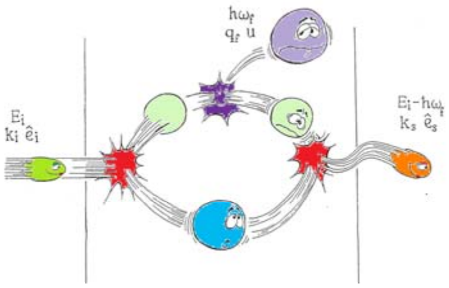
Introduction to Raman scattering



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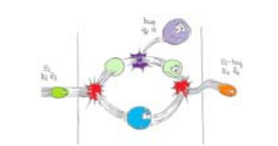
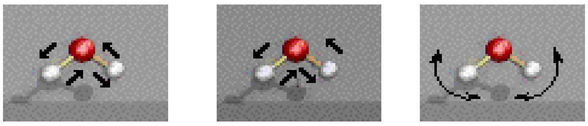
Outline



Introduction: Vibrational spectroscopy

Chemical bonds between atoms in a molecule or a crystal are not rigid ...

↳ Atoms move around their centre of gravity !
(small amplitude, up to a fraction of the atomic size)

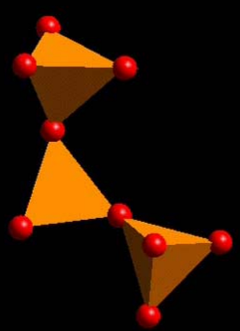


Vibrations are characteristic for a material → *« Fingerprint »*
(structure, chemistry, physics, state)

Methods:
- Infrared spectroscopy
- Raman spectroscopy
- Inelastic neutron scattering
- Ab-initio calculation

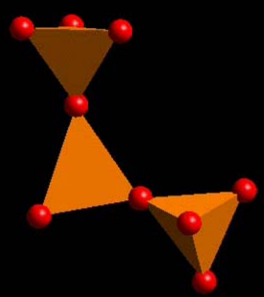
Atomic vibrations

Room temperature



SiO_4 tetrahedra in silicon

High temperature



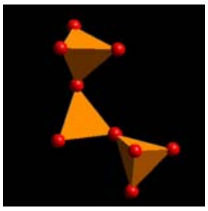
A vibration (Raman spectrum) is a unique fingerprint
for a given material, at a given external condition

Movies: M. Dove, Cambridge (UK)

Interest of vibrational spectroscopy (Raman scattering)

Vibrations are sensitive to changes of …

… external parameter (strain, temperature, pressure, E, H)
… physical properties (ferroelectric, magnetic etc.)



A probe for…

… identifying materials (solids, liquids, gas) or types of bonding (C-C ⇔ C=C)

… structural phase transitions (or changes in lattice distortion)

… investigating coupling phenomena (spin-phonon, electromagnons etc.)

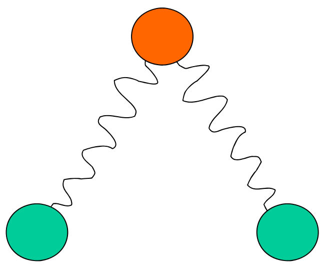
… investigating strain in thin films, nanocomposites etc.

… testing centro-symmetry etc.

Harmonic oscillator:

$$\omega = (k/\mu)^{1/2}$$

k: force constant
μ : reduced mass



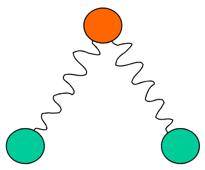
How many vibrational modes do exist ?

→ Degrees of freedom (DF)

- every atom: 3 degrees of freedom (x, y, z)
- crystal/molecule: 3*N* degrees of freedom
  (N: atoms in the unit cell/of a molecule)
- among those 3*N* : 3 DF for a translation
  3 DF for a rotation (2 for a linear molecule)
  The remaining: vibrational DF (vibrational modes)
  → 3*N* - 6 for non-linear molecules
  → 3*N* - 5 for linear molecules
  → 3*N* - 3 for crystals (no free rotation !)

Degrees of freedom (DF), examples

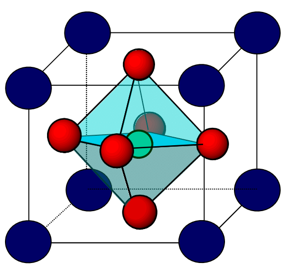
H_2O



N = 3 atoms → 3N = 9 DF
minus 3 DL (translation)
minus 3 DL (rotation)

→ 3N-6 = 3 vibrational modes

Perovskite ABO_3

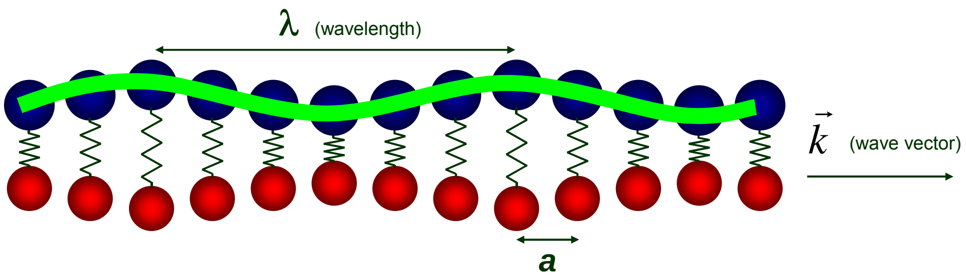


N = 5 at./uc. → 3N = 15 DF
minus 3 DF (translation)

→3N-3 = 12 vibrational DF

here a=b=c ➔ 4 triply generated modes

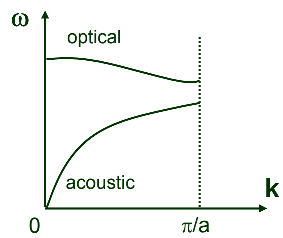
Vibrations and phonons ...



A vibrational wave can be described by a *quasi*-particle: **A phonon**
(in analogy with a photon for an electromagnetic wave)

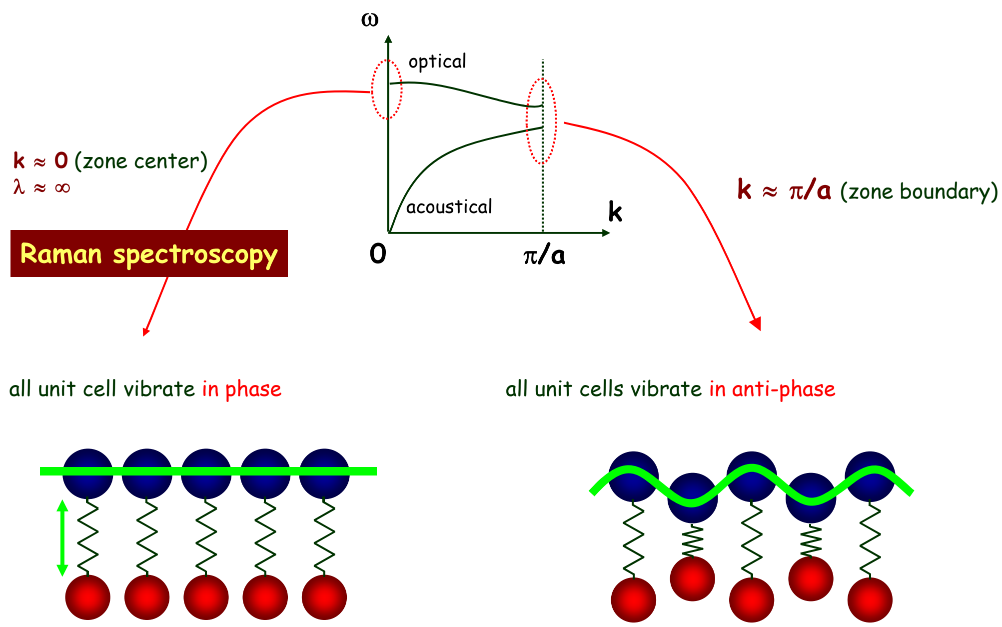
$$\omega = \omega(k)$$

(Phonon dispersion)



Phonons and Raman spectroscopy

- Optical photons: small wave-vector
- Wave-vector conservation
➔ Raman phonons: very small momentum transfer



Raman scattering, a bit of history ...

1923 Theoretical prediction by the Austrian physicist A.Smekal

"The quantum theory of dispersion" (*Naturwissenschaften* **11**, p. 873, 1923)

1928 Experimental discovery

- by the Indians C.V. Raman and K.S. Krishnan in Kalkutta

"The optical analog of the Compton effect" (*Nature* **121**, p.711, 1928)

- by the Russians G. Landsberg et L. Mandelstam à Moscou

"A novel effect of light scattering in crystals" (*Naturwissenschaften* **16**, p.557, 1928)

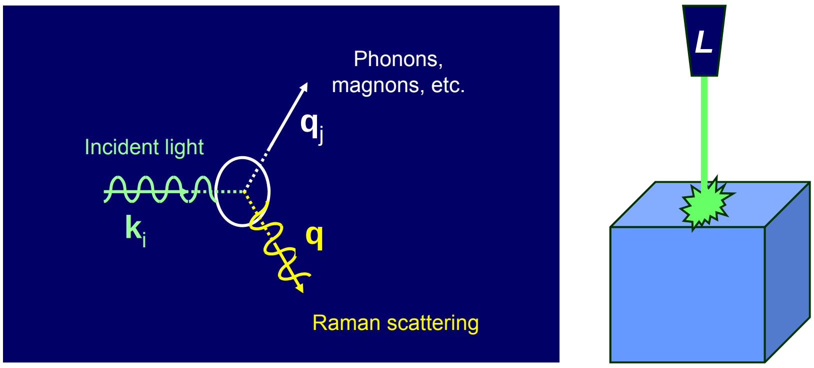
1930 Nobel price: Sir C.V. Raman (* 1888, † 1970)

"… for is work on light scattering and the discovery of the later called Raman effect ..."

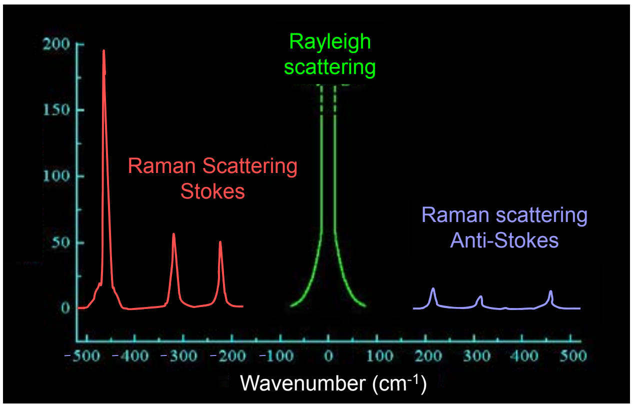
≈ 10.000 published articles using Raman scattering in the year 2011 [source WoS]

A.2 Concept & Theory: What is the Raman effect ?

