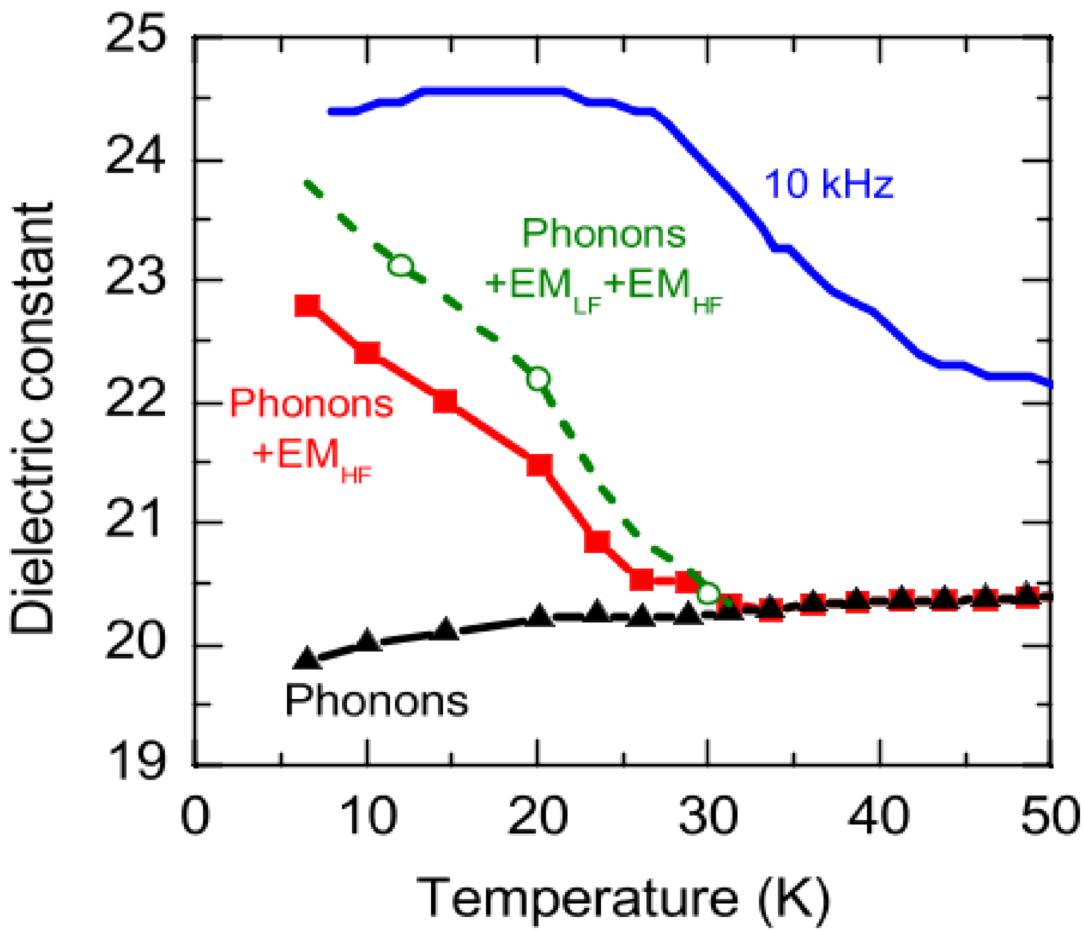


Sum-rule

$$\sum_j \Delta\varepsilon_j \Omega_{0j}^2 = const$$

The electromagnon in $TbMnO_3$ gets its strength from phonons dominated by Tb and Mn atomic movements

