Magnetoelectric coupling in isotope substituted multiferroic TbMnO3

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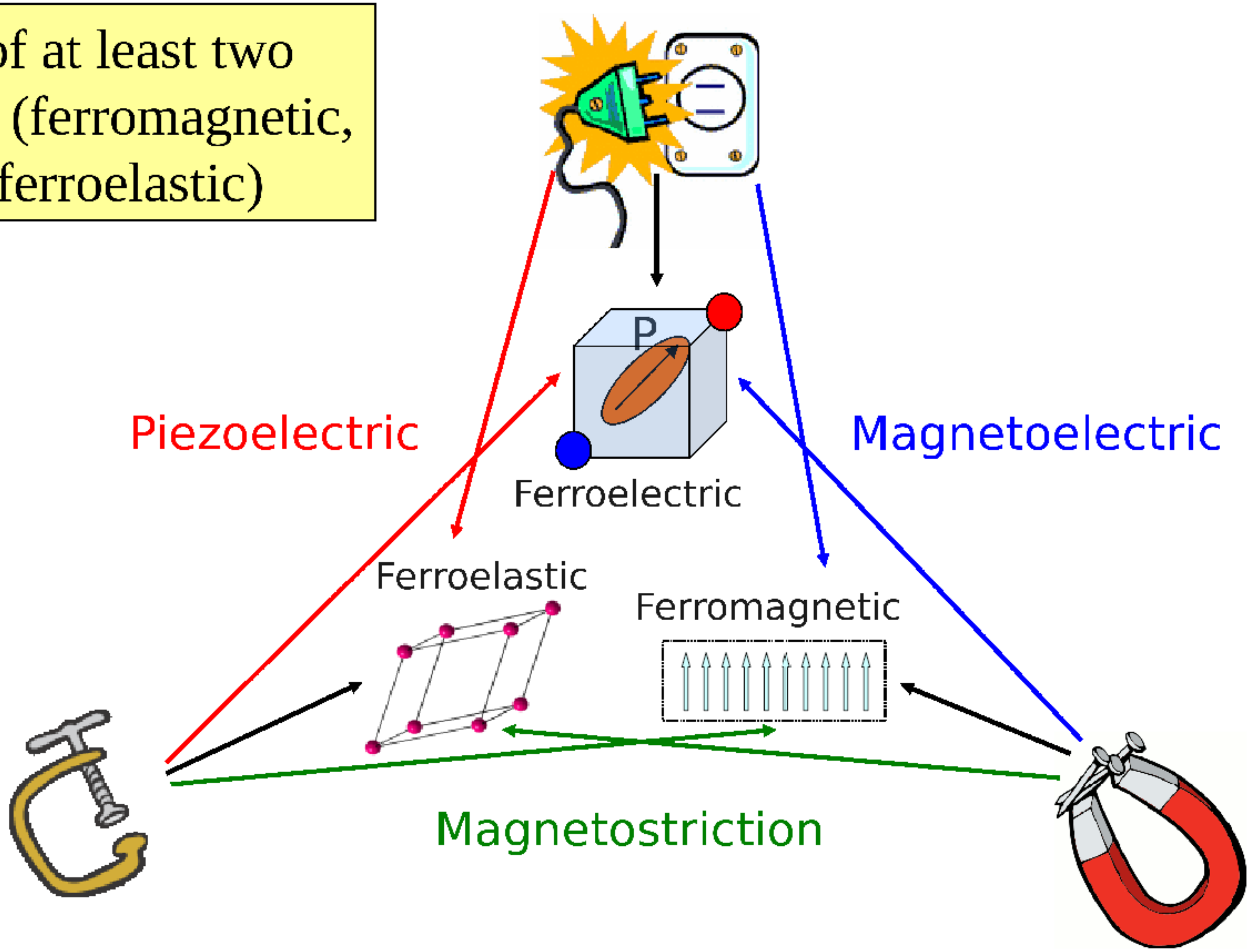
Multiferroic materials

Coexistence of at least two ferroic orders (ferromagnetic, ferroelectric, ferroelastic)



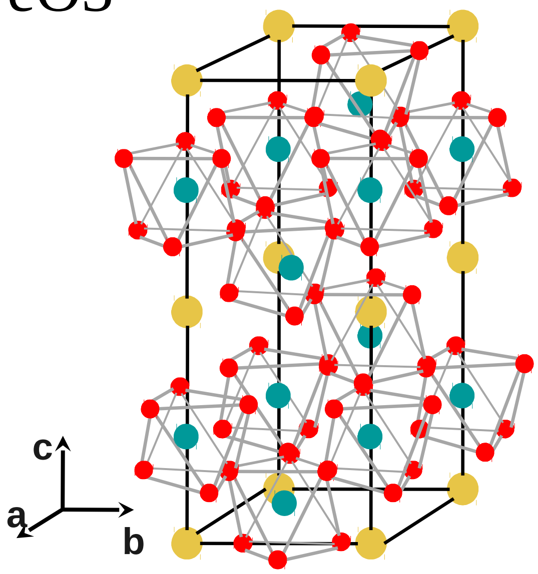
Schmid, Ferroelectrics **162**, 317 (1994)

Multiferroics type I and II

Multiferroics type I

- ✓ Strong ferroelectrics
- ✓ Order temperatures close to room temperature
- x indirect coupling between orders

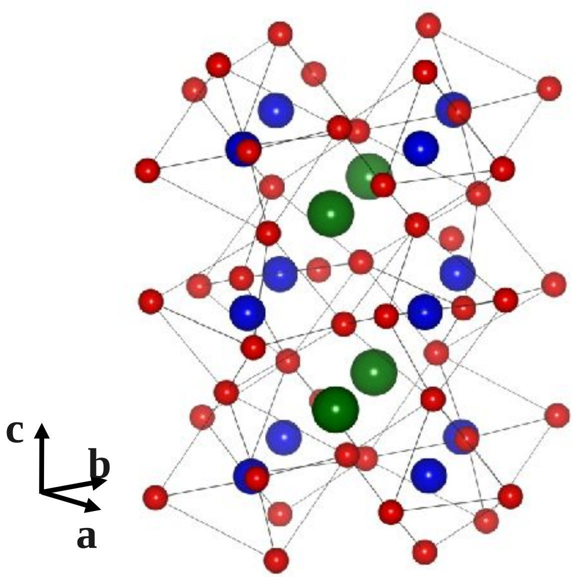
BiFeO3



Multiferroics type II

- x Weak ferroelectrics
- x Low order temperatures
- ✓ Strong direct coupling between orders

TbMnO3



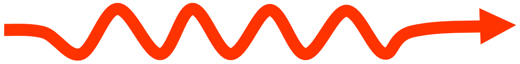
Inelastic scattering

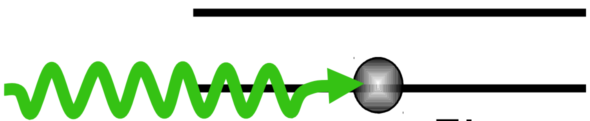
Inelastic light scattering : Sir C. Raman (1888-1970)
Nobel Price 1930