Inelastic scattering of light with a material



Example of a Raman spectrum



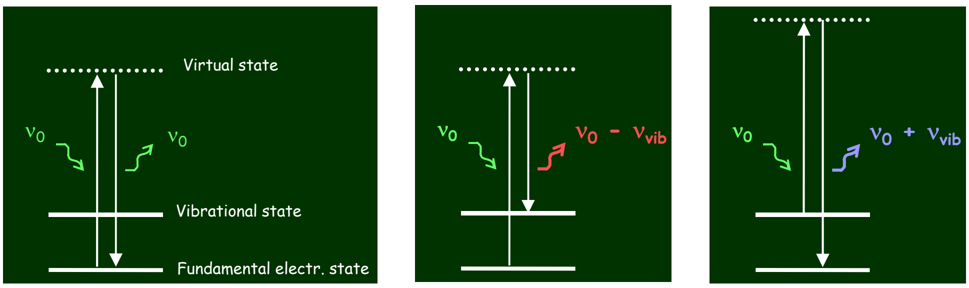
The unit of « spectroscopists », the wavenumber (cm^{-1}):

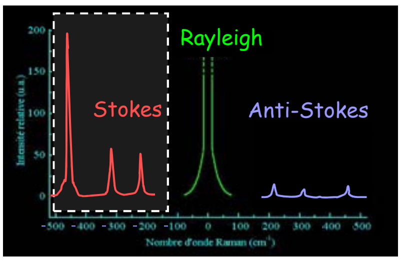
$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$$

Conversions: 1 meV= 8.051 cm^{-1} 1 THz = 33 cm^{-1} 1THz = 4.136 meV

Energy transfer model ...

Raleigh scattering (elastic) | Stokes Scattering | Anti-Stokes scattering



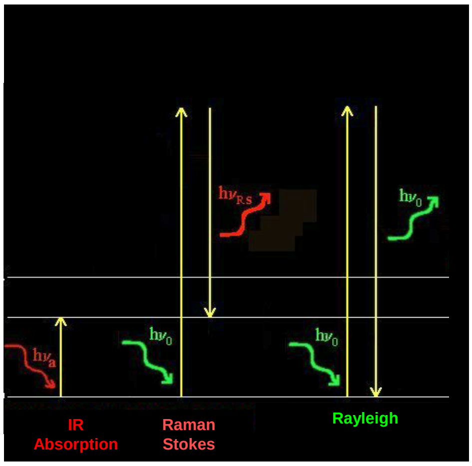


optical mode → Raman scattering
acoustic mode → Brillouin scattering

In principle, we can also study:
- rotational states
- magnetic states (→ magnons)
- electronic states (→ polarons)
- magneto-electric states (→ electromagnons)
- etc ...

Raman scattering ↔ Infrared absorption

Infrared absorption spectroscopy



IR absorption and Raman scattering are both vibrational spectroscopies

but involve different interactions (and thus selection rules)

Raman scattering- Classical treatment

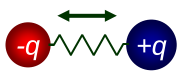
Source of the scattered light (Rayleigh and Raman):

Induced dipole of the molecule by the incident electric field

Laser

$$\vec{E} = \vec{E}_0 \cos(\omega_0 t)$$

Molecule



$$x = x_0 \cos(\omega_M t)$$

- Induced electric dipole

$$\vec{\mu} = \alpha\,\vec{E} + \frac{1}{2}\beta\,\vec{E}\vec{E} + \frac{1}{6}\gamma\,\vec{E}\vec{E}\vec{E} + \ldots$$

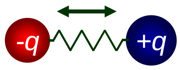
Raman scattering — Hyper-Raman scattering

a : polarisability **(tensor!)**
b : hyper-polarisability
g : 2° hyper-polarisability

- $\alpha >> \beta >> \gamma$ $\quad \vec{\mu} \cong \alpha\,\vec{E}$ $\quad$ Limitation to linear effects

Classical treatment (induced dipole)

$\vec{\mu} \cong \alpha \, \vec{E}$



Taylor development of the polarisability around x_0

$$\alpha(x) = \alpha_0 + \left.\frac{\partial \alpha}{\partial x}\right|_{x_0} x + \ldots$$

$$\vec{\mu} = \left(\alpha_0 + \left.\frac{\partial \alpha}{\partial x}\right|_{x_0} x \right) \vec{E}$$

(induced electric dipole)

Incident field

$\vec{E} = \vec{E}_0 \cos(\omega_0 t)$

$$= \left(\alpha_0 + \left.\frac{\partial \alpha}{\partial x}\right|_{x_0} x \right) \vec{E}_0 \cos(\omega_0 t)$$

Eigen-vibration of the molecule

$x = x_0 \cos(\omega_M t)$

$$= \alpha_0 \vec{E}_0 \cos(\omega_0 t) + \left.\frac{\partial \alpha}{\partial x}\right|_{x_0} \vec{E}_0 \cos(\omega_0 t) \, x_0 \cos(\omega_M t)$$

Classical treatment (result)

$$\vec{\mu} = \alpha_0 \vec{E}_0 \cos(\omega_0 t) + \frac{1}{2} \left.\frac{\partial \alpha}{\partial x}\right|_{x_0} \vec{E}_0 x \left[\cos(\omega_0 + \omega_M)t + \cos(\omega_0 - \omega_M)t \right]$$

$$\vec{\mu} = \vec{\mu}(\omega_0) + \underline{\vec{\mu}(\omega_0 + \omega_M)} + \underline{\vec{\mu}(\omega_0 - \omega_M)}$$

Raman scattering results from a modulation of the incident electric field by the vibrating molecule

… leads to two new frequencies
($\omega_0 + \omega_M$ and $\omega_0 - \omega_M$)

Classical treatment (Raman activity)

$$\vec{\mu} = \alpha_0 \vec{E}_0 \cos(\omega_0 t) + \frac{1}{2} \left. \frac{\partial \alpha}{\partial x} \right|_{x_0} \vec{E}_0 x \left[\cos(\omega_0 + \omega_M)t + \cos(\omega_0 - \omega_M)t \right]$$

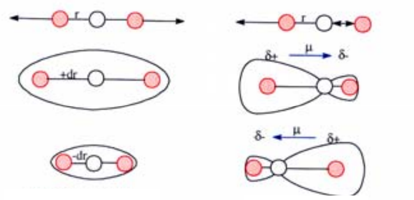
Selection rule

A mode is only active in Raman spectroscopy if

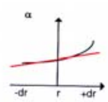
$$\left. \frac{\partial \alpha}{\partial x} \right|_{x_0} \neq 0$$

Illustration of the Raman activity & symmetry

Symmetric mode | Asymmetric mode

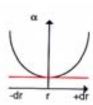


$\left. \frac{\partial \alpha}{\partial x} \right|_{x_0} \neq 0$



$\left(\frac{d\alpha}{dr}\right)_e \neq 0$

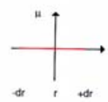
Raman active



$\left(\frac{d\alpha}{dr}\right)_e = 0$

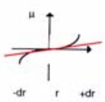
Raman inactive

$\left. \frac{\partial \mu}{\partial x} \right|_{x_0} \neq 0$



$\left(\frac{d\mu}{dr}\right)_e = 0$

IR inactive



$\left(\frac{d\mu}{dr}\right)_e \neq 0$

IR active

Raman and IR spectroscopy are **complementary**!

Exclusion rule
In a centro-symmetric molecule or crystal none of the Raman active modes is IR-active and vice versa.

The change in the molecular dipole moment when the atoms vibrate determines whether the vibration is or is not IR active.

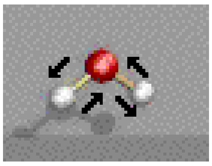
Conclusive remarks on the theoretical part

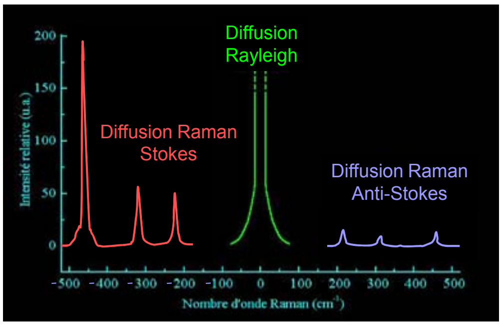
Raman scattering: Inelastic scattering of light with a material

Harmonic oscillator: $\omega = (k/\mu)^{1/2}$

k: force constant

μ : reduced mass



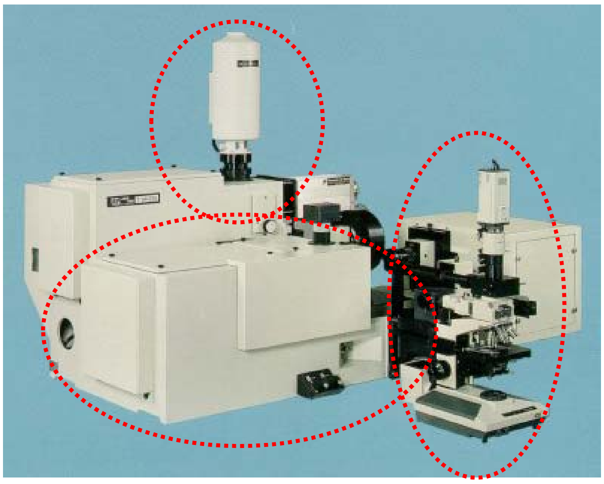


A Raman spectrum is a unique (vibrational) fingerprint for a given material

2.

Instrumental & experimental *aspects*

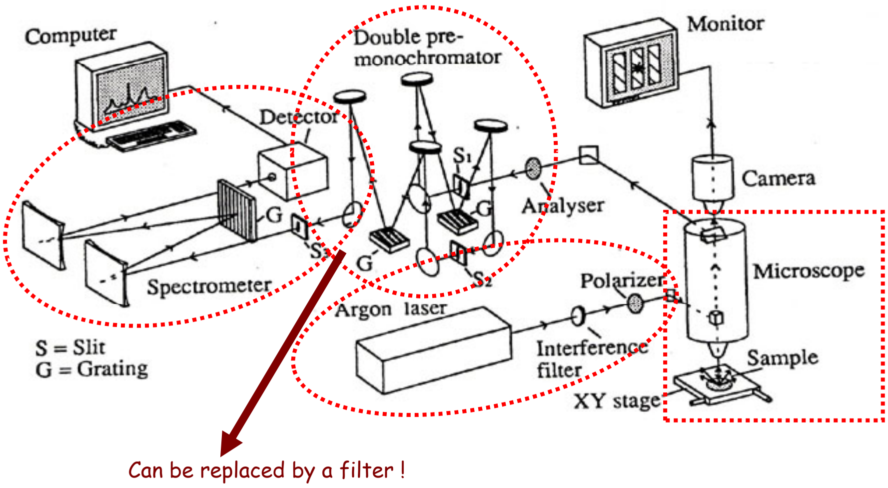
How does a Raman spectrometer look like ?



Raman Spectrometer T64000 (Jobin-Yvon)

Or more compact spectrometers

Instrumentation



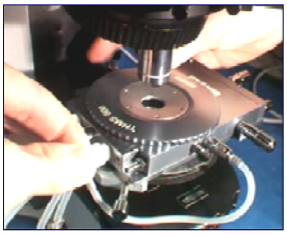
Sample preparation ?

In most cases no preparation necessary

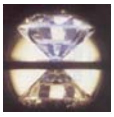
External parameters ?

Temperature (80 K to 1800 K)

- under atmosphere (Ar, O_2, N_2 or vacuum)
- simultanenous transport measurements
- simultanenous ***E*** -field



Pressure (↗ 100 GPa)



etc...

Which materials have a “nice” Raman signature ?

