Vibrational spectroscopies

With a shameless and outrageous bias towards Raman

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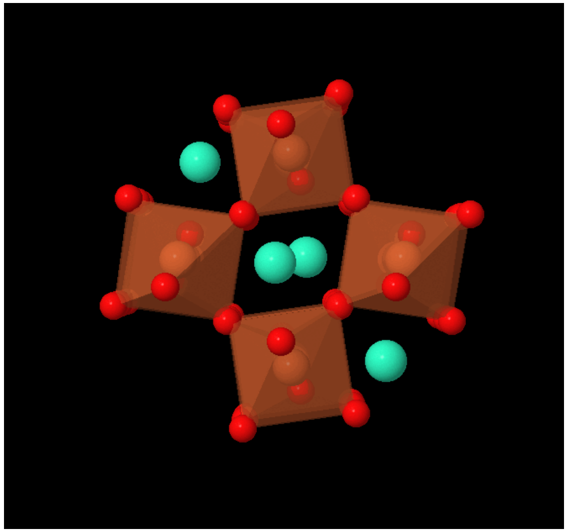
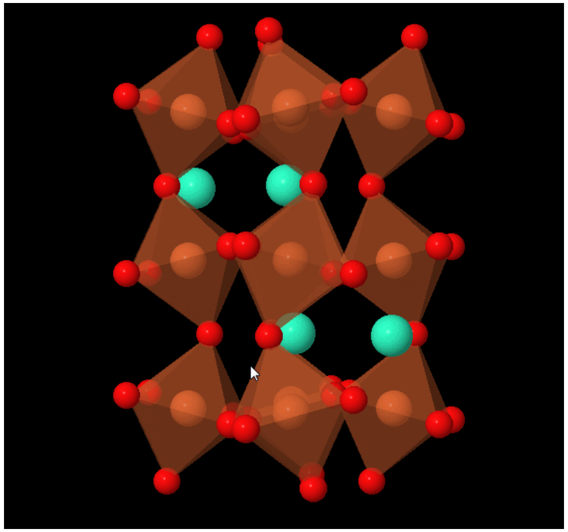
Outline

- General principles
- The soft-mode story I: ferroelectric and antiferroelectric soft mode
- The soft-mode story II: tilt modes
- Thin and ultrathin films

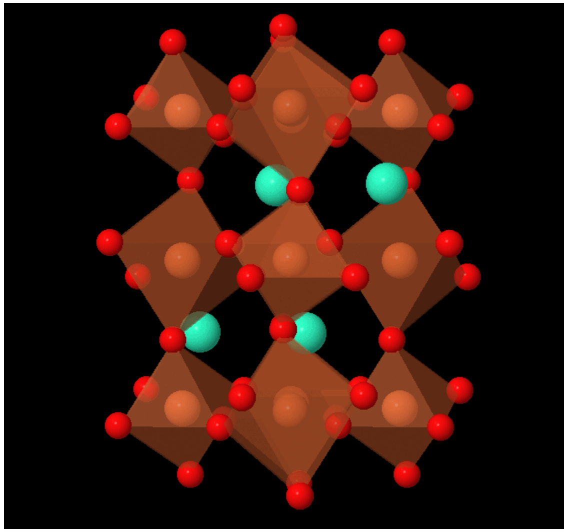
General principles



In-phase tilts



Out-of-phase tilts



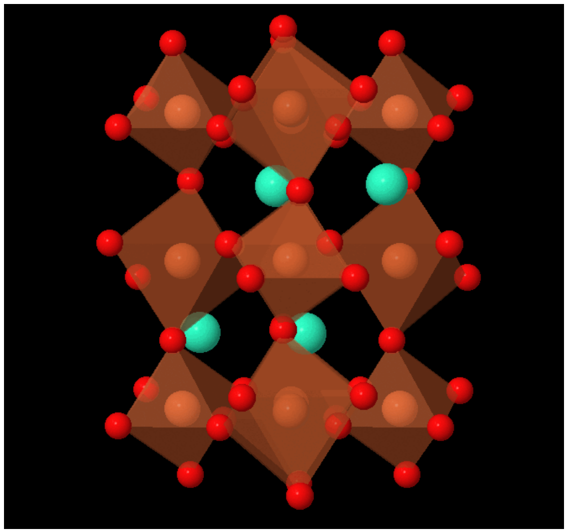
Stretching

$$\omega = \sqrt{\frac{K}{M}}$$

→ Direct access to the relevant force constants

Calculations for $TbFeO_3$ by Hongjian Zhao & Jorge Iniguez.