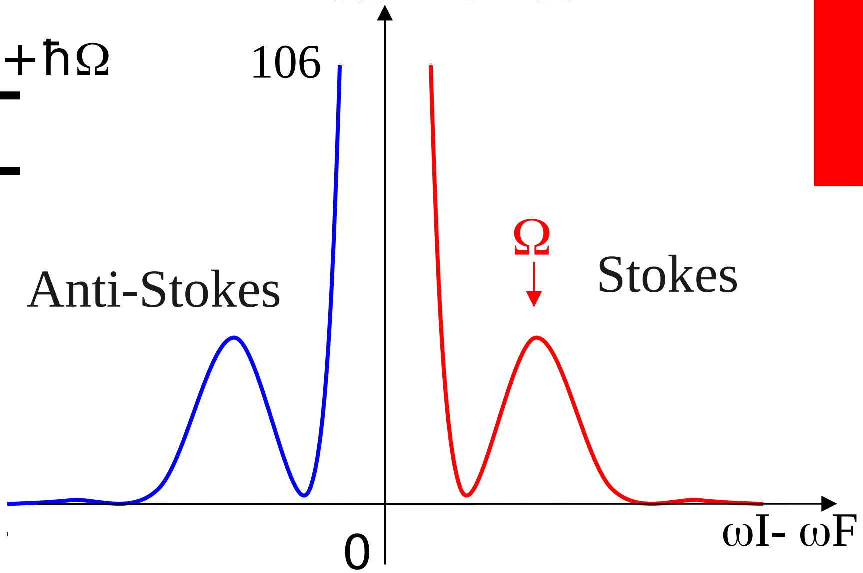
Stokes Process

$\omega F = \omega I - \Omega$

$kF = kI - q$



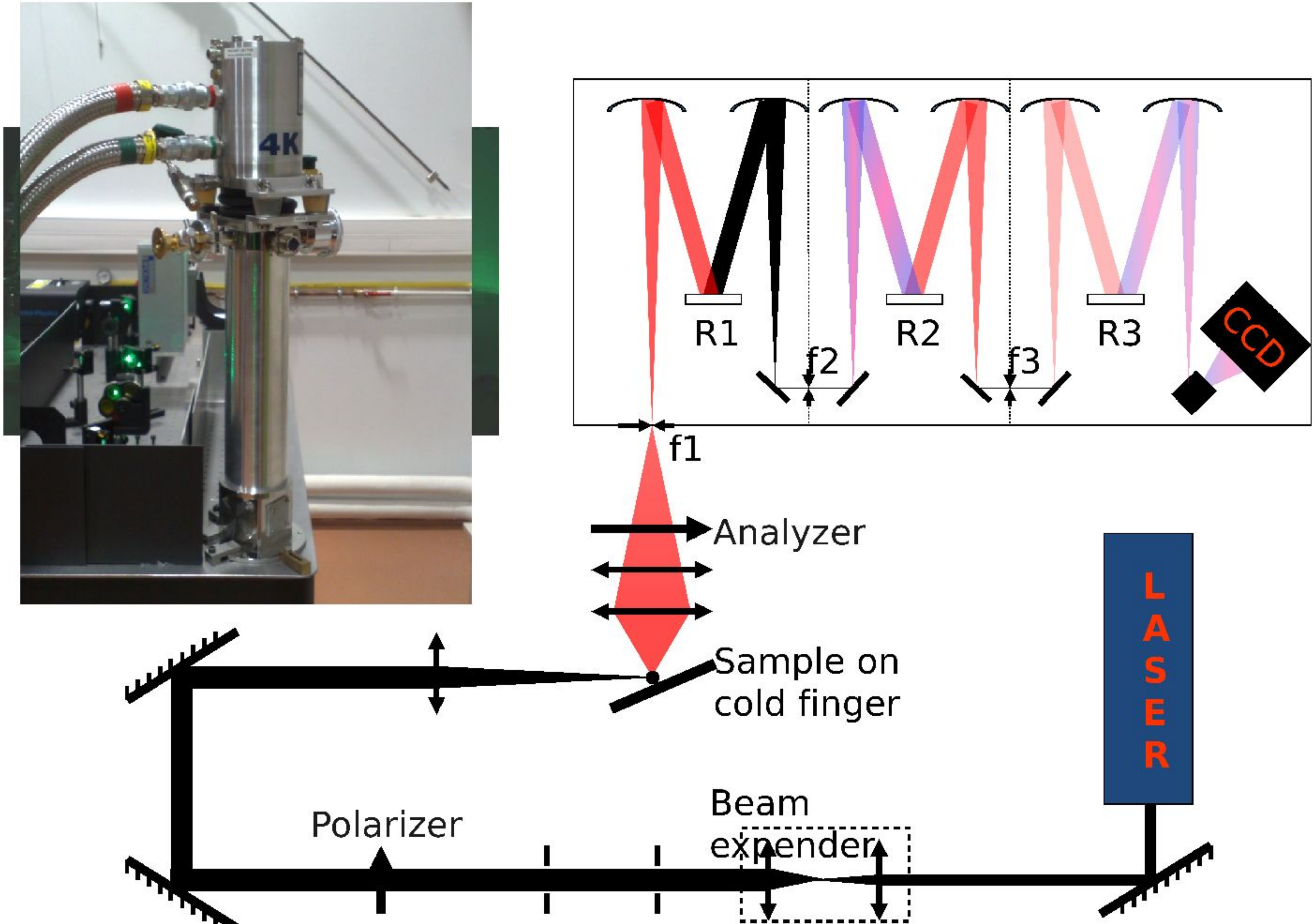




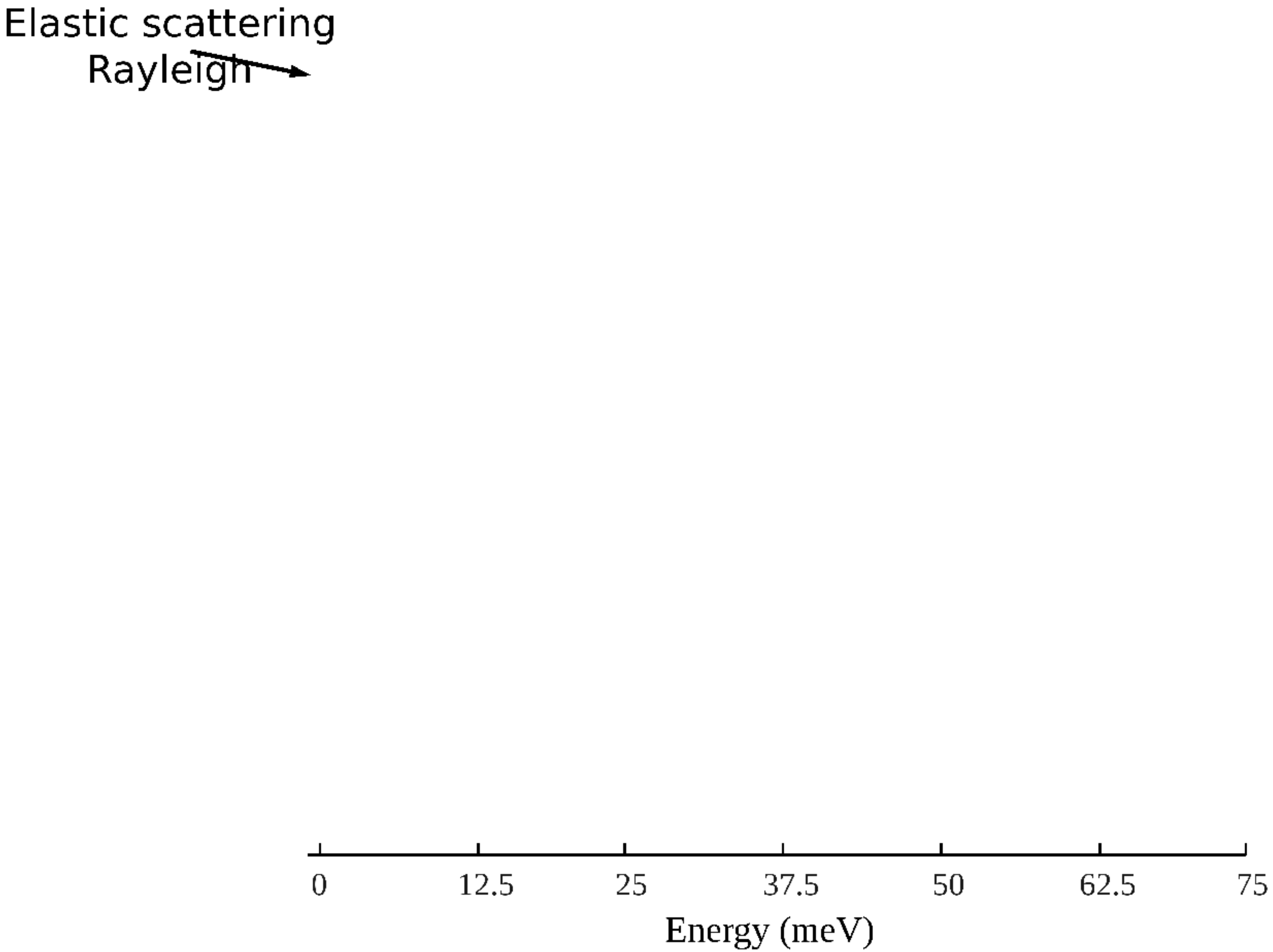
Excitations

Electrons
Magnons
Phonons

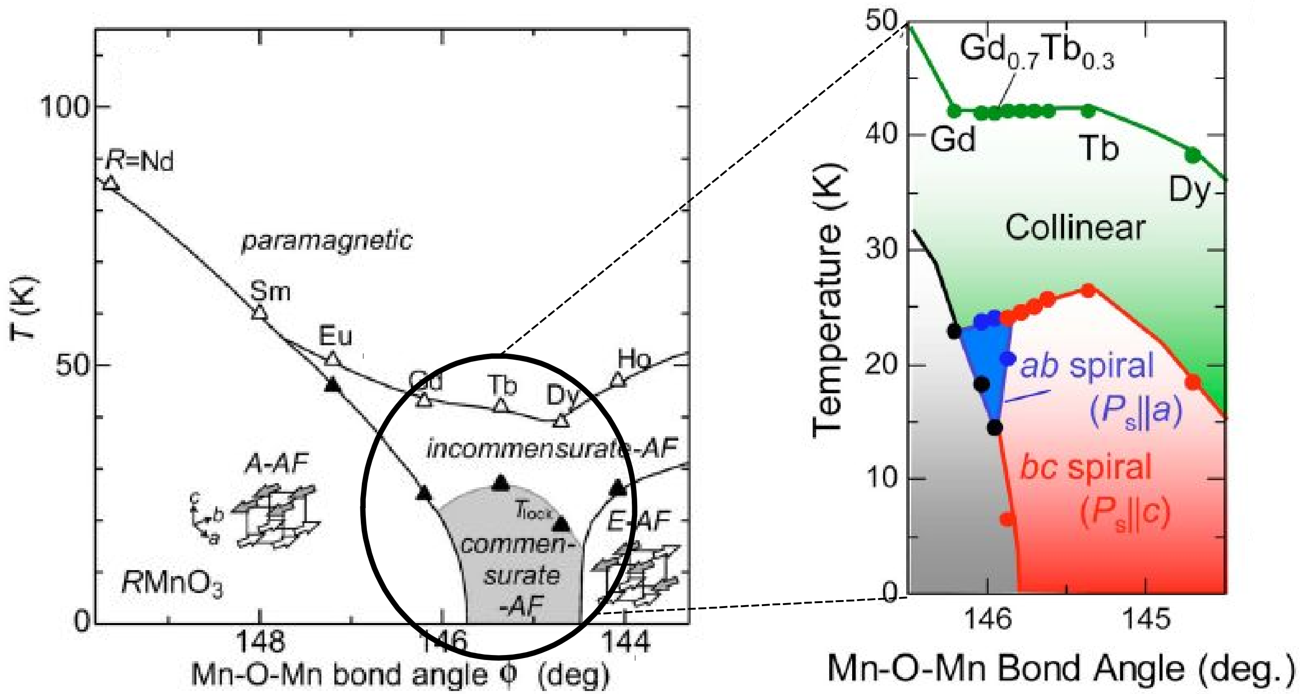
Raman scattering

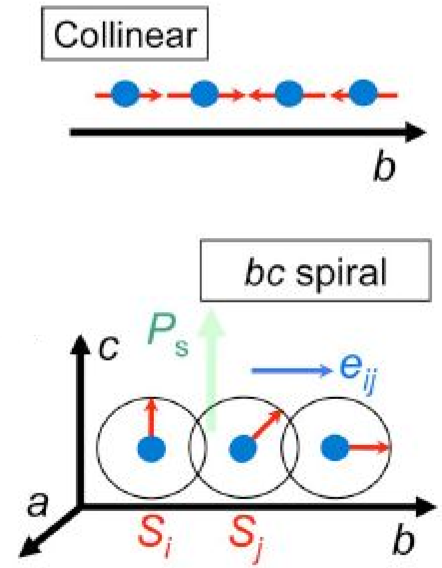


Raman spectra



RMnO3 compounds multiferroics type II





$\mathbf{P}S=\mathbf{e}ij.Si\times Sj$

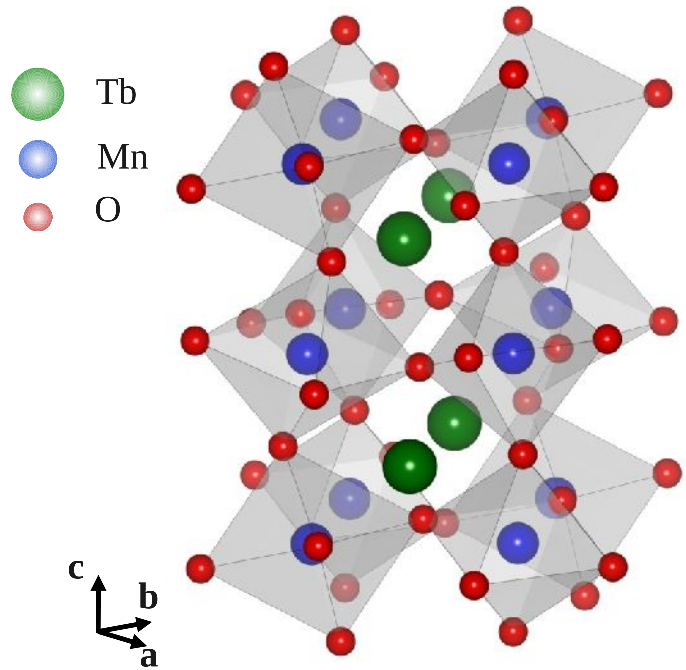
Perovskites RMnO3 : Tb, Gd, Dy

Frustrated magnet with incommensurate magnetic structure

In type II, the FE order appears after the AFM phase

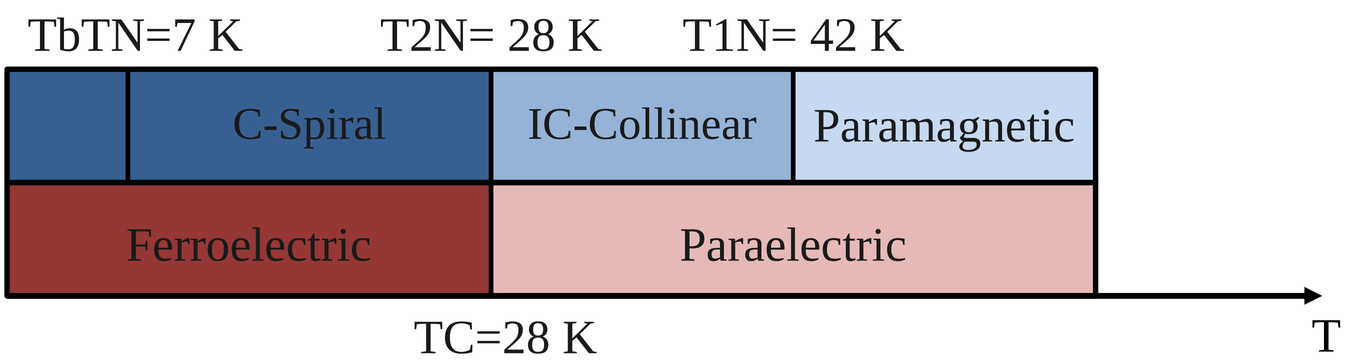
T. Kimura et al. PRB **68**, 060403(R) (2003)

The multiferroic: TbMnO3



Orthorhombic Symmetry