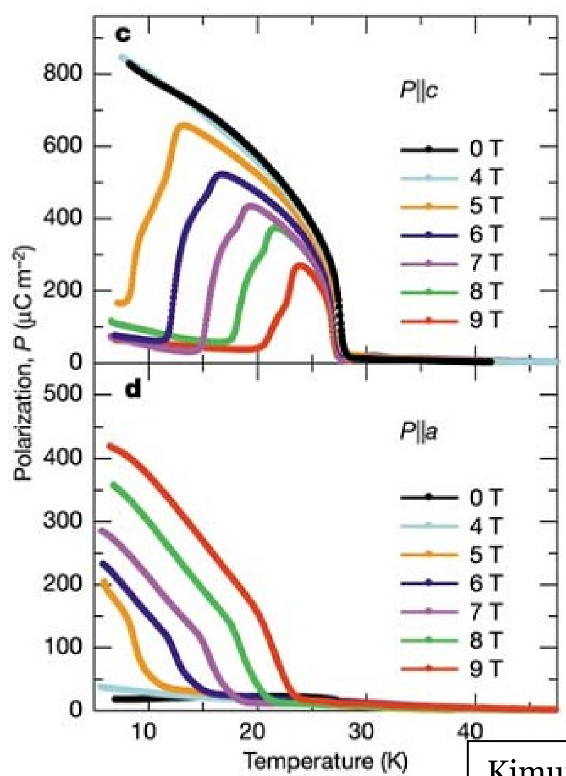
The Electromagnon contributes to ε(0)



Another confirmation that the electromagnon is excited by the electric field

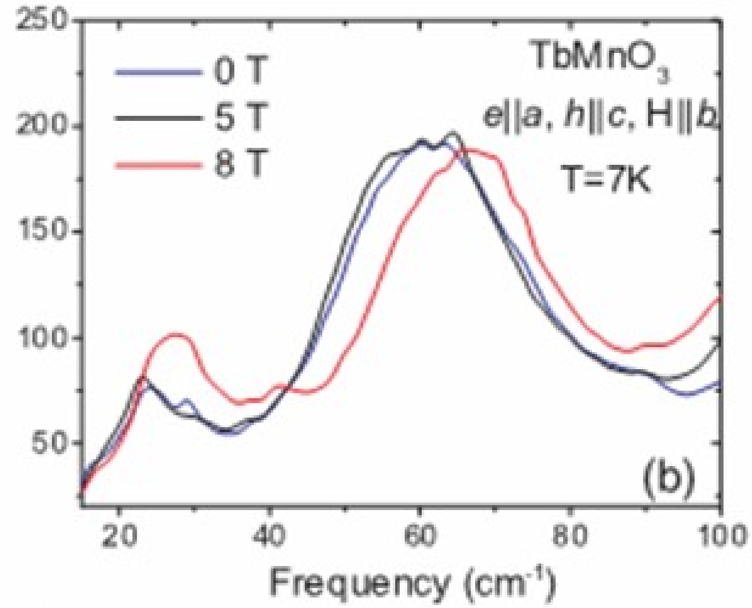
The electromagnon and polarization rotation

(Is the e-magnon related to a static coupling?)



Kimura *et al.*, *Nature* 2003

H // b

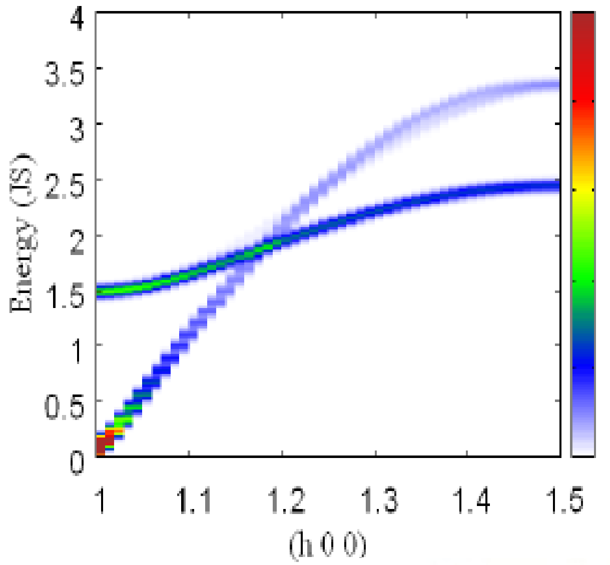


Valdés Aguilar *et al.*, *PRL*, 2009.