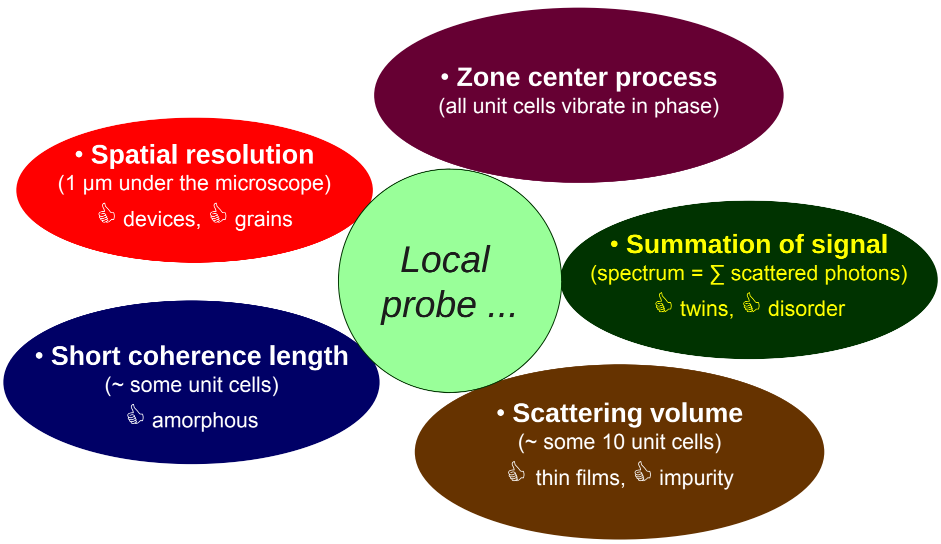
Difficult to say …, but there are indications:

• oxide, fluoride, diamond, SiC etc. (transparent materials)

• cubic (*Pm*-3*m*) materials have no Raman signature
• disorder (chemical, structural, …)
• strong metallic character
• strong absorption in the visible range
• strong reflectivity in the visible range
• bad crystalline quality

however … silicon, graphite etc … have a strong Raman signature

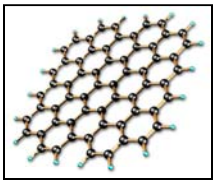
Why is Raman spectroscopy a local probe ?

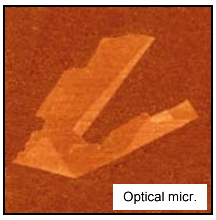


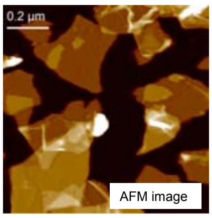
B. Illustrations 1

B.1 Raman scattering of non-oxide materials

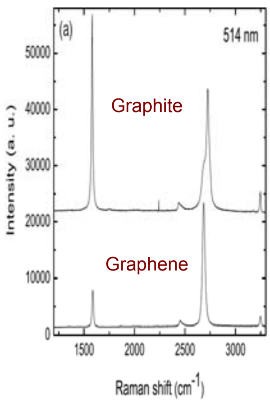
2D: Graphene

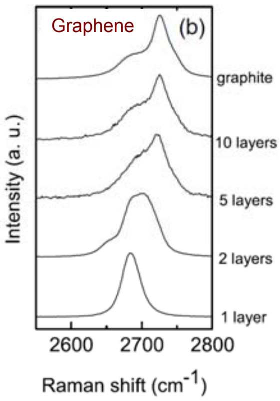


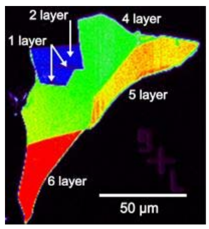




Identification of single atomic layers of graphene

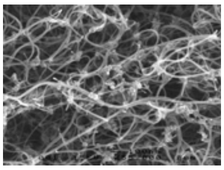


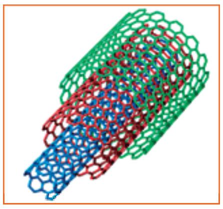


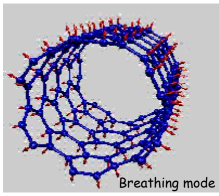


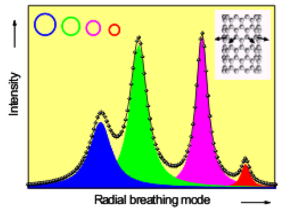
A. C. Ferrari, et al., Phys. Rev. Lett. 97, 187401 (2006)

1D: Carbon nanotubes

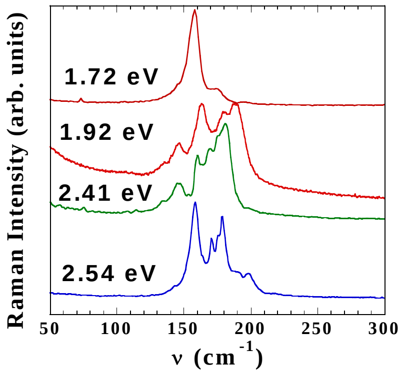








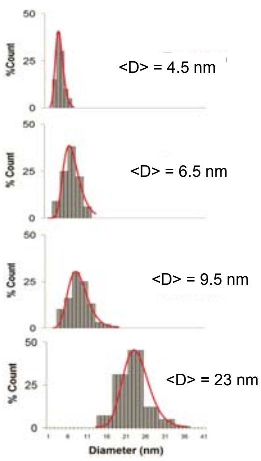
Determination of nanotube diameter !



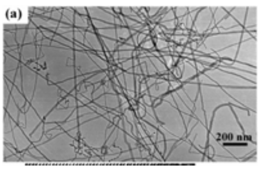
Nano-Size effects in Si nanowires

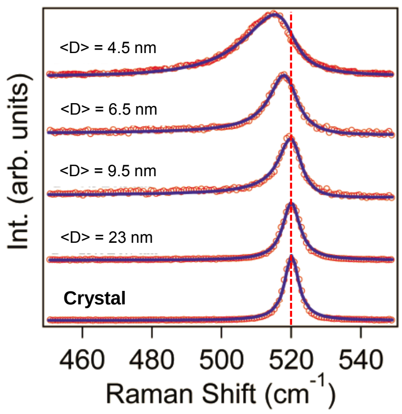
K. W. Adu et al., Nanolett. 5, 409 (2005)

Distribution of diameters



TEM image of Si nanowires

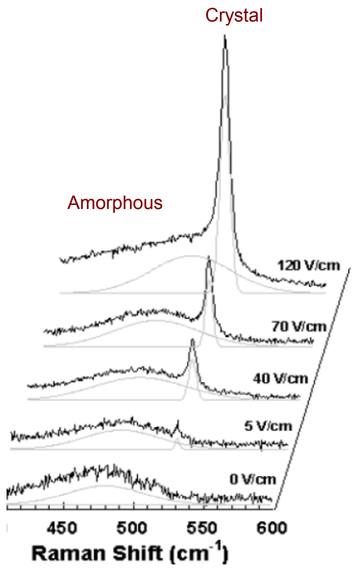




➔ Identification and characterization of nano-size effects

Amorphous samples

Do amorphous samples have a Raman signature ?

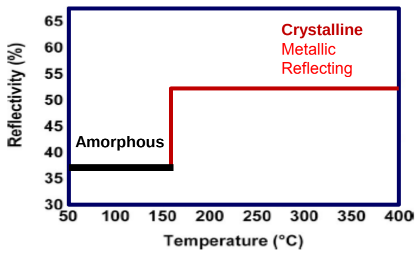


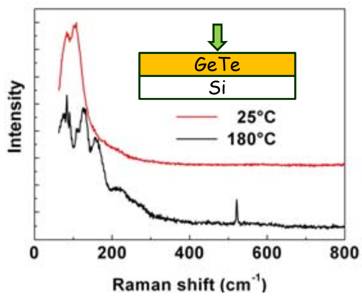
Example

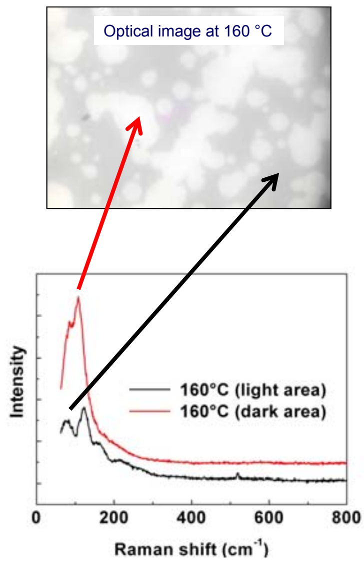
Amorphous vs. nano-crystalline Si

S. Jin Park et al., J. Korean Phys. Soc. 42, S466 (2005)

Phase Change Materials/Memories (PCM's), e.g. GeTe







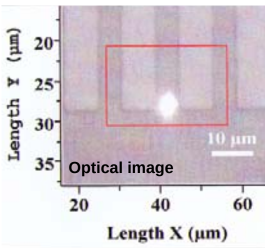
➔ Probing of phase transition

➔ Probing transition region

E. Gourvest, J. Kreisel, M. Armand, S. Maitrejean, A. Roule, S. Lhostis,C. Vallée, Appl. Phys. Lett. 95, 031908 (2009).

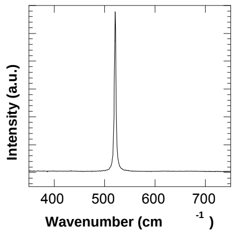
Raman imaging in micro- and nano-technology

Contacts on a Si wafer



Do the contacts induce strain ?

Reference Si: 523.34 cm^{-1}

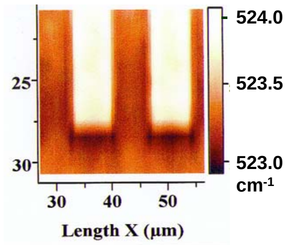


Change in band position

↓

Strain !