P*bnm* space group

Sample growth by zone fusion



Strong polarization (type II) P=0.08μC/cm2 (BiFeO3=100μC/cm2)

Giant magnetoelectric effect

TbMnO3 : the static properties

How to explain the strong coupling between the ferroelectric and magnetic orders ?

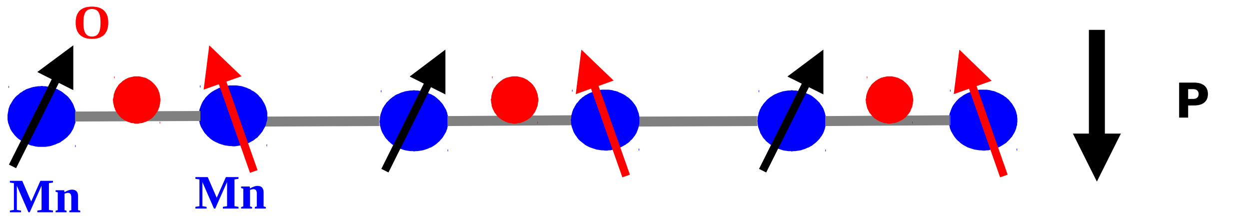
Magnetic ferroelectricity

Spiral spin structure

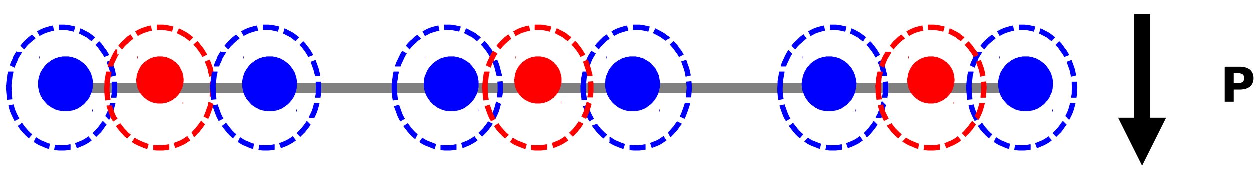
The spiral spin structure breaks simultaneously the time and spatial inversion → Magnetoelectric effect

….. microscopic scale …..

Dzyaloshinskii-Moriya Interaction



Charge displacement



Sergienko and Dagotto, PRB 73, 094434 (2006)

Katsura, Nagaosa and Baltasky, PRL **95**, 057205 (2005)

Which interaction is at the origin of the ferroelectricity?