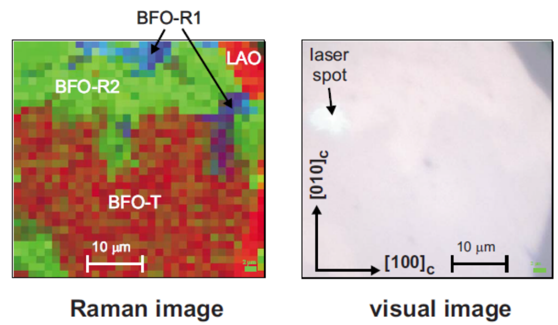
General principles

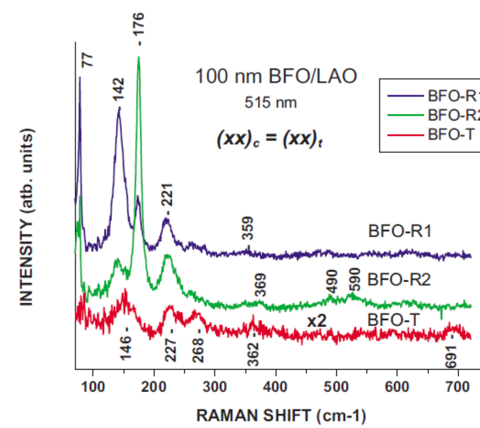


Vibrational spectroscopy

Vibration frequencies are a unique fingerprint

for a given material, at given external conditions

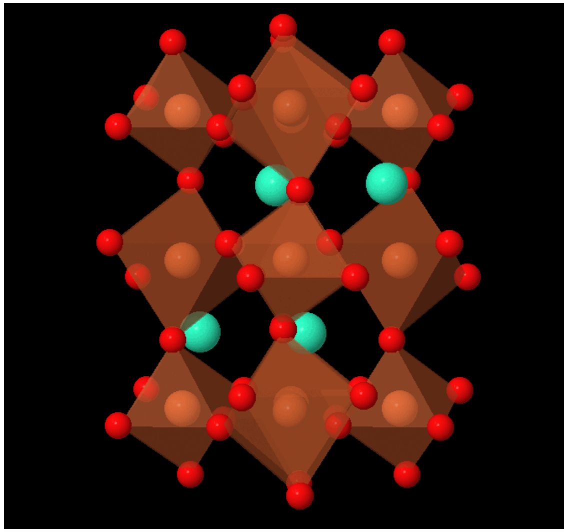




The fingerprint approach

- Quality control for sample processing
- Identification of phases specific chemical bonds (C-C, C=C…)
- Locate phase transitions
- In-situ chemical reaction / crystallisation

General principles



Vibrational spectroscopy

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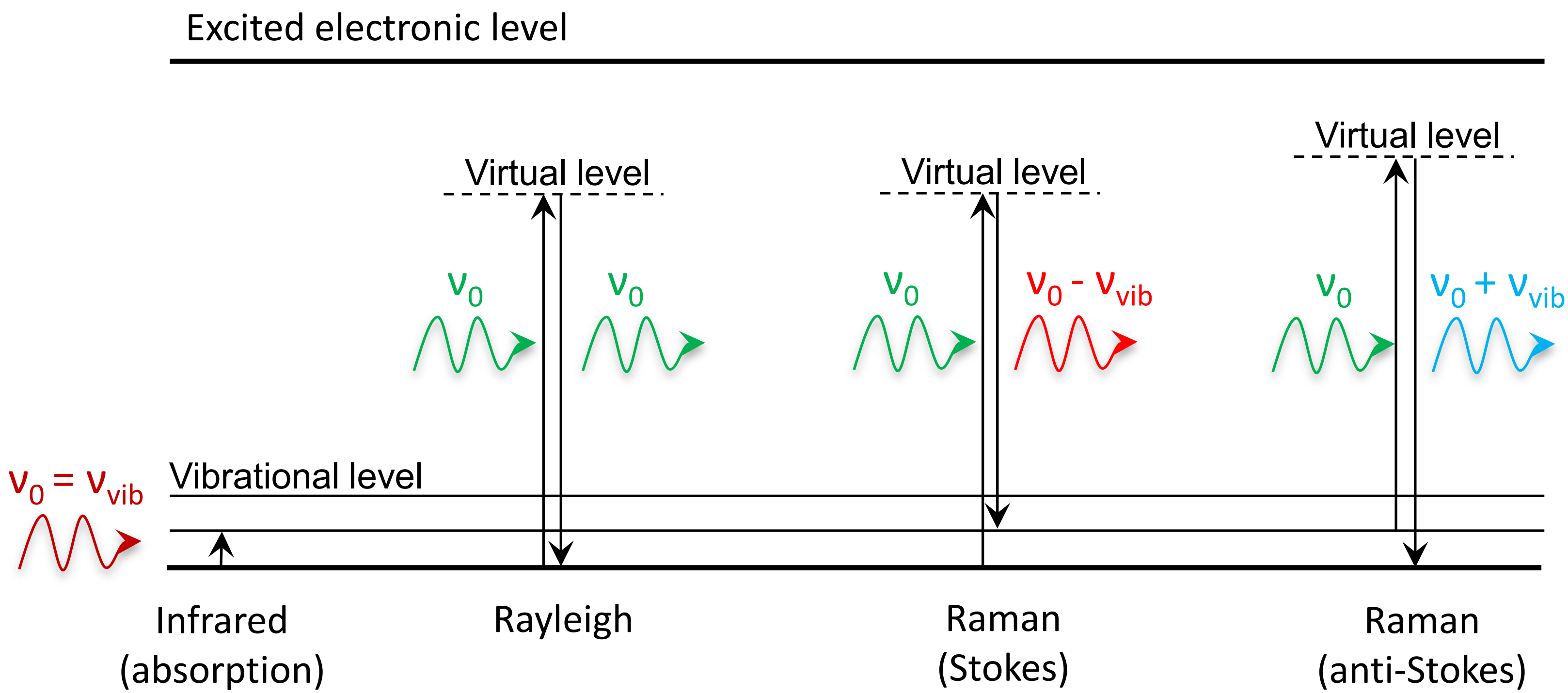
The in-depth approach

- Spectra fitting
- Interpretation of the Raman shifts, widths etc.
- Identification of atomic displacements patterns
- Comparison with calculations
- Relation to other physical properties
- Strain effects, coupling to magnetism…