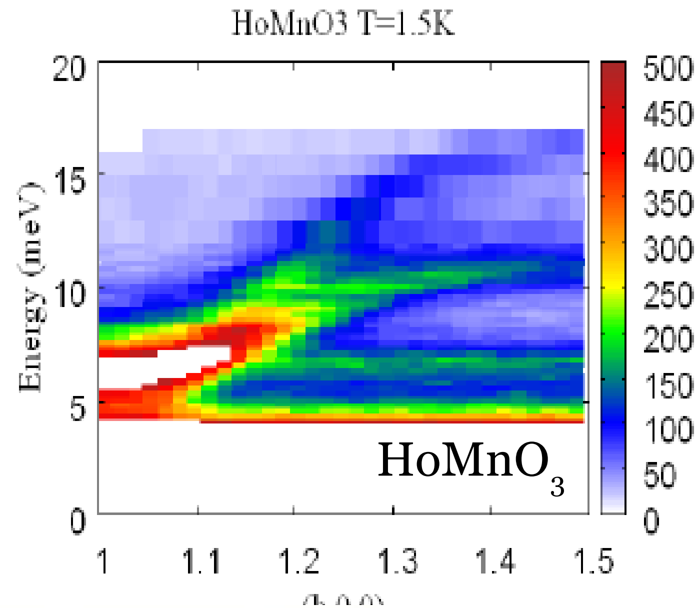
The rotation of the polarization does not have a large effect on the electromagnon