Raman (strain) image



Strain underneath & at corner of contacts

Potential effect on dopants …

Michel Mermoux, Grenoble, unpublished

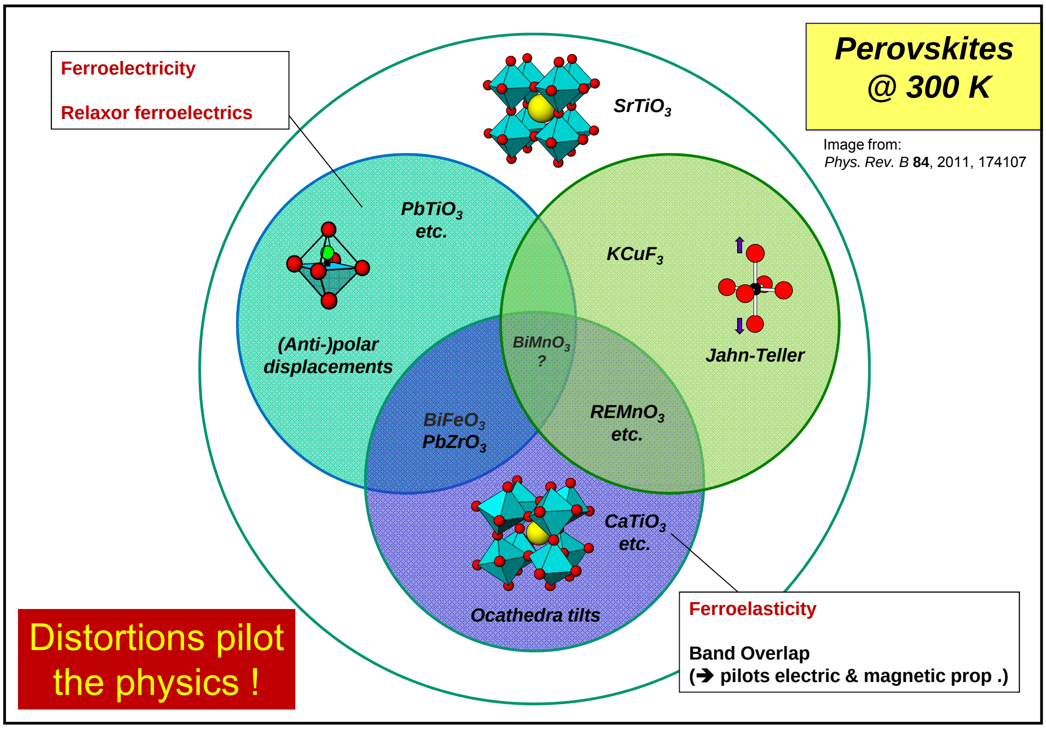
C. Illustrations 2

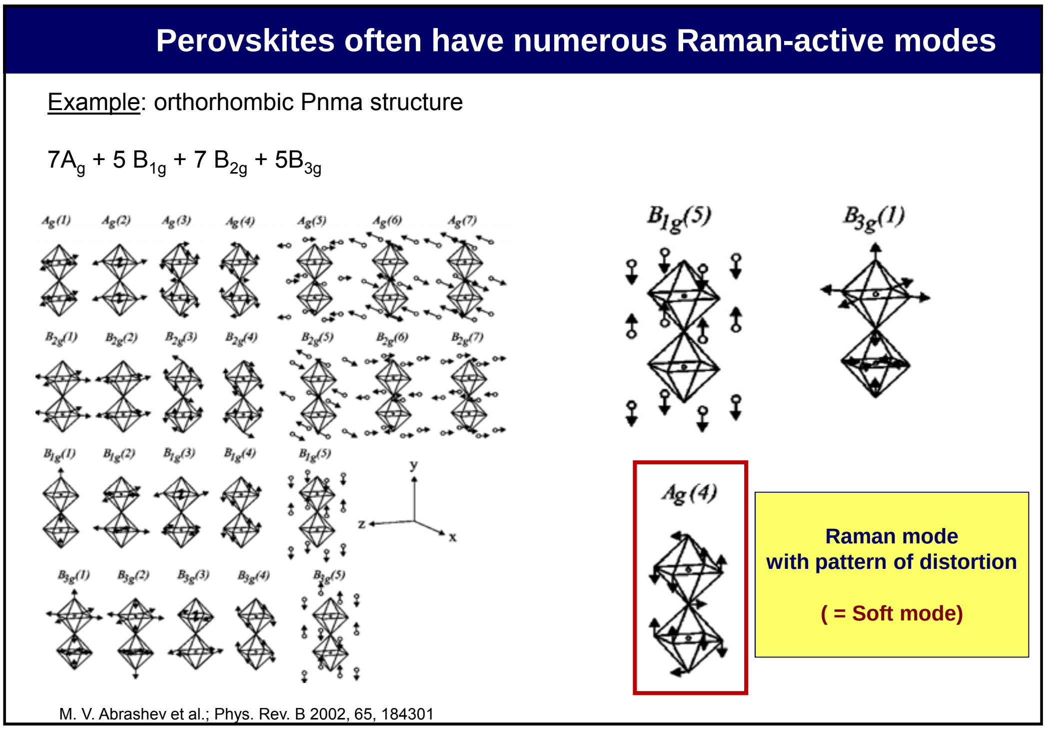
Raman scattering of ferroic oxides

(or … Treating individual ferroic orders before looking at multiferroics)

1. Octahedra tilts (ferroelasticity)
2. Cation displacements (ferroelectricity)

(The notion of "soft modes" & "hard modes")

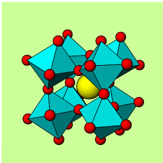

Perovskites
@ 300 K
Image from:
Phys. Rev. B 84, 2011, 174107
Ferroelectricity
Relaxor ferroelectrics
SrTiO3
PbTiO3
etc.
KCuF3
(Anti-)polar
displacements
BiMnO3
?
Jahn-Teller
BiFeO3
PbZrO3
REMnO3
etc.
CaTiO3
etc.
Ocathedra tilts
Ferroelasticity
Band Overlap
(➔ pilots electric & magnetic prop .)
Distortions pilot
the physics !


Perovskites often have numerous Raman-active modes
Example: orthorhombic Pnma structure
7Ag + 5 B1g + 7 B2g + 5B3g
B1g(5)
B3g(1)
Ag(4)
Raman mode
with pattern of distortion
(= Soft mode)
M. V. Abrashev et al.; Phys. Rev. B 2002, 65, 184301

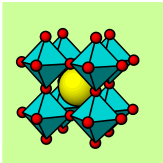
Probing the structural distortion & phase transition of perovskites

Structural distorsion

Raman mode with pattern of distortion (= Soft mode = Instability)



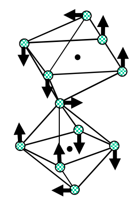
ferroelastic
non-cubic

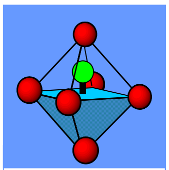


cubic

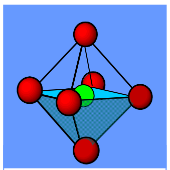
Following rotation angle of octahedra

(➔ orbital overlap)





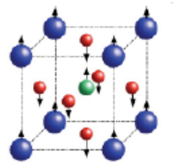
ferroelectric
non-cubic



paraelectric
cubic

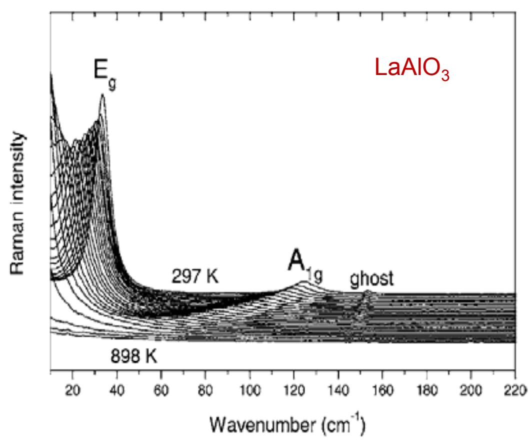
Following polar displacements

(➔ ferroelectricity)

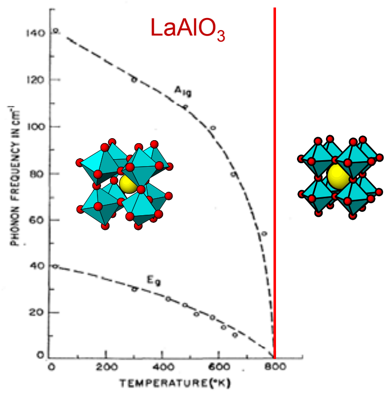


Prototype example for octahedra rotations: $LaAlO_3$

S. A. Hayward et al., Physical Review B 72, 054110 (2005).



J. F. Scott, Physical Review 183, 823 (1969).



Landau theory:

$\omega^2(T) = \omega_0^2 (T_c - T) = \theta(T)^2$

Position of soft mode ➔ Tilt angle θ

See also the textbook example: $SrTiO_3$

[P. A. Fleury, J. F. Scott, and J. M. Worlock, Physical Review Letters 21, 16 (1968).]S

Effect of high-pressure on octahedra tilts: $LaAlO_3$

P. Bouvier & J. Kreisel J. Phys.: Condens. Matter **14**, 3981 (2002)

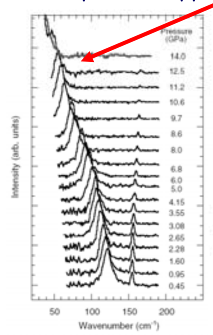
Raman spectroscopy

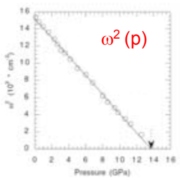
"soft mode"

$\omega^2(p) = \omega_0^2 (P_c - P) = \theta^2 (P)$

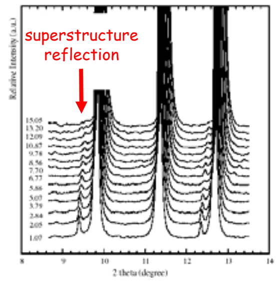
↓

Rotation of octahedra



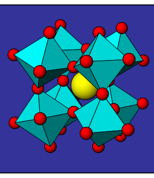


Powder diffraction at a synchrotron source

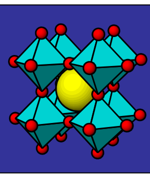


Tilt

paraelectric non-cubic



under pressure →

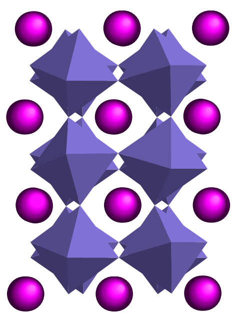


~~Tilt~~

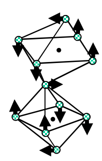
paraelectric <u>cubic</u>

Octahedra tilts in "stable" perovskites

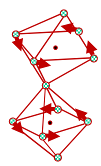
- Orthorhombic space group Pnma (a≠b≠c, α=β=γ=90°)
- Most common structure of perovskites
- Examples:
  → othomanganites ($RMnO_3$)
  → orthoferrites ($RFeO_3$)
  → othoscandates ($RScO_3$)
  → orthochromites ($RCrO_3$)
- Tilt system: $a^-a^-c^+$
  ➔ can be described by <u>two</u> octahedra rotations



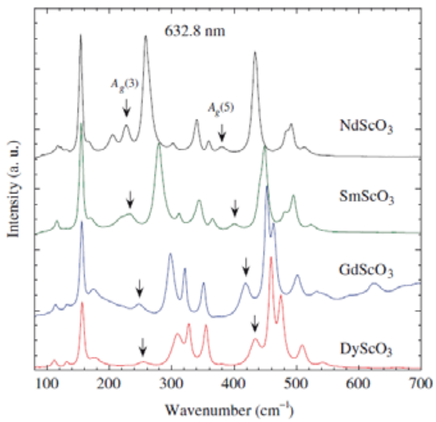
$A_g(5)$ [101] rotation

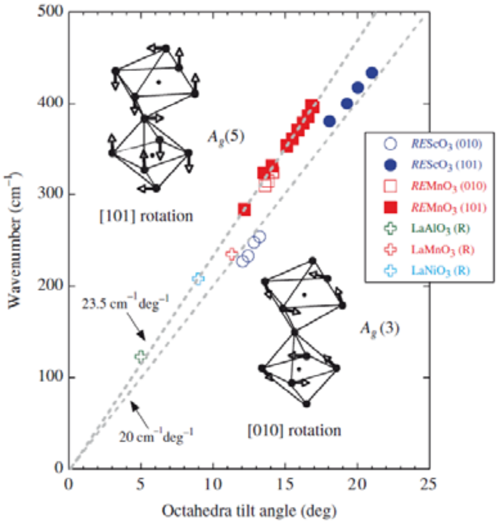


$A_g(3)$ [010] rotation



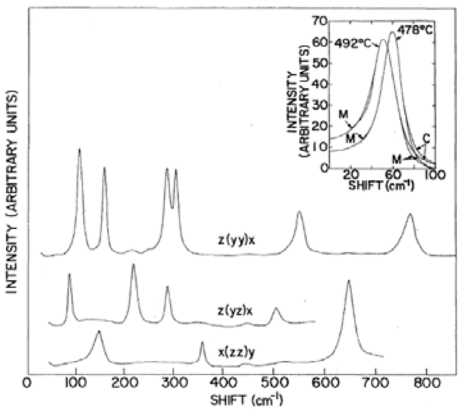
Position of Raman phonons scale with tilting angle