General principles

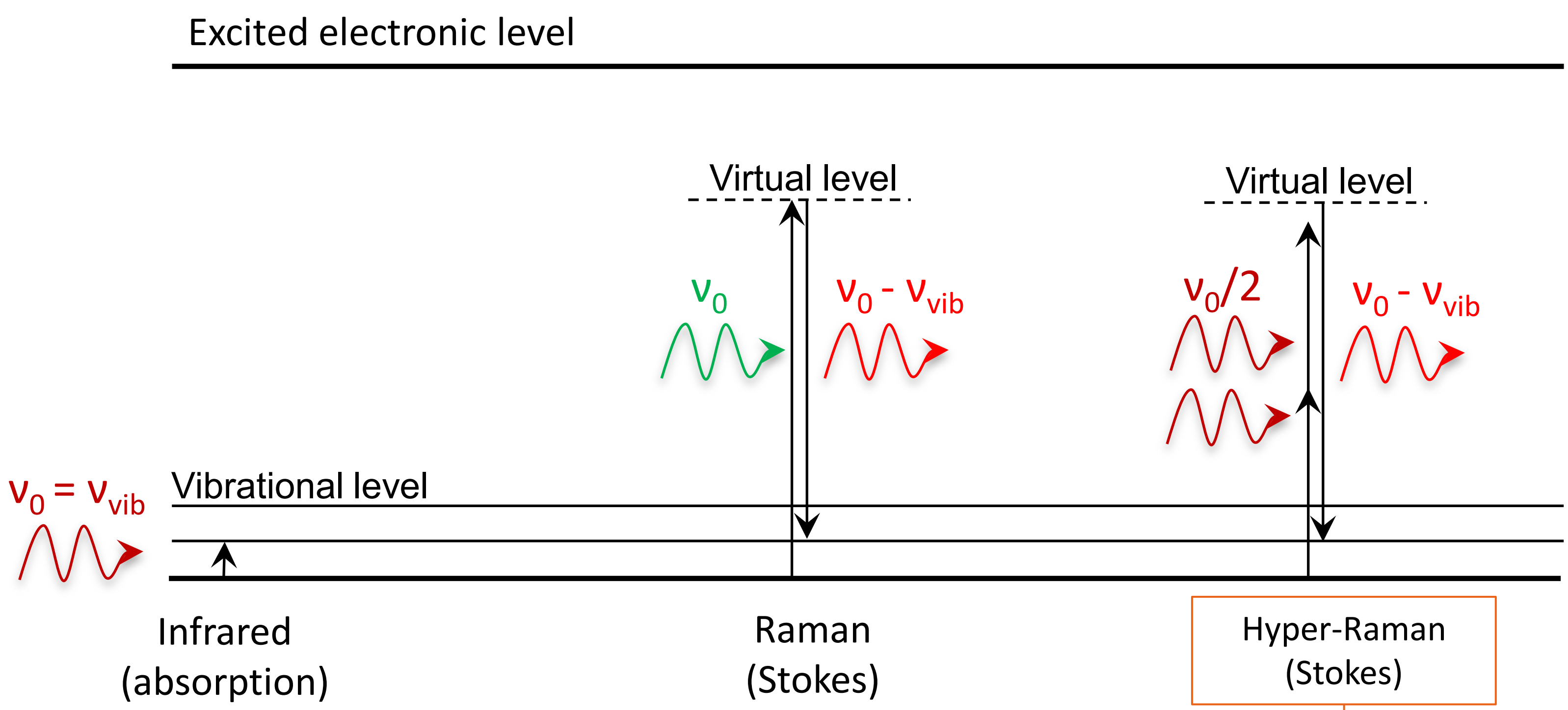


$\Delta E_{rot} << \Delta E_{vib} << h\nu_0 << \Delta E_{elec}$

The unit of « spectroscopists », the wavenumber (cm^{-1}): $\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$

Other common units:
- 1 meV = 8 cm^{-1}
- 1 THz = 33 cm^{-1}

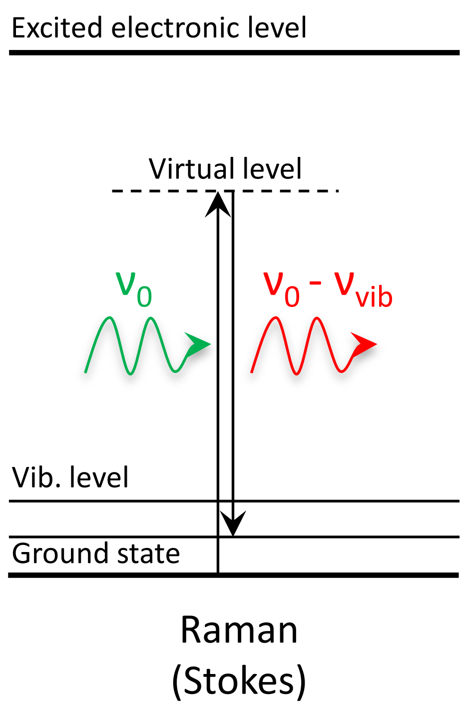
General principles



More permissive selection rules:

- All IR active modes are Hyper-Raman active
- Non IR/Raman active modes can be Hyper-Raman active