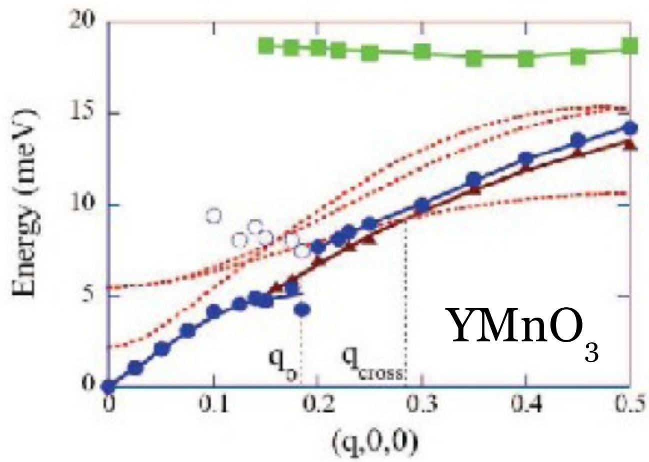
Hybrid Mode – Netrons

Calcul



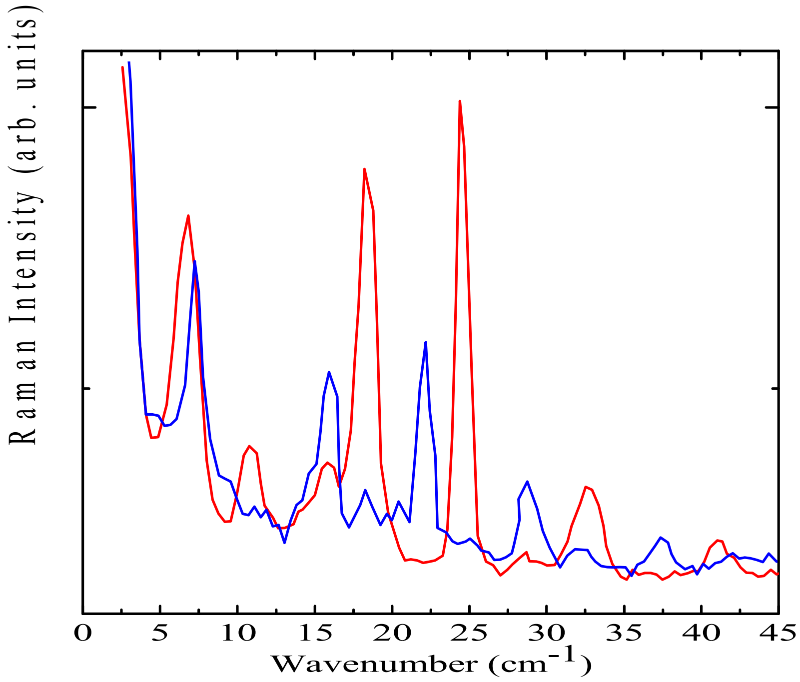
Mesures

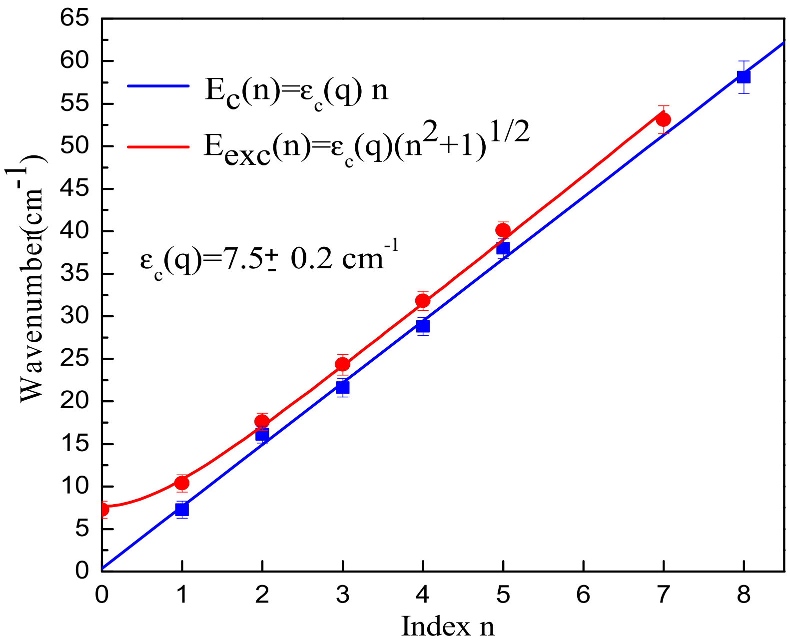




S. Petit, LLB, Saclay

(Electro?)mangons in $BiFeO_3$

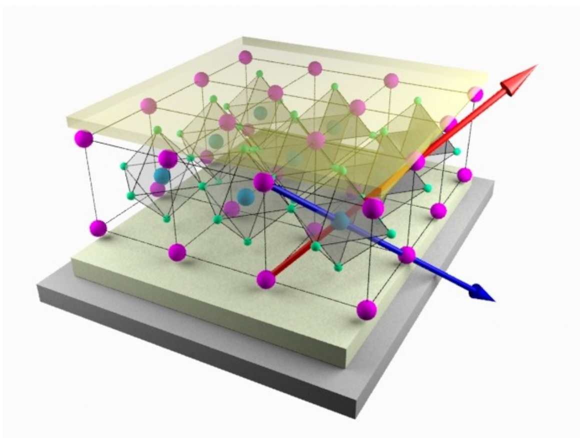


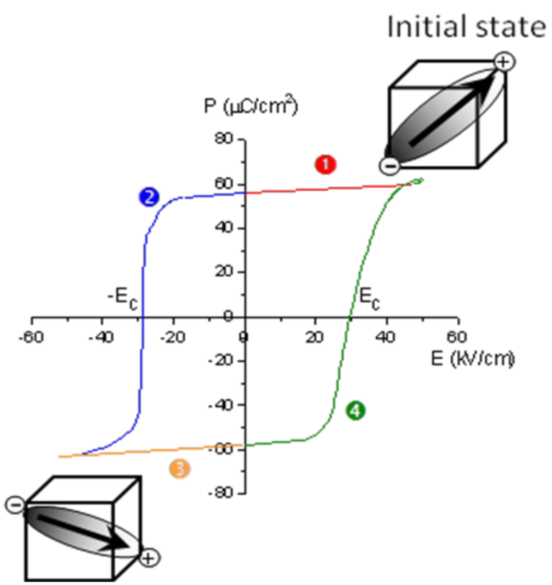


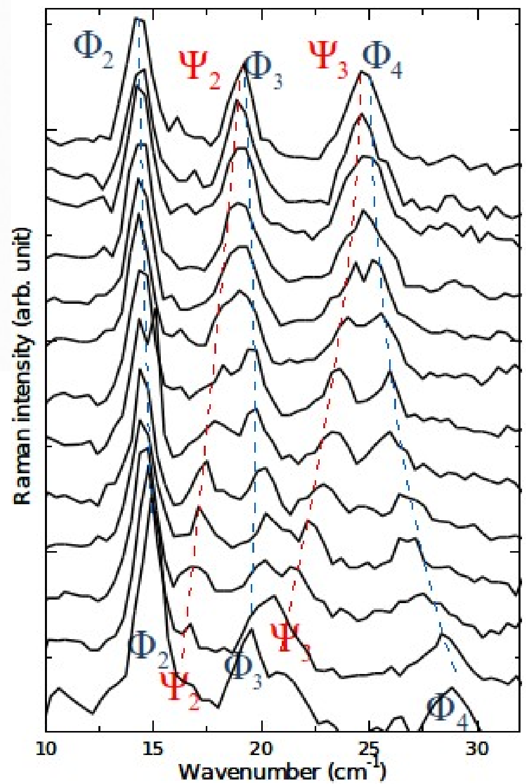
- Two different spin waves
- Dispersion compatible with calculations for electromagnon