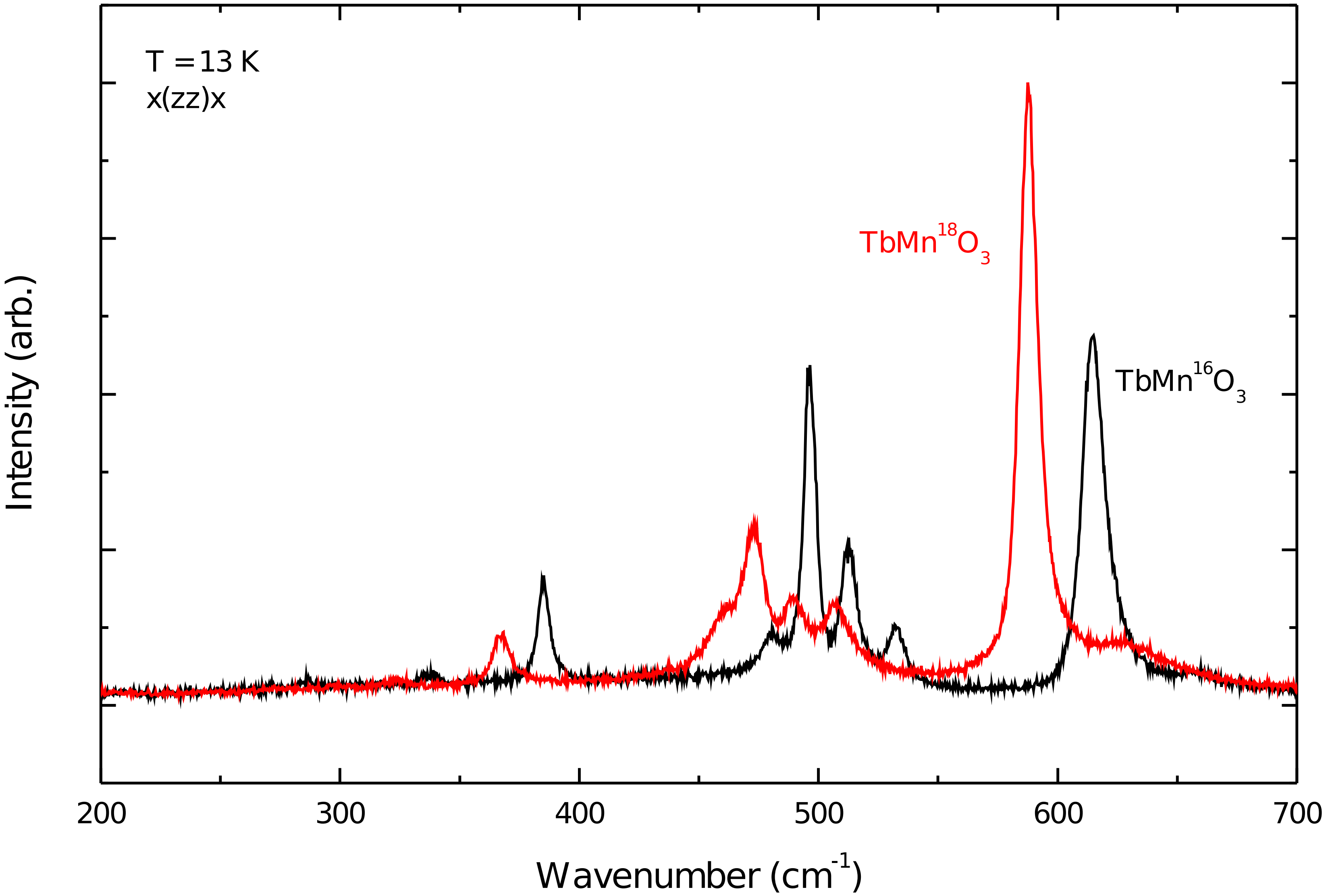
? ?

Dzyaloshinskii-Moriya Interaction

Charge displacement

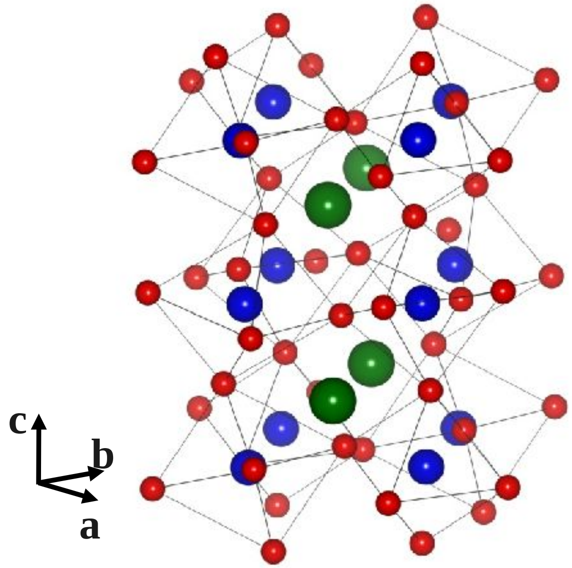
- **Oxygen substitution 18O □ 16O**
- **Temperature dependence of phonon frequencies**