General principles



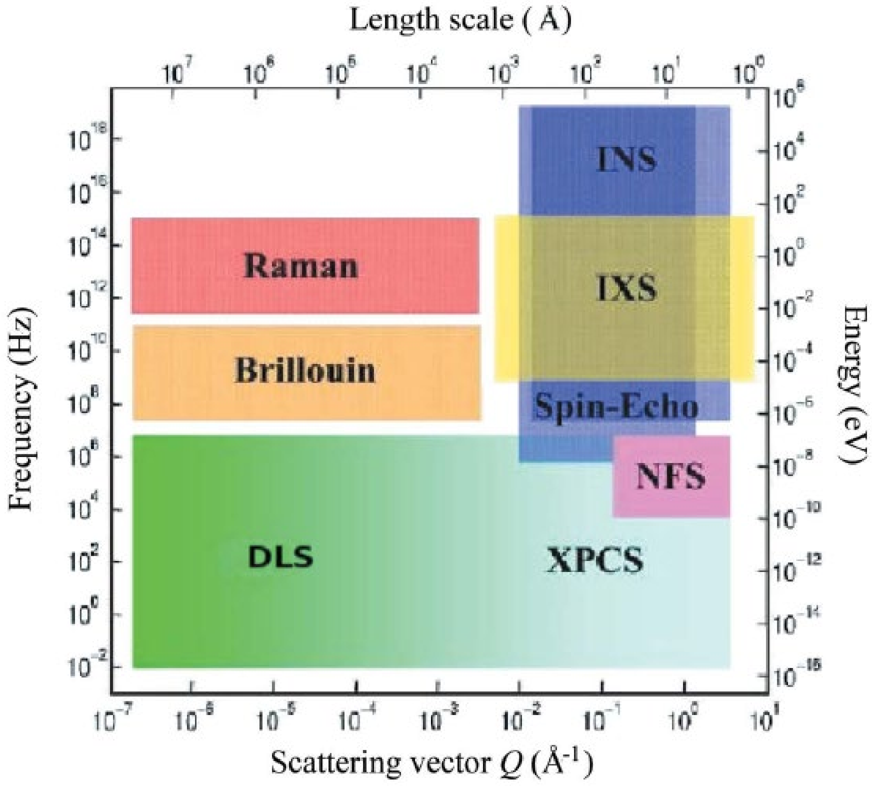
Conservation of energy: $\nu_{vib} = \nu_0 - \nu_{scattered}$

Conservation of momentum: $p_{vib} = p_0 - p_{scattered}$

- Momentum of a phonon mode: $0 \leq p_{\text{phonon}} \leq h/a$
- Momentum of light $p_{\text{light}} = \hbar k = h/\lambda$

Only phonons at the Γ point (long wavelength) participate in the Raman scattering and IR absorption process.

General principles



DLS: Dynamic light scattering

INS: Inelastic neutron scattering

IXS: Inelastic X-ray scattering

NFS: Nuclear forward scattering

XPCS: X-ray Photon Correlation Spectroscopy

Grübel & Zontone, Journal of Alloys and Compounds **362**, 3–11 (2004)

General principles

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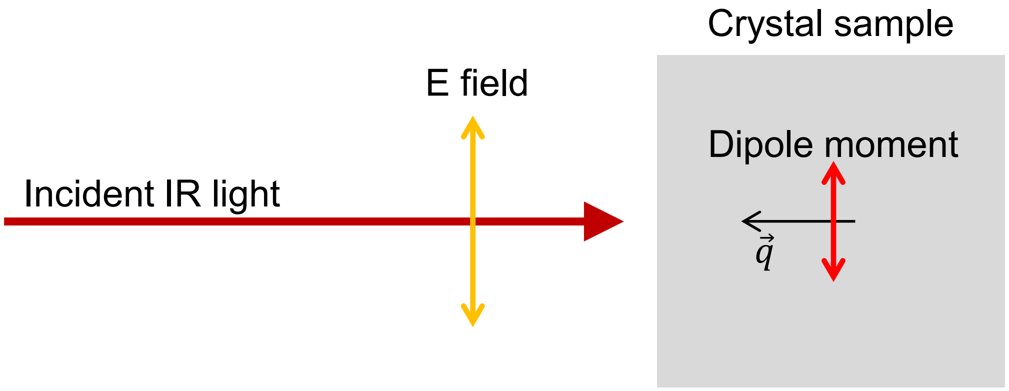
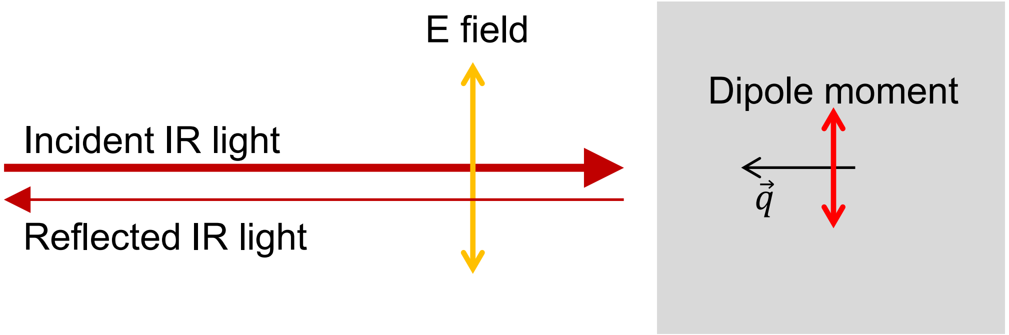