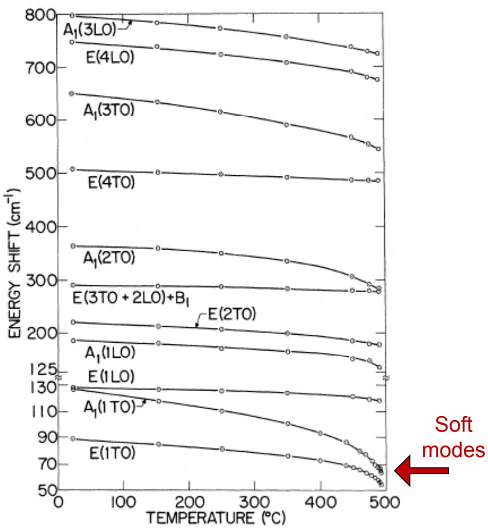




ReMnO3: M. N. Iliev et al., Physical Review B 73, 064302 (2006).
ReScO3: O. Chaix-Pluchery, & J. Kreisel, Phase Transitions 48, 542 (2011).
ReCrO3: M. Weber, J. Kreisel et al., arXiv:1112.3618v1 (2012)

C.2 Cation displacements (ferroelectricity): $BaTiO_3$





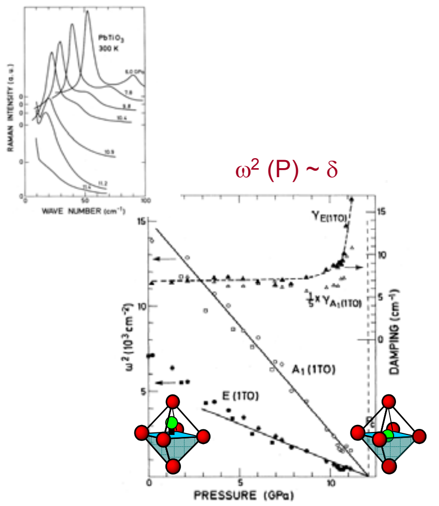
C. H. Perry, and D. B. Hall, Physical Review Letters 15, 700 (1965).

High-pressure studies of $PbTiO_3$

High-Pressure Raman data

J.A. Sanjurjo, E. Lopez-Cruz, G. Burns

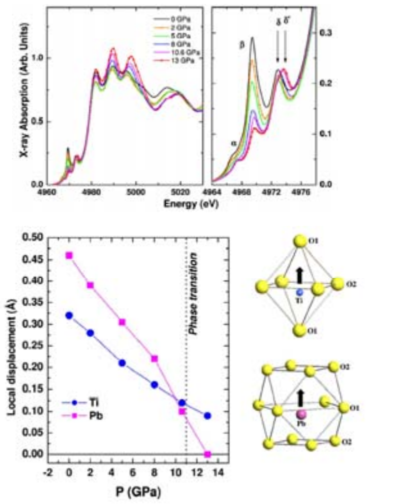
Phys. Rev. B **28**, (1983), p. 7260



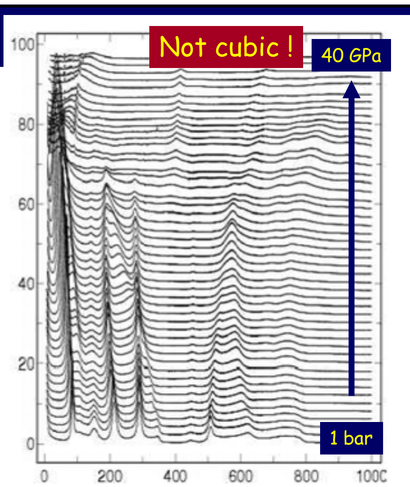
High-pressure X-ray absorption data

N.Jaouen, A.C.Dhaussy, J.P.Itié, A.Rogalev, S.Marinel, Y.Joly

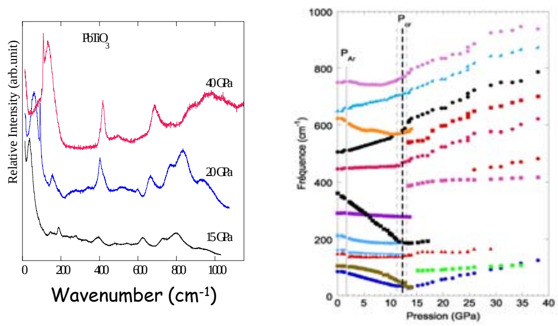
Phys. Rev. B **75** (2007) p. 224115



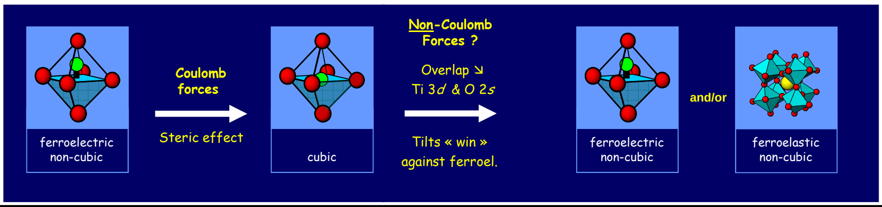
The ferroelectric $PbTiO_3$



P. Bouvier, B. Dkhil, J.Kreisel et al. Phys. Rev. Lett. **95** (2005) & Phys. Rev. Lett. **101** (2008)

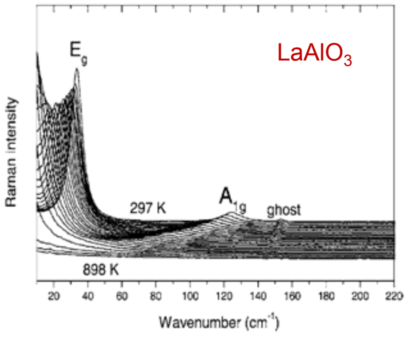


Not cubic at high pressure ! ➔ New mechanisms

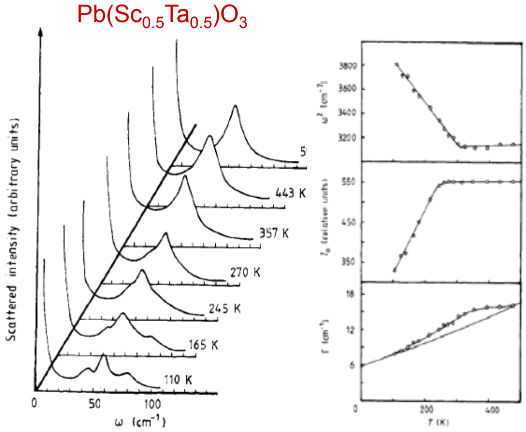


Soft ⇔ Hard mode spectroscopy

S. A. Hayward et al., Physical Review B 72, 054110 (2005).



U. Bismayer, V. Devarajan, and P. Groves, Journal of Physics: Condensed Matter 1, 6977 (1989).



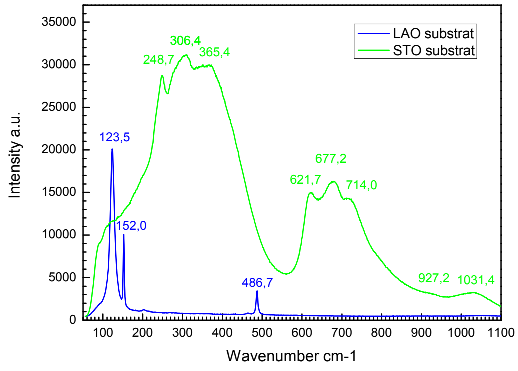
See also:
U. Bismayer, Hard Mode Raman Spectroscopy and Its Application to Ferroelastic and Ferroelectric Transitions, *Phase Transitions* 27 (1990) pp. 211
E. K. H. Salje and U. Bismayer, Hard Mode Spectroscopy: The Concept and Applications, *Phase Transitions* 63 (1997) pp. 1

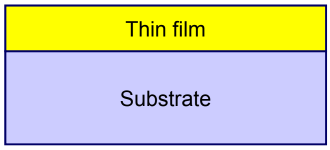
D. Illustrations 3

Raman scattering of multiferroic oxides

1. Thin films & Phase Transitions
2. Hetero-structures
3. Spin phonon-coupling
4. Electromagnons

D.1. Thin films & their substrate …



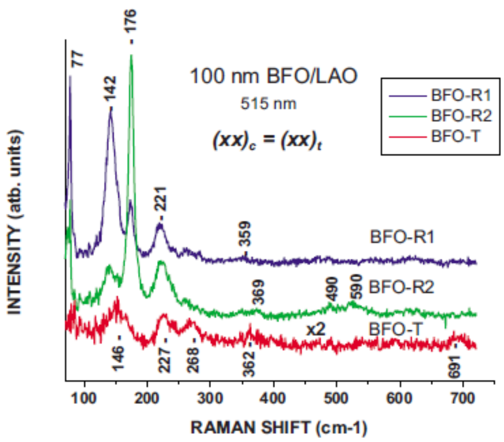


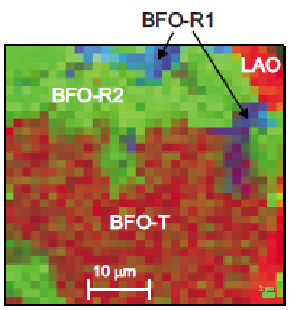
Strongly scattering substrate
➔ a potential problem for investigating very thin films (can be overcome by UV –Raman)

Raman spectra & imaging of inhomogenous films

Example: Highly-strained $BiFeO_3$ films on LAO with phase coexistence

Potential lead-free piezoelectric [J. X. Zhang et al., Nat Nano 6, 98 (2011)]



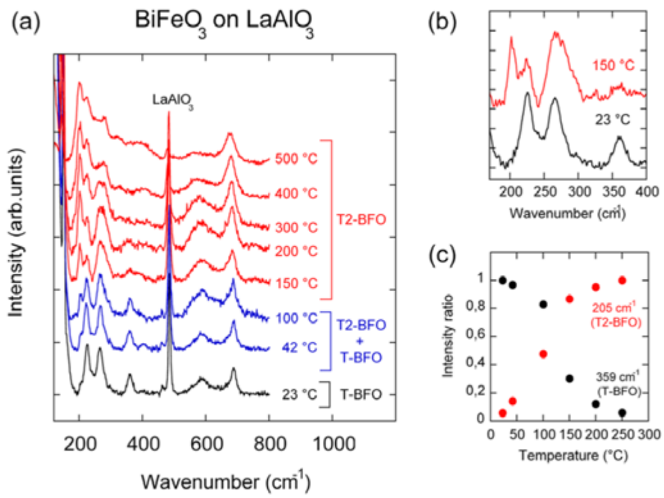


Raman image

M. N. Iliev, M. V. Abrashev, D. Mazumdar, V. Shelke, and A. Gupta, Physical Review B 82, 014107 (2010)

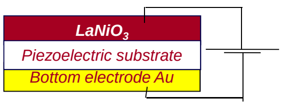
Probing a phase transition in tetragonal-like BFO by Raman scattring

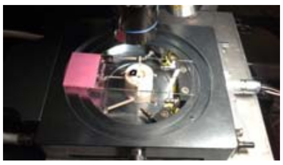
J. Kreisel, P. Jadhav, O. Chaix-Pluchery, M. Varela, N. Dix, F. Sánchez, and J. Fontcuberta, Journal of Physics: Condensed Matter 23, 342202 (2011).