Effect of the substitution on the phonon frequencies

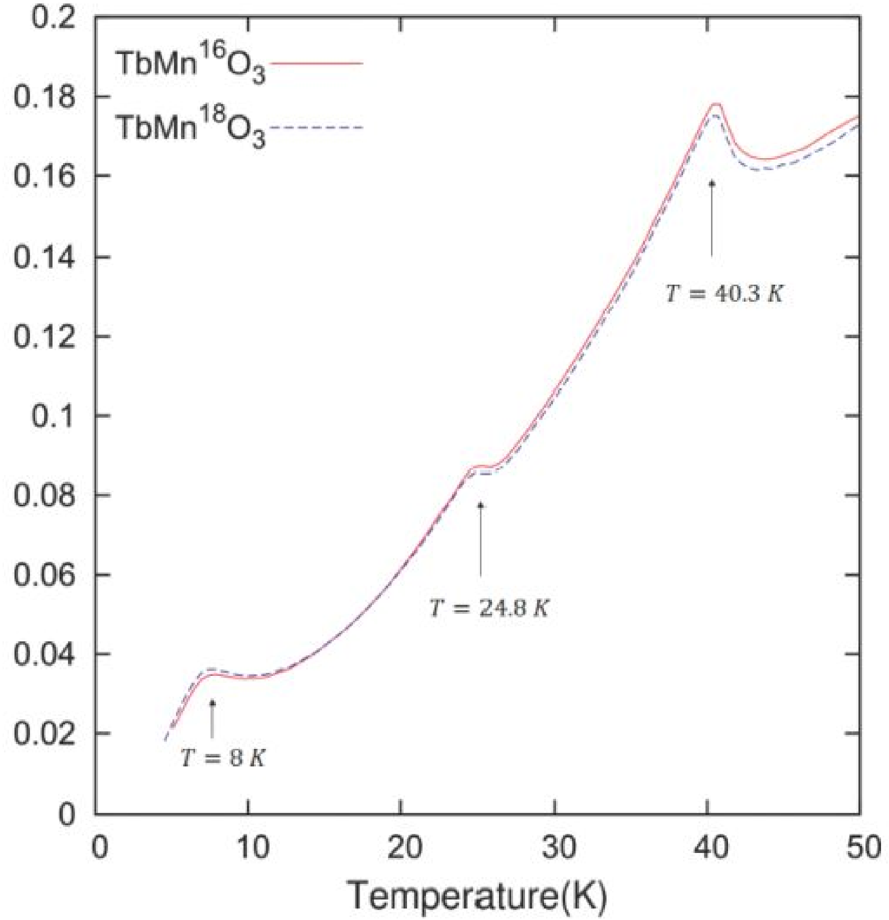


Phonon frequency shift related to: $\sqrt{\frac{k}{m}}$

Effect of the substitution on the magnetism transition



Specific heat measurements

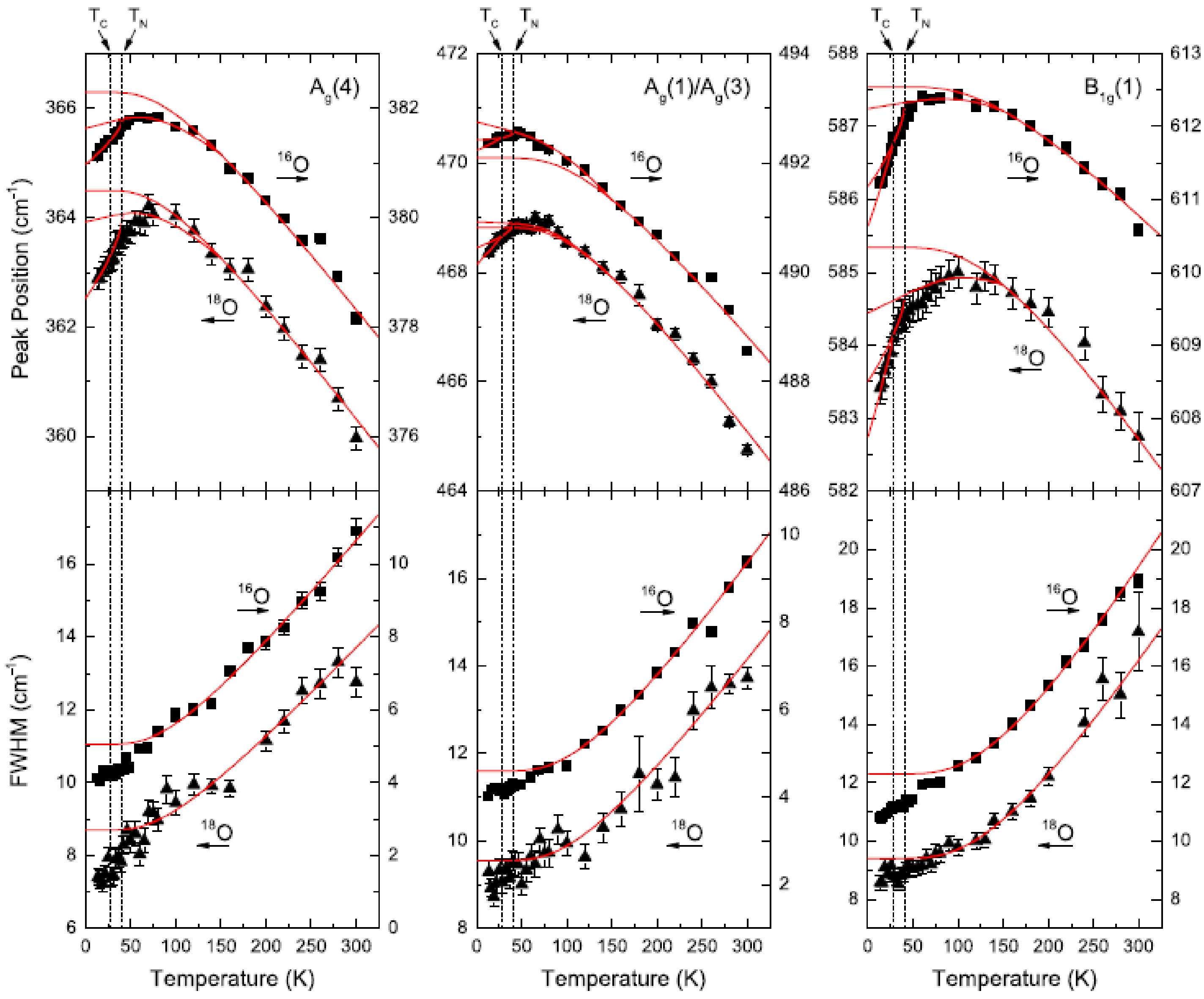


No effect of the substitution in the magnetic temperature transition

 the Jahn Teller distortion play no role in ferroelectric and magnetism order

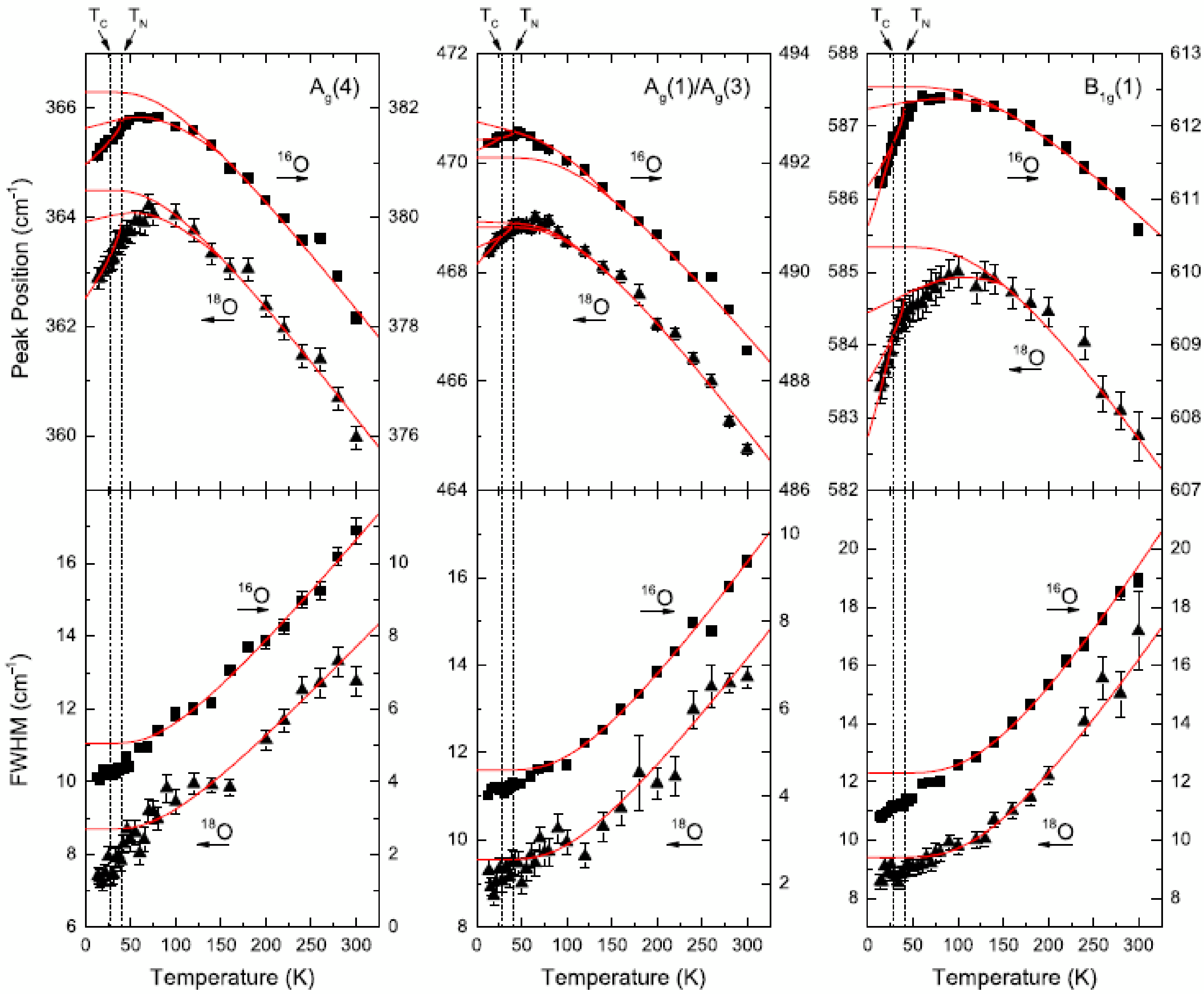
Alonso et al. *Inorg. Chem.*, *39*, 917 (2000)

Temperature dependence of phonon frequencies



Do not follow the empirical law: phonon phonon interaction $\omega_{ph}(T) = -A\left(1+\frac{2a}{\exp(\hbar\omega_0/2k_BT)-1}\right)+\omega_0$