Absorption measurement

Sensitive to TO modes only

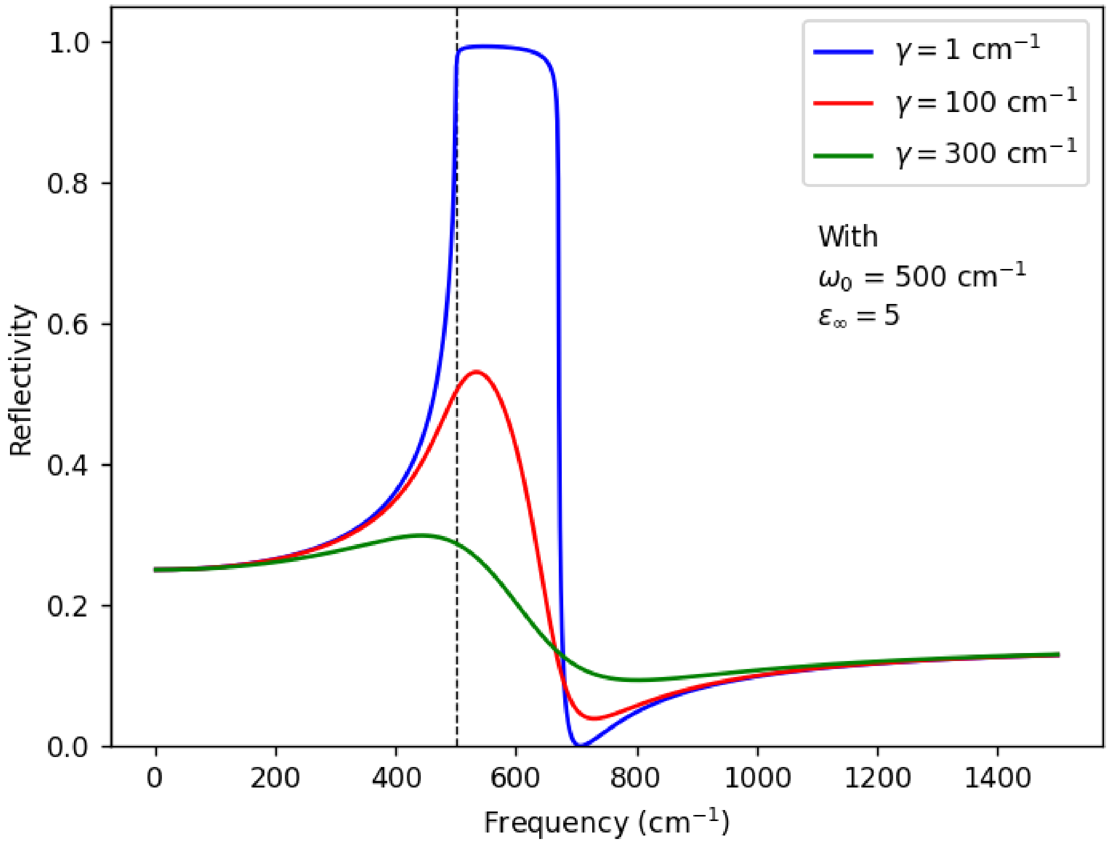


Reflectivity measurement
Sensitive to TO+LO modes
Requires fitting

- Polar mode frequencies and damping
- Complex dielectric response

Experimental techniques

Signature of a damped harmonic oscillator in a FTIR reflectivity spectrum

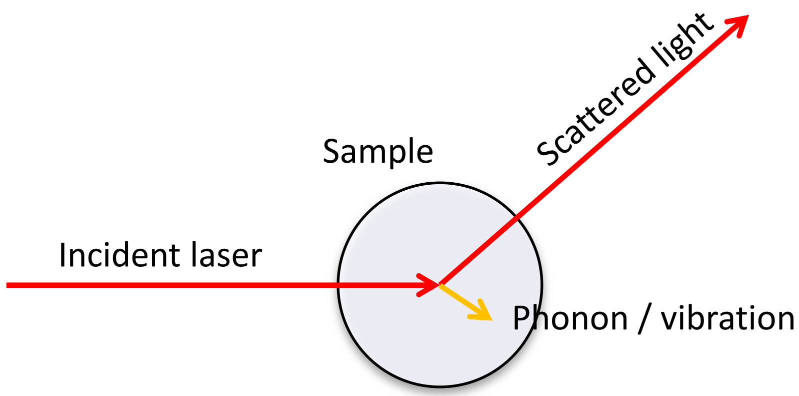


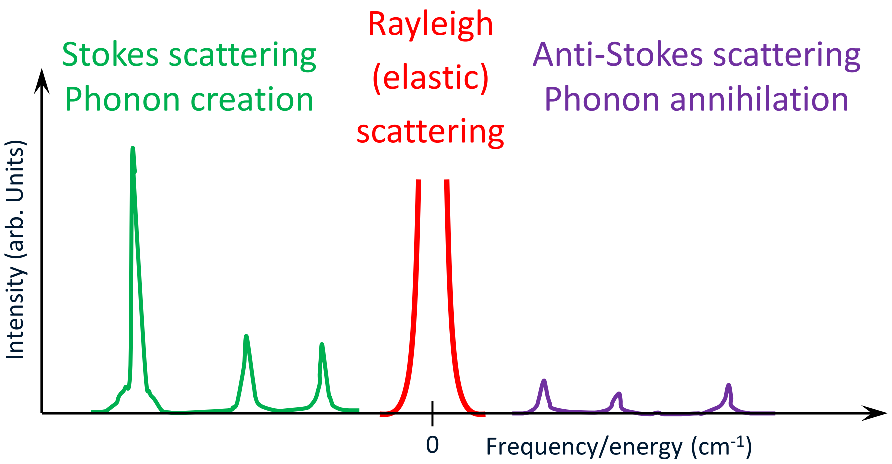
Reflectivity at normal incidence:

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

The complex response function is obtained by fitting R(ω).