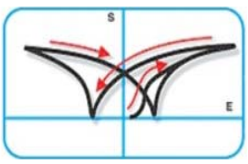
Structural transition close to 300 K in multiferroic $BiFeO_3$ thin films

Following the strain engineering of films on a piezoelectric substrate

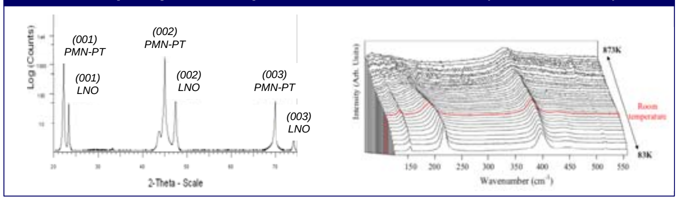




Strain as a fct. of E
(piezo substrate)

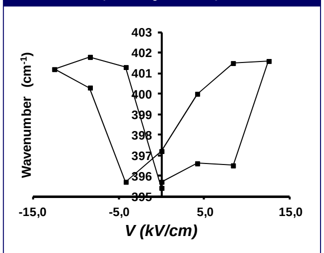


Good quality films on piezoelectric substrate (XRD & Raman)



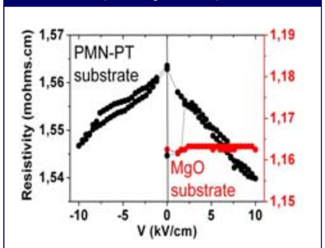
N. Chaban, M. Weber, J. Kreisel, S. Pignard *Appl. Phys. Lett.* **97**, 031915 (2010)

Raman phonon frequency as a fct. of E
($LaNiO_3$ thin film)



Transmission of strain to thin film !

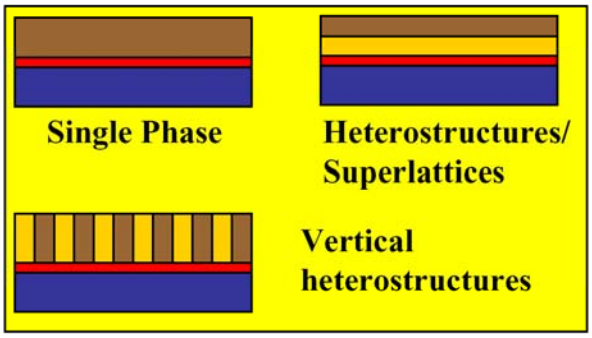
Resistivity as a fct. of E
($LaNiO_3$ thin film)



➔ 2% change in resistivity

N. Chaban, J. Kreisel, S. Pignard, unpublished

D.2 Heterostructures



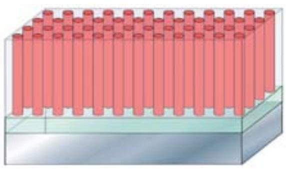
Raman scattering of self-organized Multiferroic Nano-composites

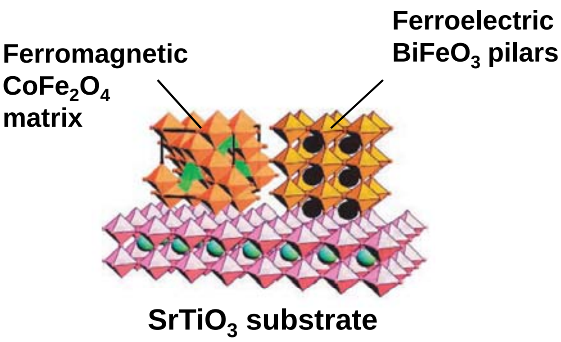
H. Zheng, J. Kreisel, Y.-H. Chu, R. Ramesh, and L. Salamanca-Riba, Appl. Phys. Lett. 90, 113113 (2007).

O. Chaix-Pluchery, C. Cochard, P. Jadhav, J. Kreisel, N. Dix, F. Sánchez, and J. Fontcuberta, Appl. Phys. Lett. 99, 072901 (2011).

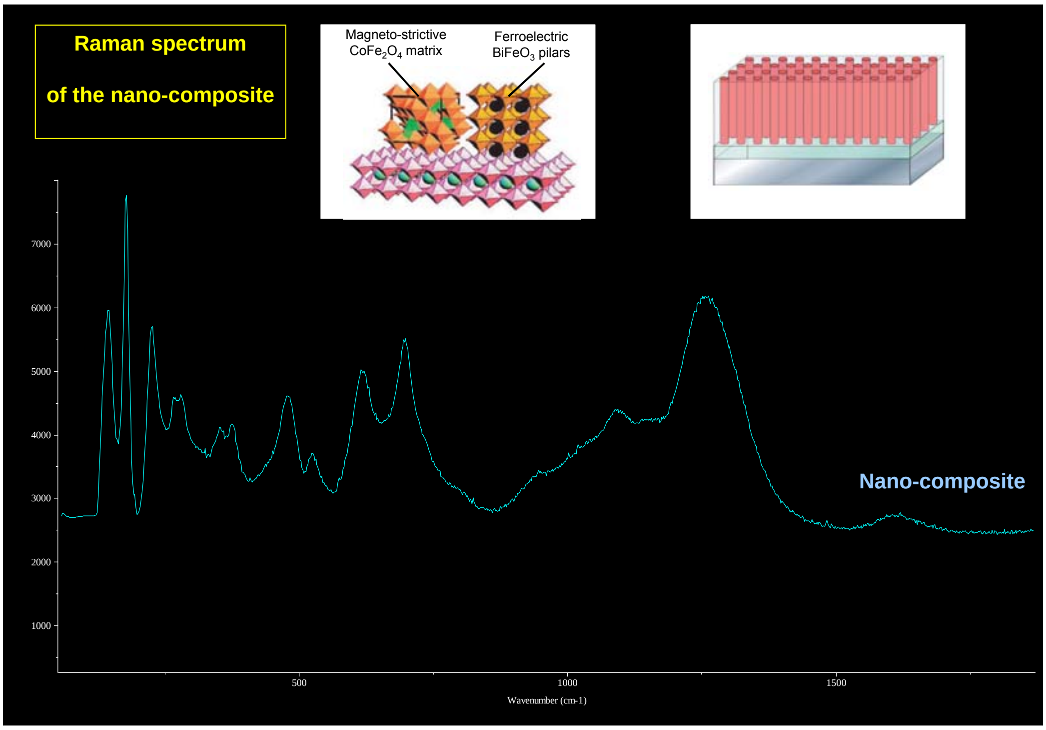
Exploiting strain coupling

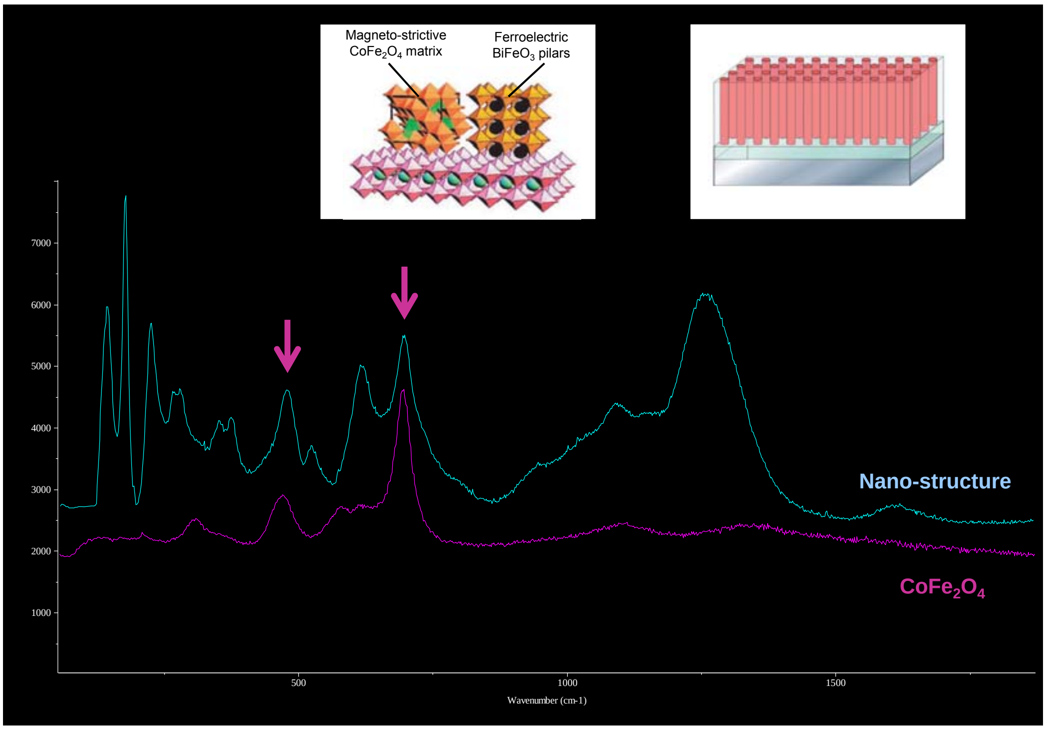
- Magneto-electric memories
- Energy harvesting