Temperature dependence of phonon frequencies

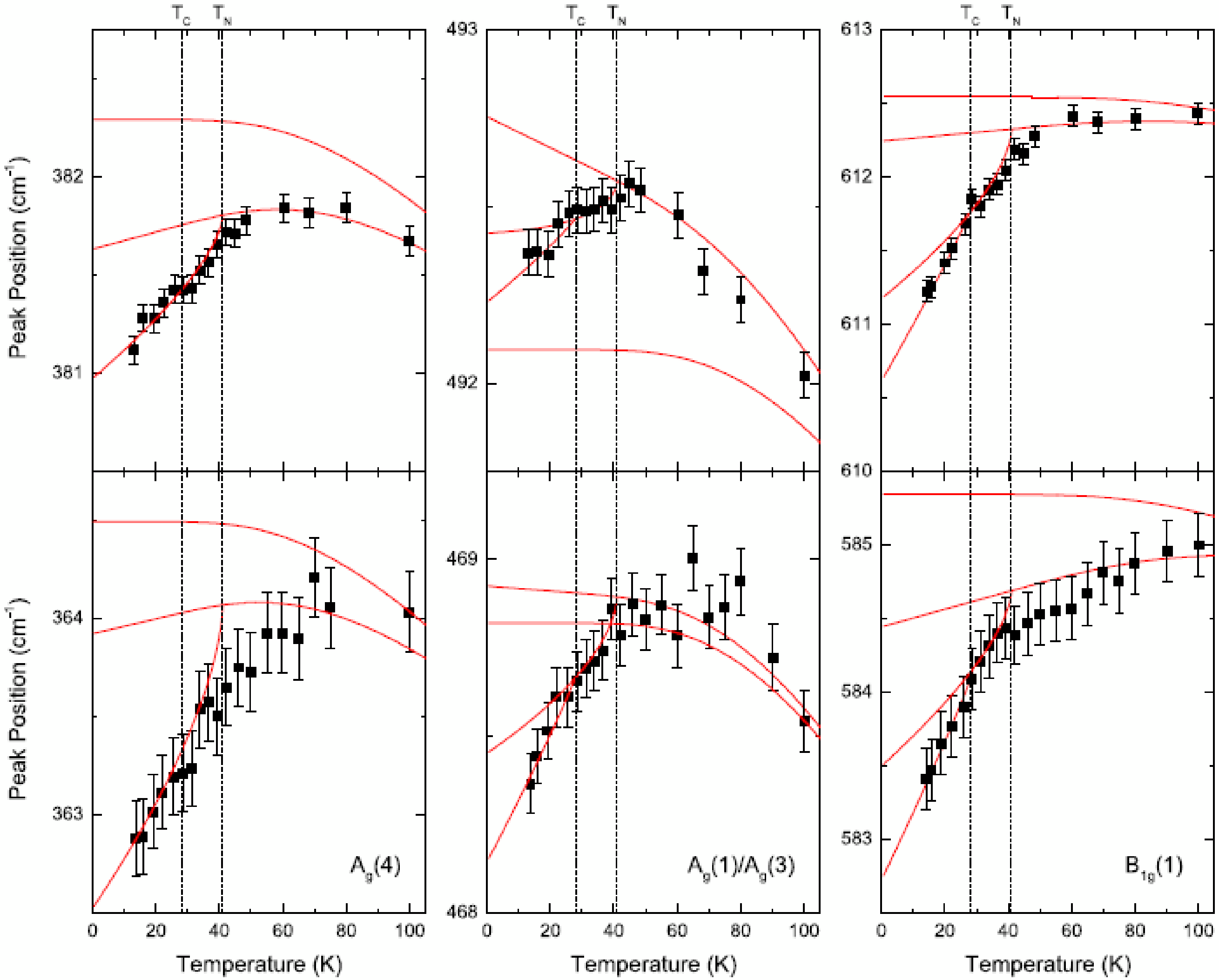


Do not follow the empirical law

Lattice distortion ?

Meier et al. New Journal of Physics 9, 100 (2007)

Temperature dependence of phonon frequencies



Spin-phonon coupling

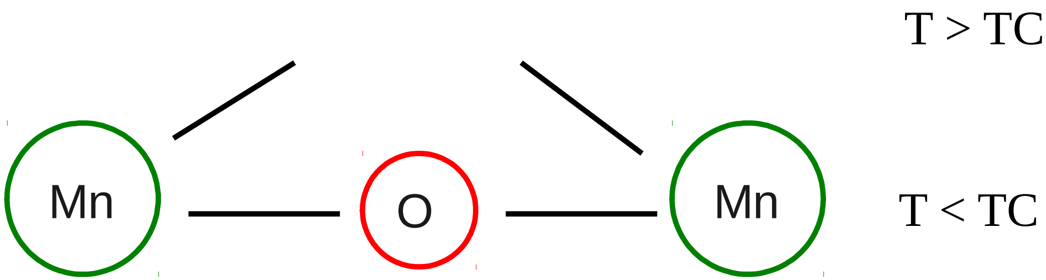
Coupling between the spin and the lattice

Granado et al. PRB 60, 11879 (1999)

Temperature dependence of phonon frequencies

<u>Spin- phonon coupling</u> : phonon modulating the exchange integral between interacting atomic spins.

TbMnO3 : Mn3+ ions interact via superexchange (O2-)
Mn-O-Mn □ ≠ 180° in the multiferroic phase (T > TC)



Which interaction is at the origin of the ferroelectricity?

? **?**

Dzyaloshinskii-Moriya Interaction

~~Charge displacement~~

Conclusion and Outlooks

Oxygen substitution 18O □16O

Heat capacity measurements:

No effect of the substitution in the magnetic temperature transition

□ the Jahn Teller distortion play no role in ferroelectric and magnetism order

Raman scattering:

Observation of a spin-phonon coupling in TbMnO3

□ Dzyaloshinskii-Moriya Interaction is at the origin of the ferroelectricity

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What append to the electromagnons with the substitution ?

Collaborators

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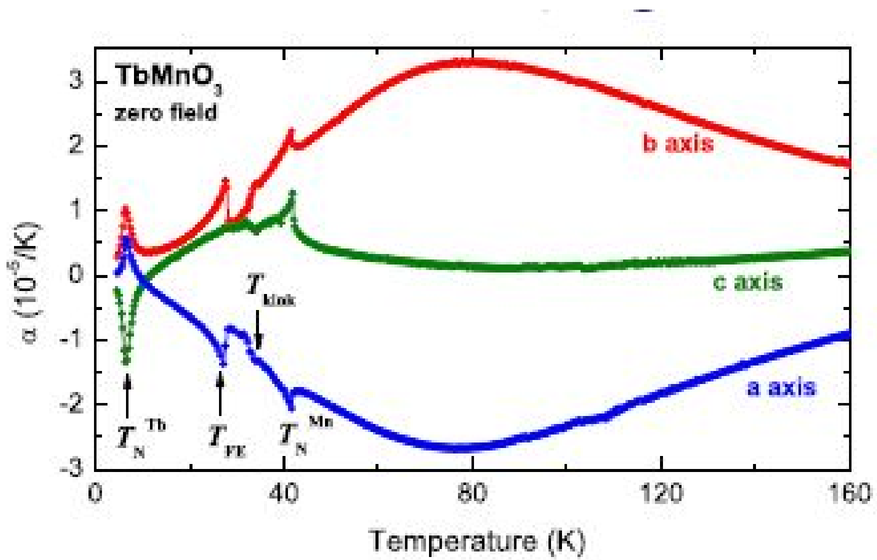
Spin-phonon interaction

$$(\Delta\omega_{stret})_{s\text{-}ph} \approx -\frac{2}{m\omega_\alpha}\frac{\partial^2 J_{xz}}{\partial u_{stret}^2}\left(\frac{M_{sublatt}(T)}{4\mu_B}\right)^2$$

Granado et al. PRB 60, 11879 (1999)

Lattice distortion



Meier et al. New Journal of Physics 9, 100 (2007)

TbMnO3 : the dynamical properties

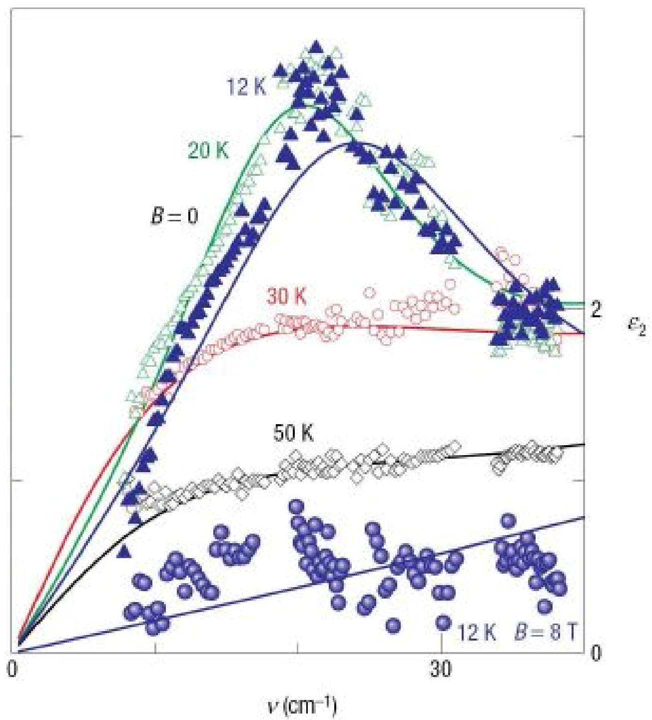
Degree of freedom

(magnon) Magnetic ⟷ Lattice (optical phonons)

Strong coupling

« New » excitations: electromagnons

Magnon with an electric dipole that can be strongly coupled to the electric field of light



Optical conductivity

New peak of spin excitation with a polar activity

↓

Electromagnon

Pimenov et al. Nature Phys **2**, 97 (2006)