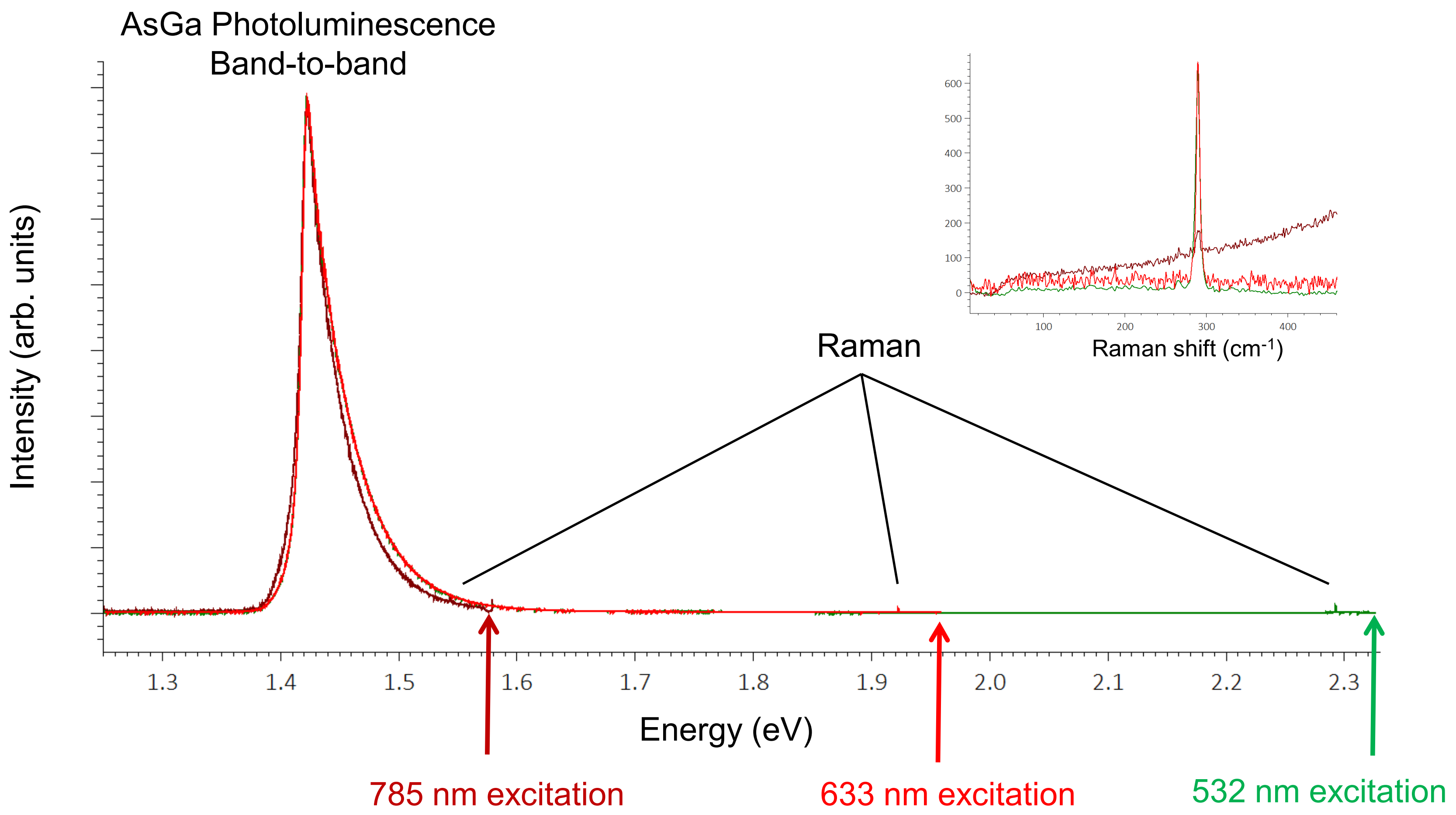
General principles





General principles

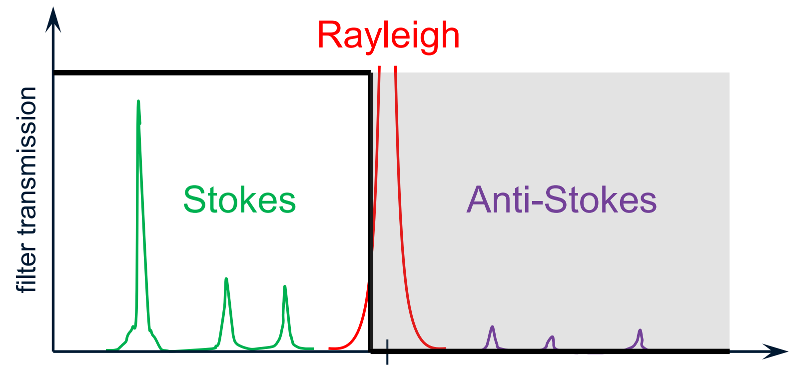
The Raman signal is small!