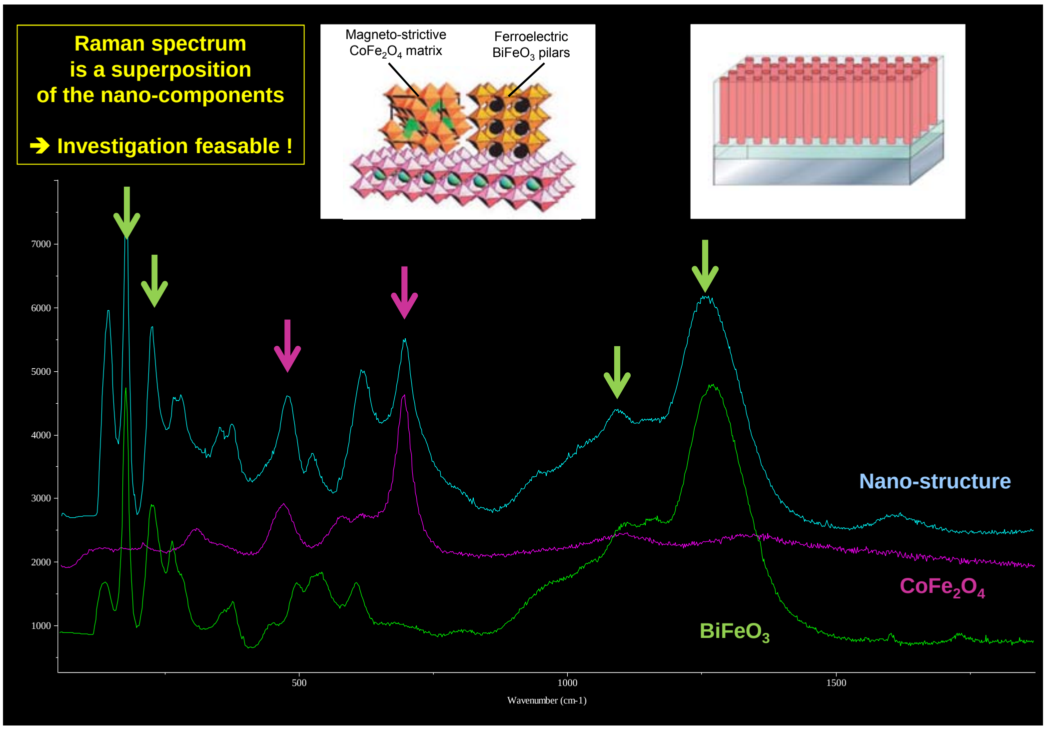




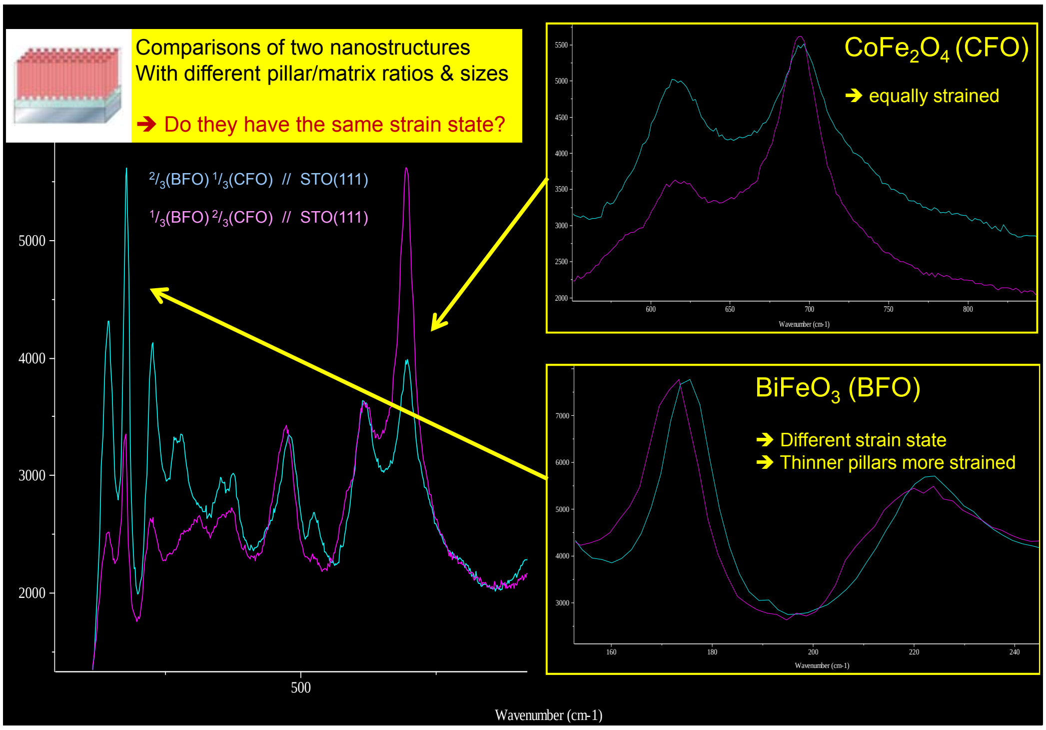
Strain-state and strain-coupling in multiferroic perovskite/spinel nano-composite ?


Raman spectrum
of the nano-composite
Magneto-strictive
$CoFe_2O_4$ matrix
Ferroelectric
$BiFeO_3$ pilars
7000
6000
5000
4000
3000
2000
1000
500
1000
1500
Wavenumber (cm-1)
Nano-composite


Magneto-strictive
$CoFe_2O_4$ matrix
Ferroelectric
$BiFeO_3$ pilars
7000
6000
5000
4000
3000
2000
1000
500
1000
1500
Wavenumber (cm-1)
Nano-structure
$CoFe_2O_4$



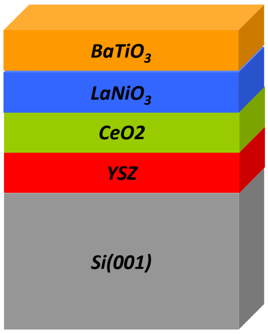
Raman spectrum
is a superposition
of the nano-components
➔ Investigation feasable !
Magneto-strictive
CoFe2O4 matrix
Ferroelectric
BiFeO3 pilars
Nano-structure
CoFe2O4
BiFeO3
Wavenumber (cm-1)

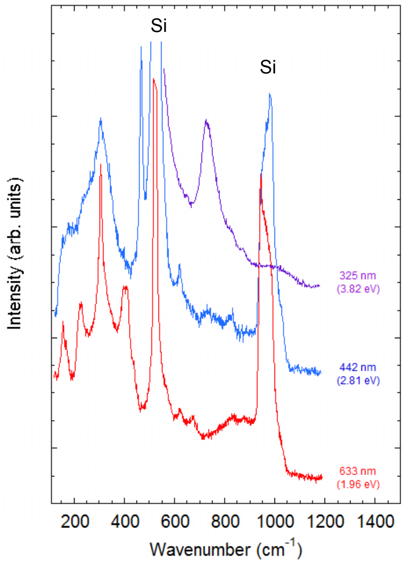


Comparisons of two nanostructures
With different pillar/matrix ratios & sizes
➔ Do they have the same strain state?
2/3(BFO) 1/3(CFO) // STO(111)
1/3(BFO) 2/3(CFO) // STO(111)
CoFe2O4 (CFO)
➔ equally strained
BiFeO3 (BFO)
➔ Different strain state
➔ Thinner pillars more strained
Wavenumber (cm-1)

Raman scattering of complex heterostructures

J. Kreisel, M. Weber, J. Fontcuberta (Barcelona), unpublished



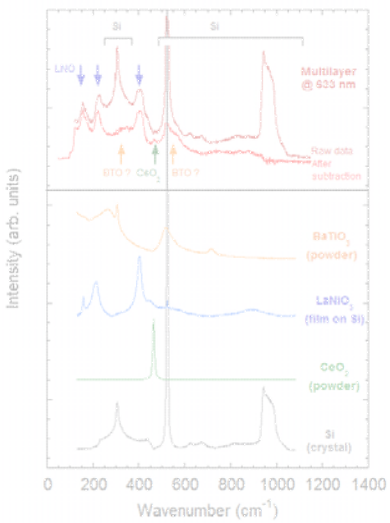


Use of different wavelenghts

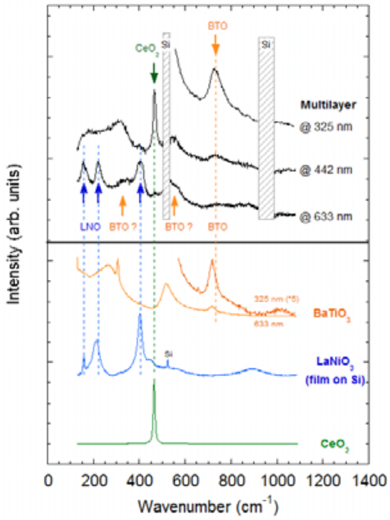
➔ Different optical depths
➔ Different absorption
➔ Different Raman cross sections

Raman scattering of complex heterostructures

Reference spectra & Si-subtraction

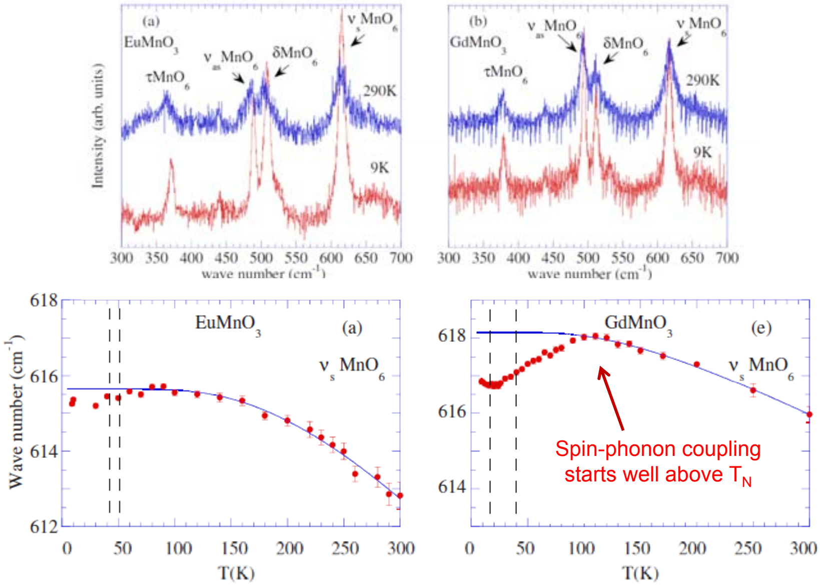


Final mode assignment ➔ Evidence for strain



D.3 Spin-Phonon coupling (always present, but usually small)

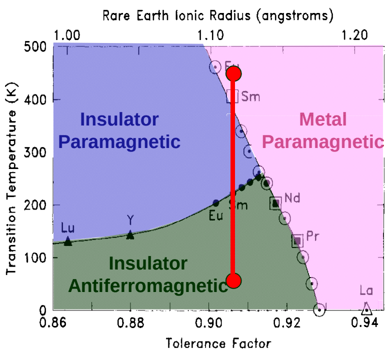
J. A. Moreira, A. Almeida, J. Kreisel et al. *Phys. Rev. B* **79**, 054303 (2009), *Phys. Rev. B* **81**, 054447 (2010), *Phys. Rev. B* **82**, 094418 (2010).



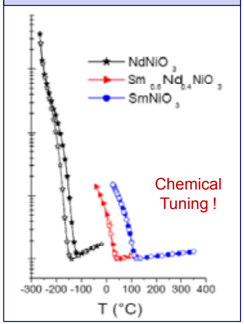
Look at : J. Laverdière, S. Jandl, A. A. Mukhin, V. Y. Ivanov, V. G. Ivanov, and M. N. Iliev, Physical Review B 73 (2006) pp. 214301

Phase transitions in $ReNiO_3$

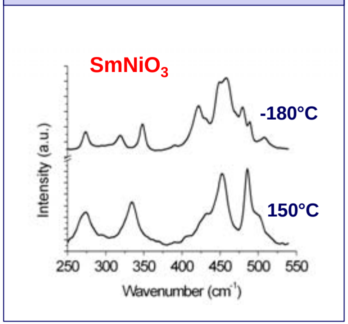
MI & magnetic phase transition ➔ Structural transition ?

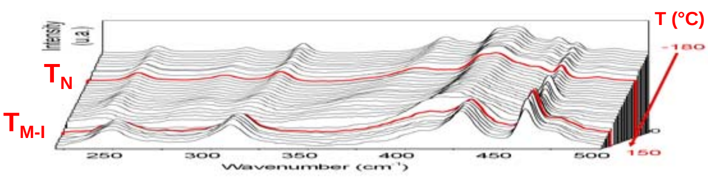


Metal-insulator transitions



Raman scattering





Structural phase trans. @ at T_{MI}

Strong spin-phonon coupling

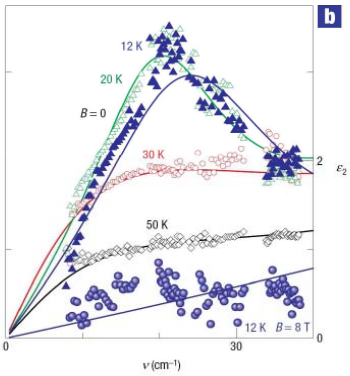
Multiferroic coupling ?