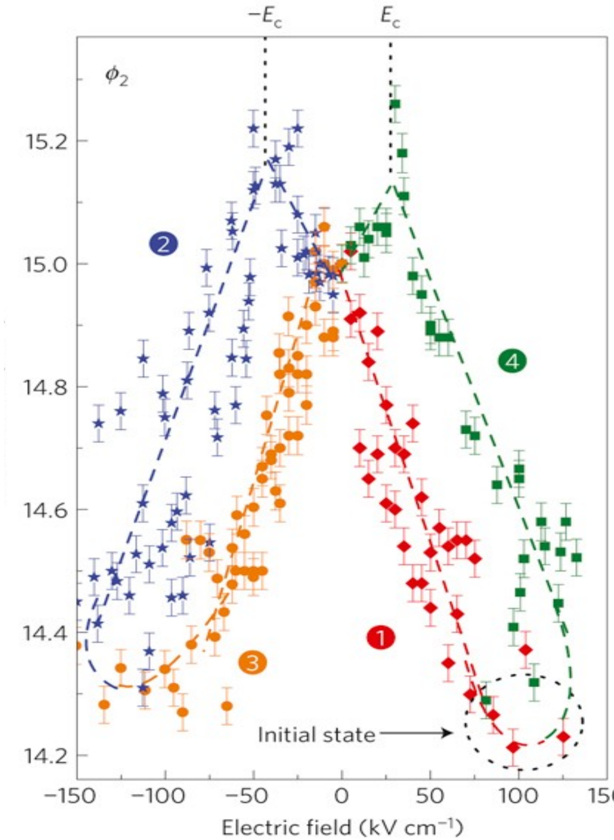
M. Cazayous et al., PRL **101**, 03760(2008)

Electric Control of Spin Waves ($BiFeO_3$)



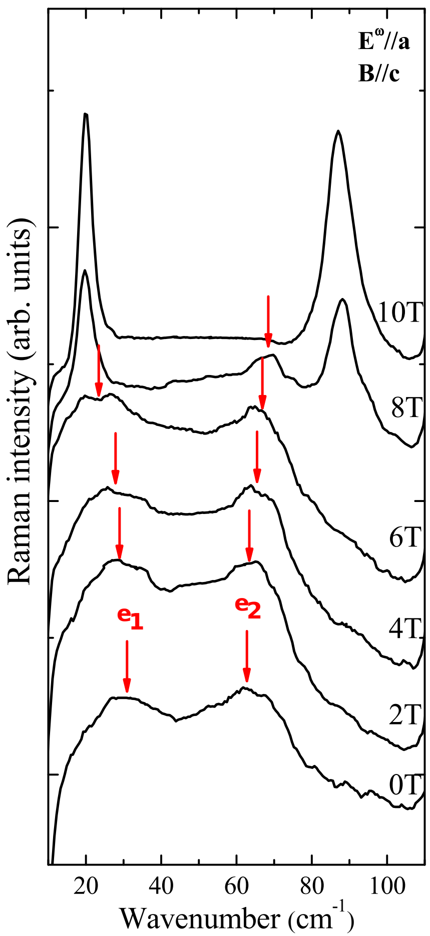






P. Rovillain et al. Nat. Mater. **9**, 979 (2010)

Magnetic Control of the Electromagnon ($TbMnO_3$)



- In $TbMnO_3$ under magnetic field
- Hybrid magnon-mode phonon
- De-hybridation of electromagnon

Rovillain et al. PRL **107**, 027202 (2011)

Open questions

- ✓ Every good theorist can put together a Landau-like theory for the magneto-electric coupling, but what is its microscopic nature?
- ✓ What is the role of the lattice in the interaction?
- ✓ How important is ferroelasticity in the magneto-electric coupling?
- ✓ Do strong correlations have any saying in the matter?
- ✓ Is "magnetic" spatial symmetry breaking enough to create ferroelectricity?
- ✓ Where and what is the damn electromagnon?
- ✓ Is there a difference between static and dynamic coupling?