A. B. Sushkov, PRL **98,** 027202 (2007)

TbMnO3 : difference between experiments and theory

Observation

Infrared : 2 excitations e1: 20 cm-1 e2: 60 cm-1

AFMR = 1M = energy of e1

Takahashi *et al.* PRL **101**, 187201 (2008)

Neutron : e1 at 20 cm-1 associated with 1M and e2 at 60 cm-1 associated with zone edge

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

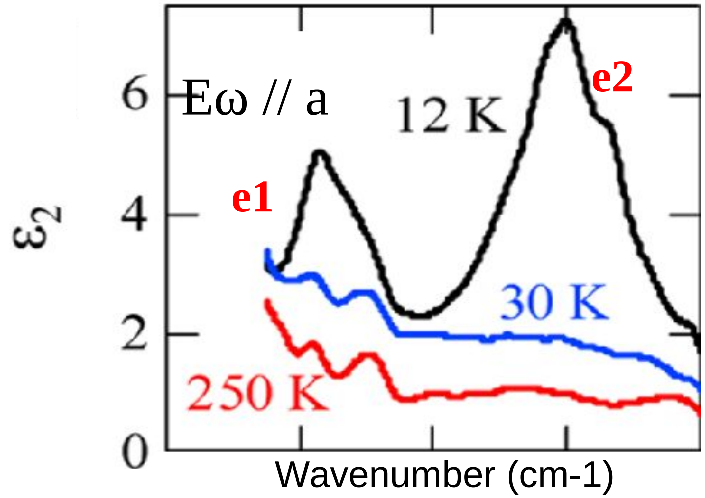
Theory

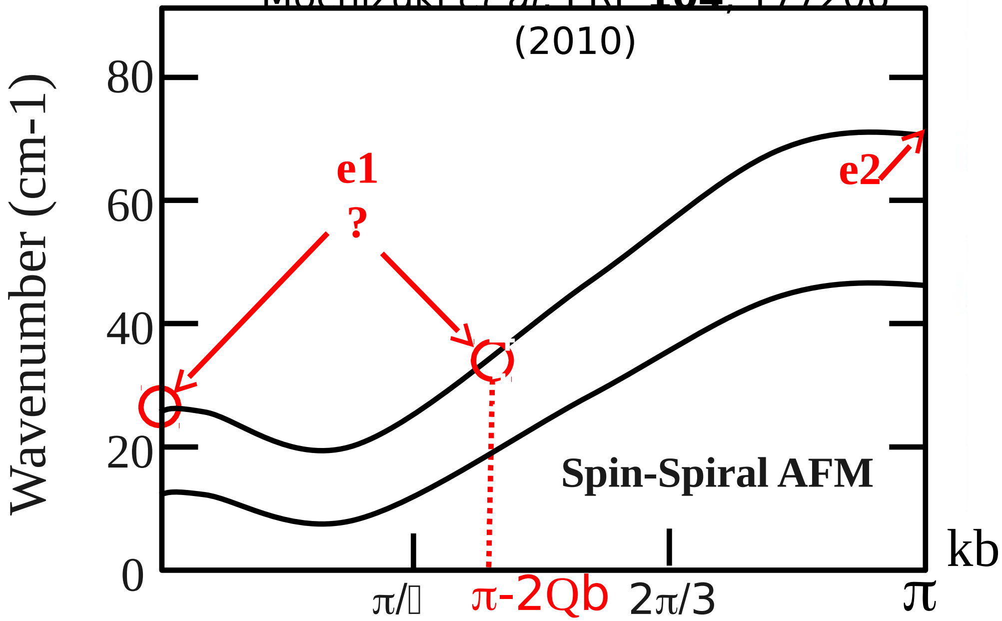
e1 at 25 cm-1 with a wave-vector π-2Qb

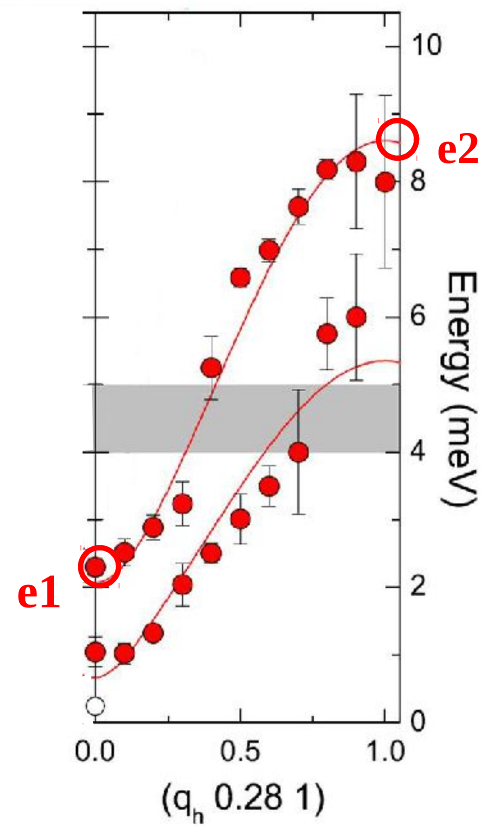
e2 at 60 cm-1 with a wave-vector π

Stenberg *et al.* PRB **80**, 094419 (2009)

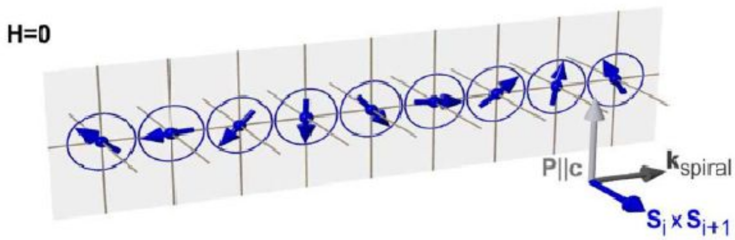
Mochizuki *et al.* PRL **104**, 177206 (2010)





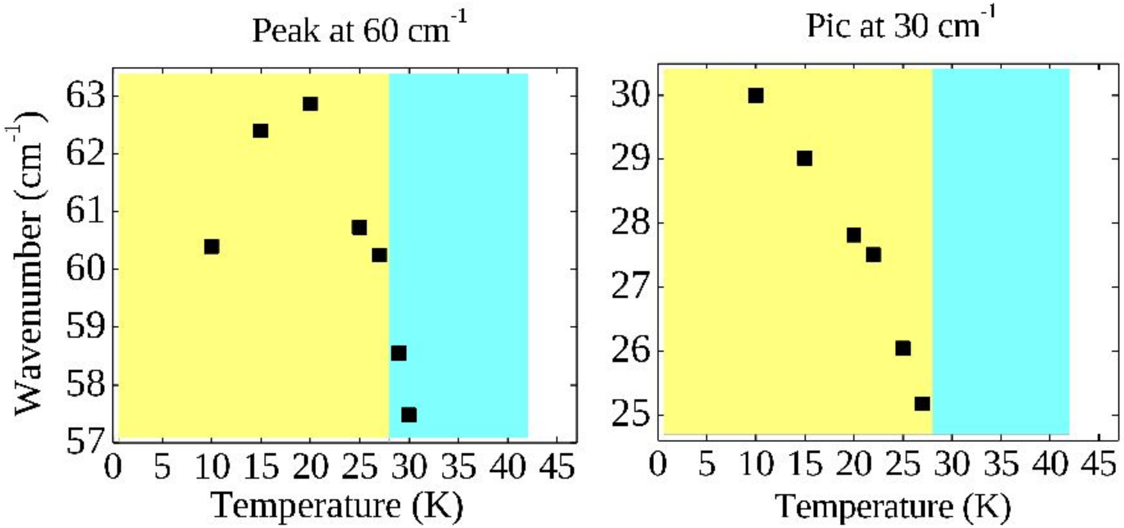


The Raman point of view



2 peaks at 30 (3.5) and 60 (7.5) cm-1 (meV)

Magnons or electromagnons ?