C. Girardot, J. Kreisel, S. Pignard et al. *Phys. Rev. B* **78**, 104101 (2008)

D.4 Electromagnons

Spin waves excited by ac E-fields [Pimenov]

New excitations of mixed magnetic (magnons) and lattice (phonons) character ?



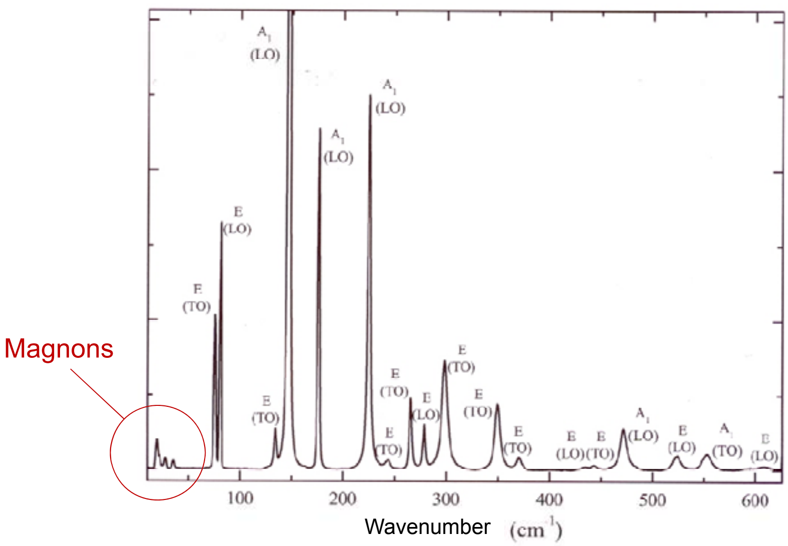
Optical conductivity

New peaks with dipolar activity

Electromagnon

Pimenov et al. Nature Phys 2, 97 (2006)
A. B. Sushkov, PRL 98, 027202 (2007)

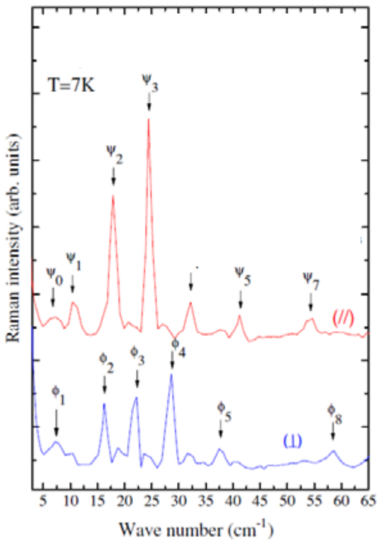
Raman signature of $BiFeO_3$



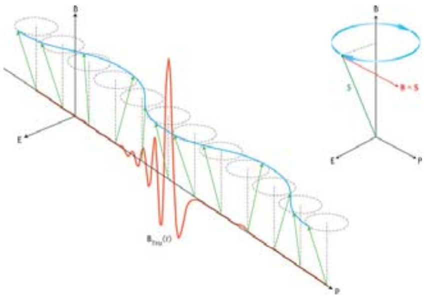
Taken from PhD thesis P. Rovillain, Paris (F)

Beyond phonons ➔ Magnons & Electromagnons

M. Cazayous, et al. Physical Review Letters 101, 037601 (2008).



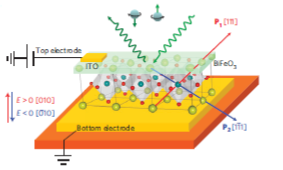
Magnetic excitations (magnons)

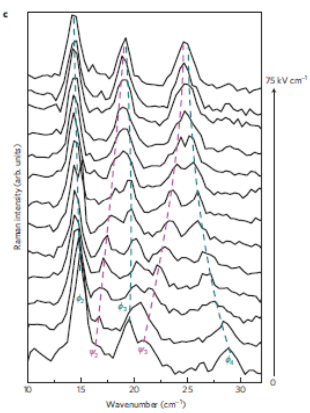


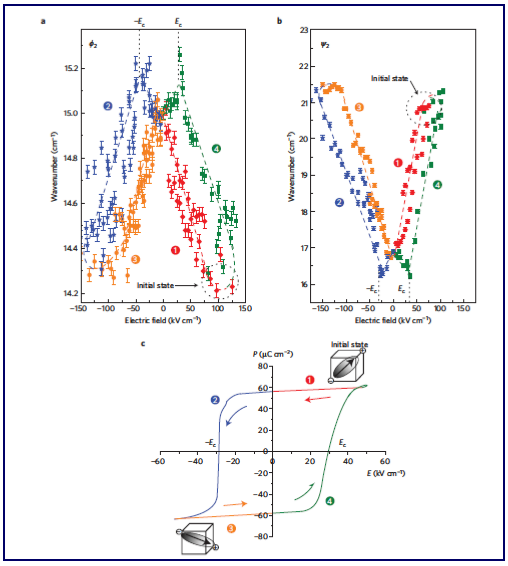
Possible electromagnons ?!

Electric-field control of spin waves in multiferroic $BiFeO_3$

P. Rovillain et al., Nat Mater 9, 975 (2010).



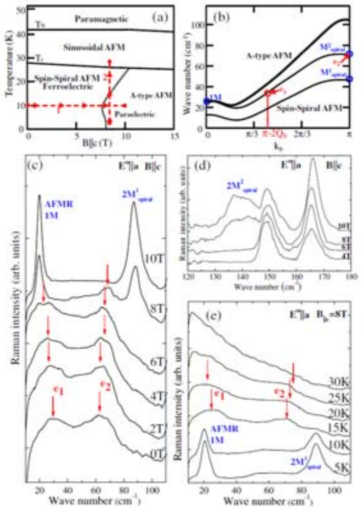


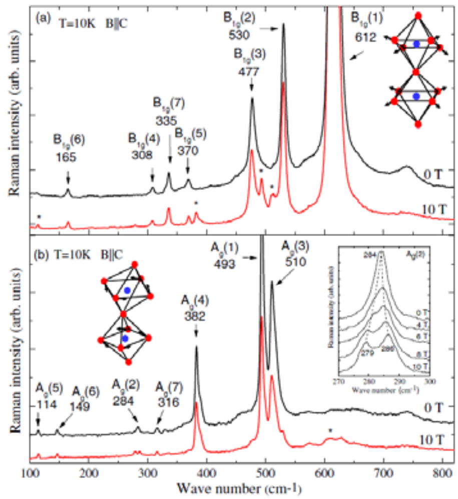


PRL 107, 027202 (2011) PHYSICAL REVIEW LETTERS week ending 8 JULY 2011

Magnetic Field Induced Dehybridization of the Electromagnons in Multiferroic $TbMnO_3$

P. Rovillain,[1] M. Cazayous,[1] Y. Gallais,[1] M-A. Measson,[1] A. Sacuto,[1] H. Sakata,[2] and M. Mochizuki[3]





D.

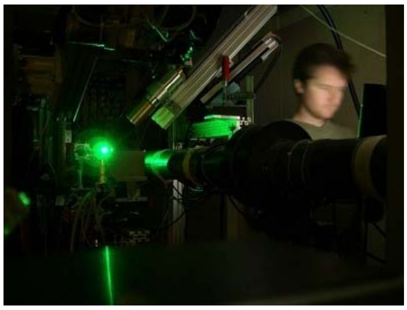
Emerging techniques & fields

Simultaneous use of Raman spectroscopie & synchrotron radiation

Now at almost all synchrotrons sources

3 beamlines @ ESRF

+ mobile spectrometers



See proceedings of the 2008 & 2011 international workshops:

" Workshop on Simultaneous studies of Raman spectroscopy with Syncrotron X-ray Absorption, Scattering and Diffraction "

Emerging 1 … Imaging & Enhancing the Raman signal

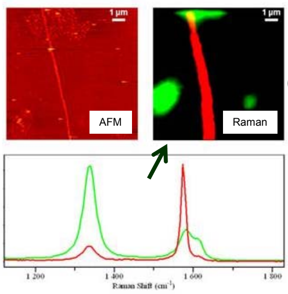
2 emerging techniques with sub-μ resolution

Coupled Raman-AFM

Co-localisation
&
analysis of sub-μ objects

Tip-enhanced Raman scattering (TERS)

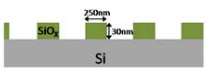
NanoRaman:
Spatial resolution <100nm
(mechanism not yet understood)

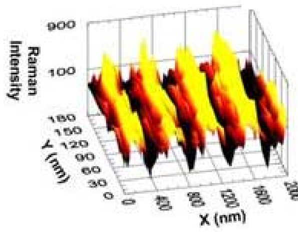


Carbon nanotubes (AFM & Raman imaging)

Raman spectra of different regions

TERS Imaging of Nano-structured Silicon





SiO$_x$ on a Si substrate imaged by TERS

Emerging 2 … Raman scattering of biological & pharmaceutical samples

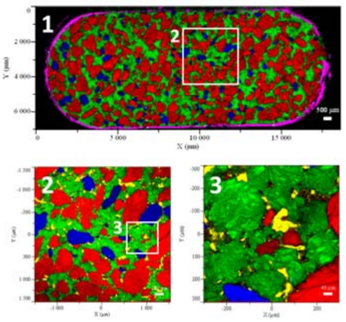
Raman Spectroscopy, the Sleeping Giant in Structural Biology, Awakes*

Paul R. Carey‡

From the Department of Biochemistry, Case Western Reserve University, Cleveland, Ohio 44106

Example 1

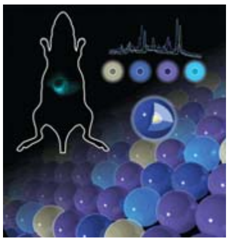
Raman image of whole pharmaceutical tablet
48,081 spectra ➔ 8m:55s total acquisition

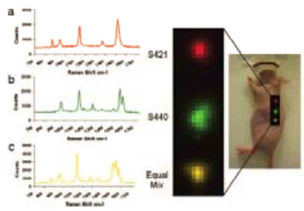


Noninvasive molecular imaging of small living subjects using Raman spectroscopy

S. Keren, C. Zavaleta, Z. Cheng, A. de la Zerda, O. Gheysens, and S. S. Gambhir*

Molecular Imaging Program at Stanford, Departments of Radiology and Bioengineering, Bio-X Program, Stanford University, 1201 Welch Road, Stanford, CA 94305-5484





S. Keren et al. PNAS 2008,

Concluding remarks …

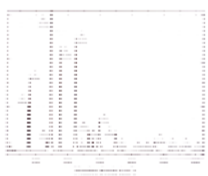
Raman spectroscopy …

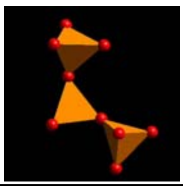
… is a versatile technique for the study of various materials

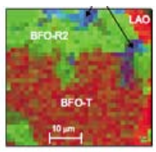
… is versatile for characterization *and* fundamental research

… complimentary to other techniques (diffraction etc.)

… versatile for investigating phase transitions and coupling mechanism







Raman image