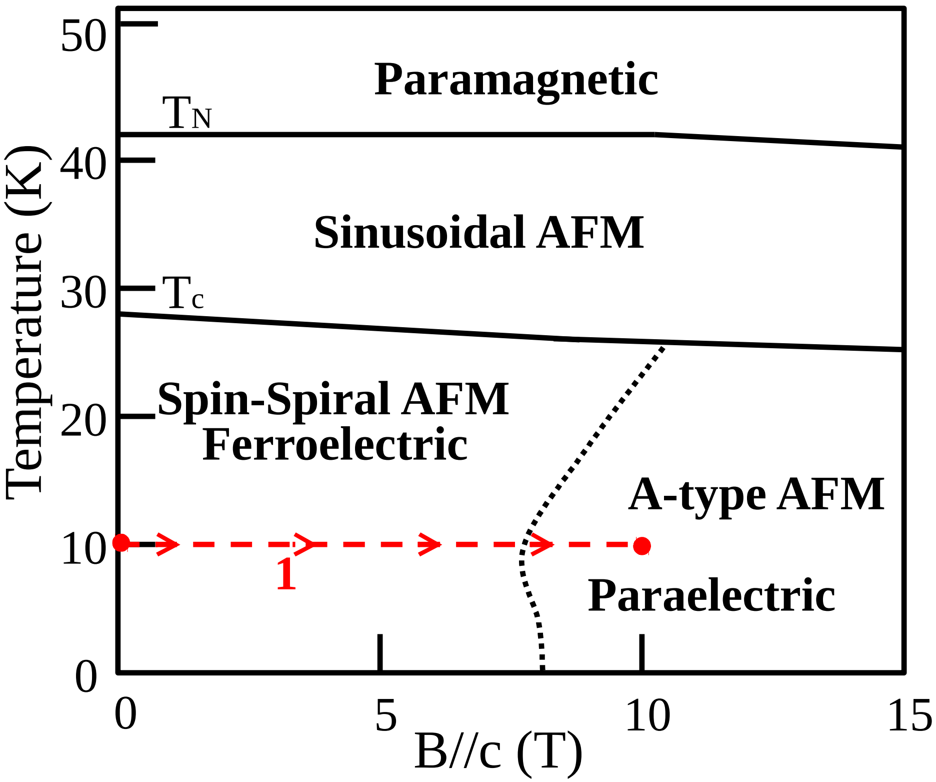


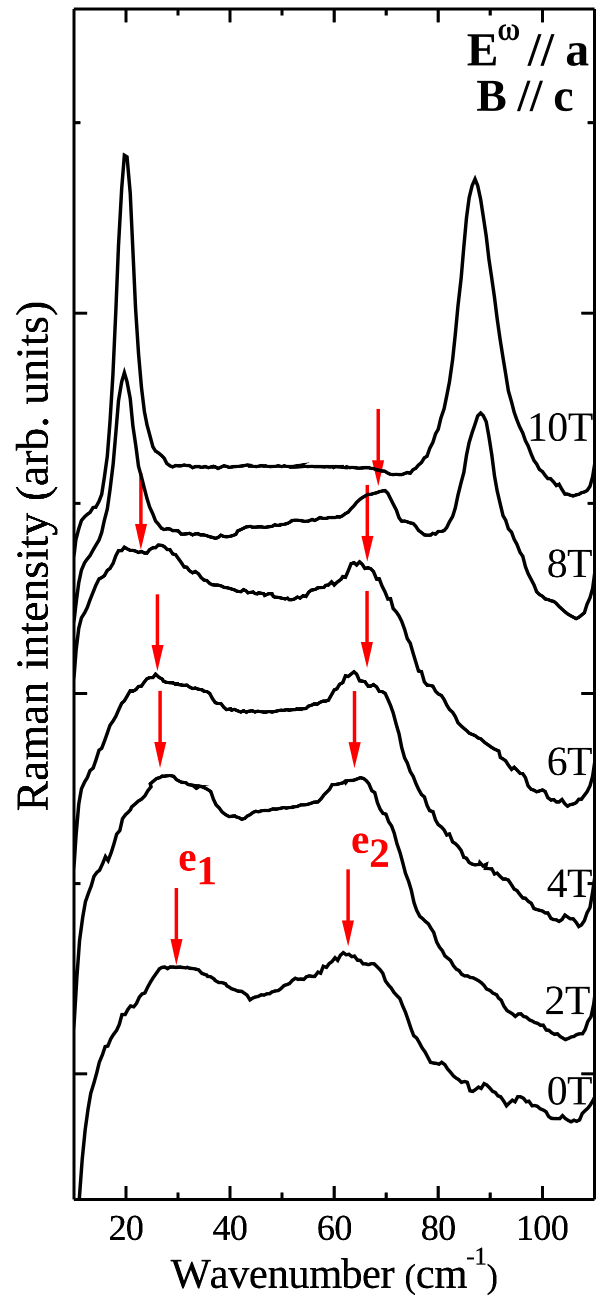
The peaks disappear at Tc

→ Electromagnons

P. Rovillain et al. PRB **81**, 054428 (2010)

TbMnO3 : electromagnons under magnetic field



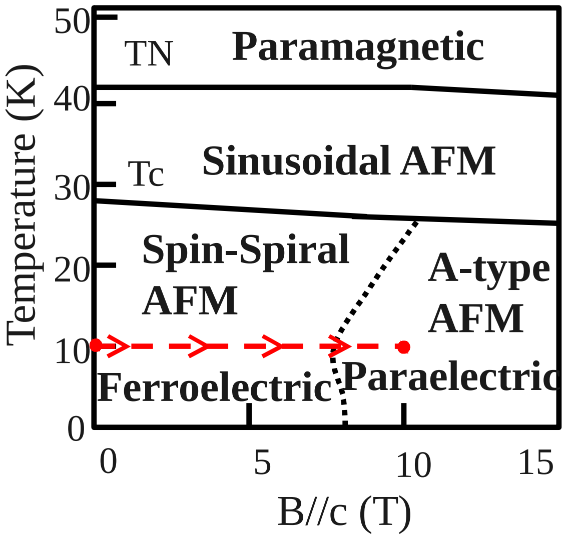


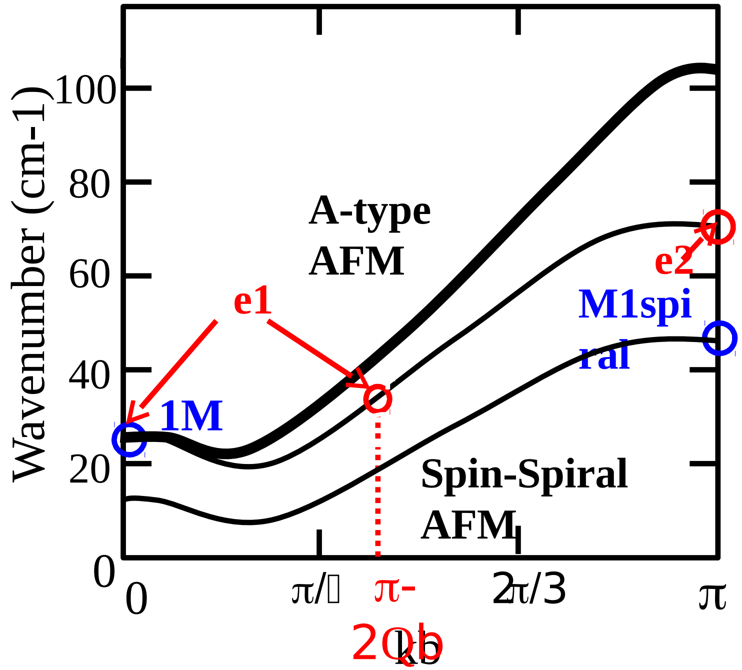
At high field, the e1 and e2 electromagnons disappear quickly

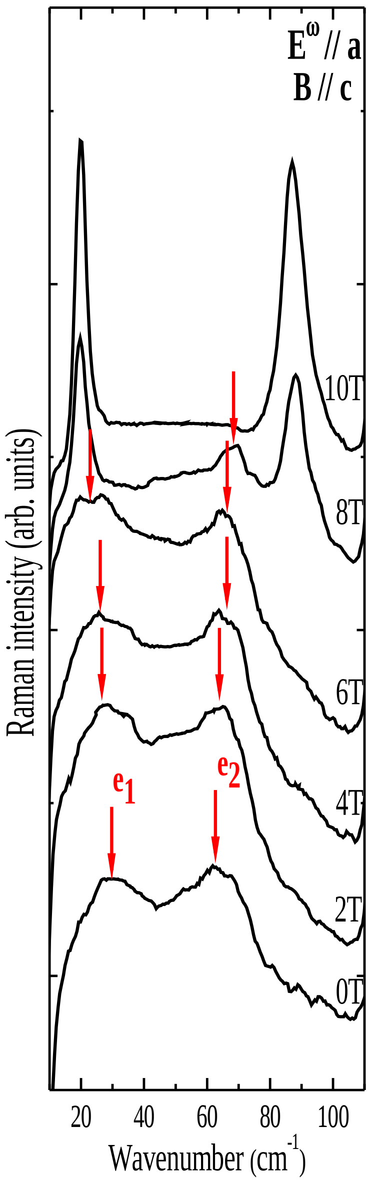
At 8T, 2 new peaks blow up located at 21 cm-1 and 85 cm-1

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

TbMnO3 : electromagnons







- Spectral weight transfer: electromagnon magnon
- High field, the polarization vanishes
   Deshybridization of electromagnons
- Excitations and wave vector of e1 and e2

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