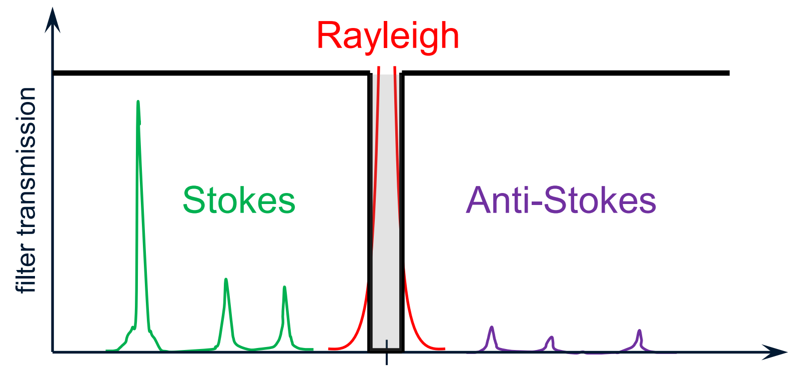
General principles

With rejection filters

- Edge filters → down to 50 cm^{-1}

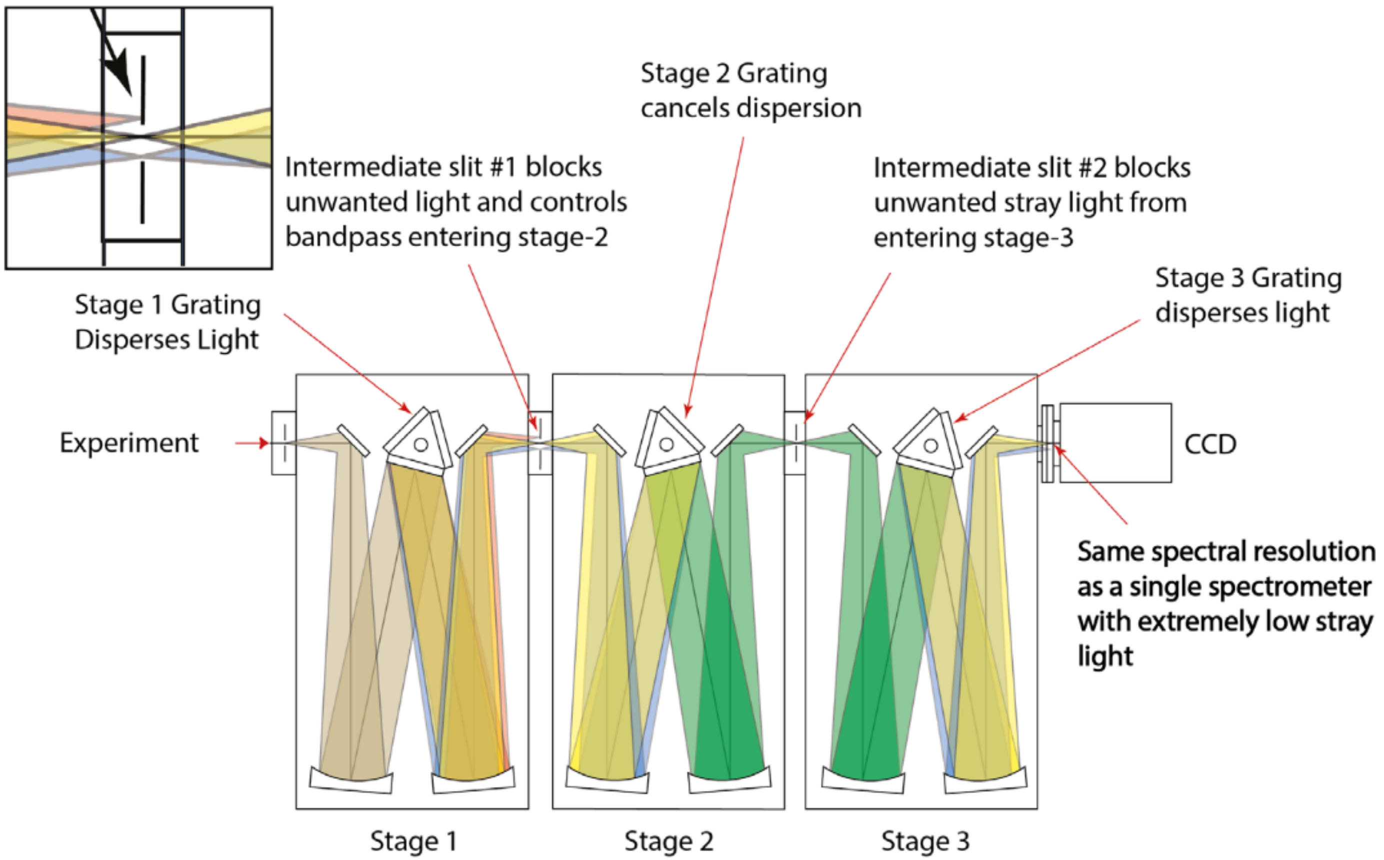


- Notch filters / Bragg filters → down to 10 cm^{-1}



General principles

With multiple gratings



General principles

A vibration mode is **infrared active** if it modulates the dipole moment of the molecule (resp. polarization of the crystal).

$$\left.\frac{\partial P}{\partial Q}\right|_0 \neq 0$$

⇕

A vibration is **infrared active** if it transforms like a polarization vector, i.e. if its symmetry is that an irrep associated to a basis function x, y or z.

A vibration mode is **Raman active** if it modulates the polarizability of the molecule (resp. crystal).

$$\left.\frac{\partial \alpha}{\partial Q}\right|_0 \neq 0$$

⇕

A vibration is **Raman-active** if it transforms like a second-rank tensor, i.e. if its symmetry is that of an irrep associated to a basis function xy, xz, yz, x^2, y^2 or z^2.

(Q = normal mode coordinate)

General principles

A given mode may be
- Raman and IR active
- Raman active only
- IR active only
- « Silent »

→ Raman and infrared activity can be predicted from group theory

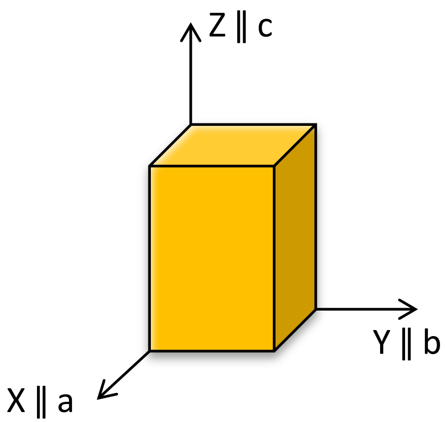
Some symmetry rules:

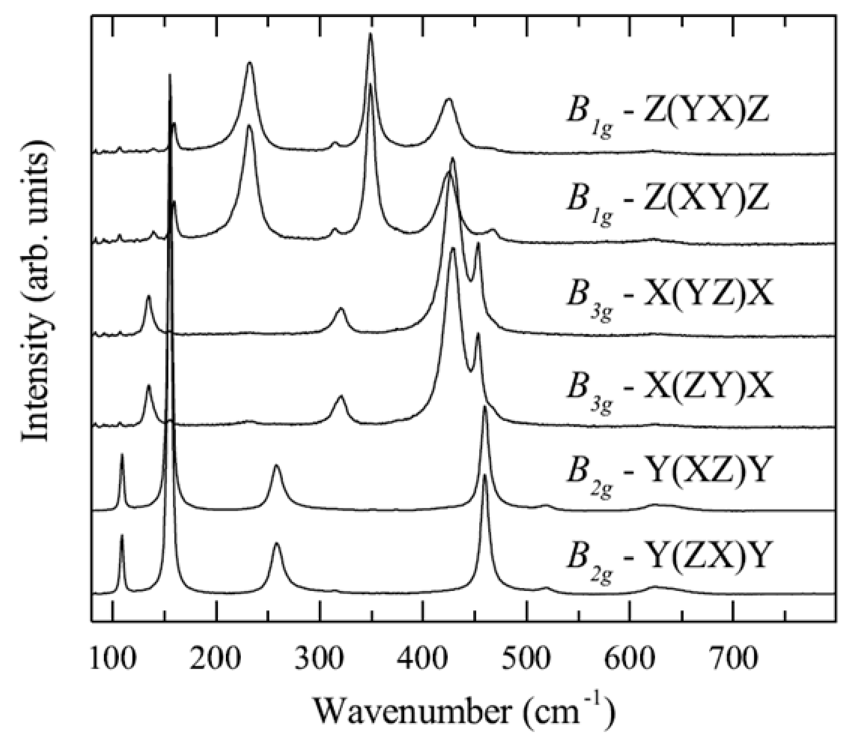
- A fully symmetric vibration is always Raman active
- A vibration breaking inversion symmetry is always Raman inactive and infrared active.
- In a centro-symmetric molecule or crystal none of the Raman active modes is IR-active and vice versa.
- In our ferroelectric materials, most modes are Raman active.

General principles

Example of $SmFeO_3$
(orthorhombic Pnma)

24 Raman active phonons = $7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}$



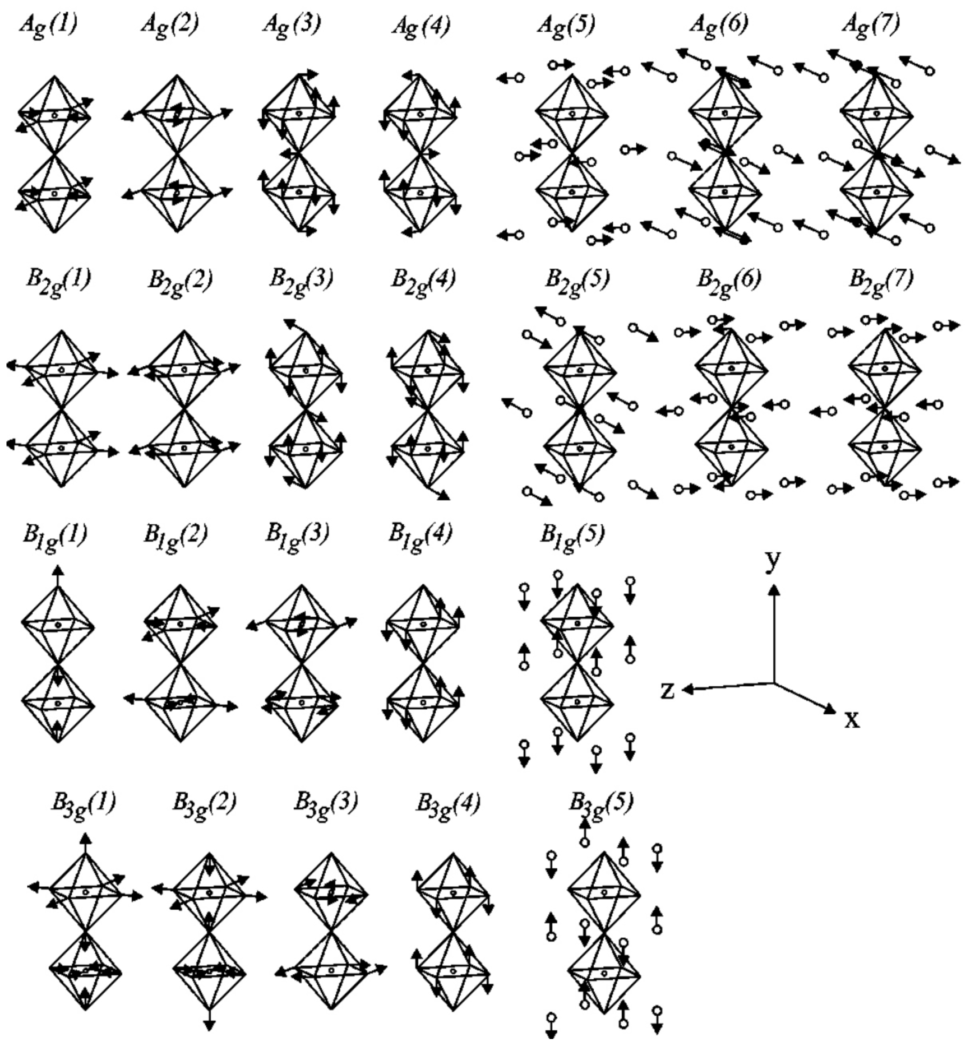


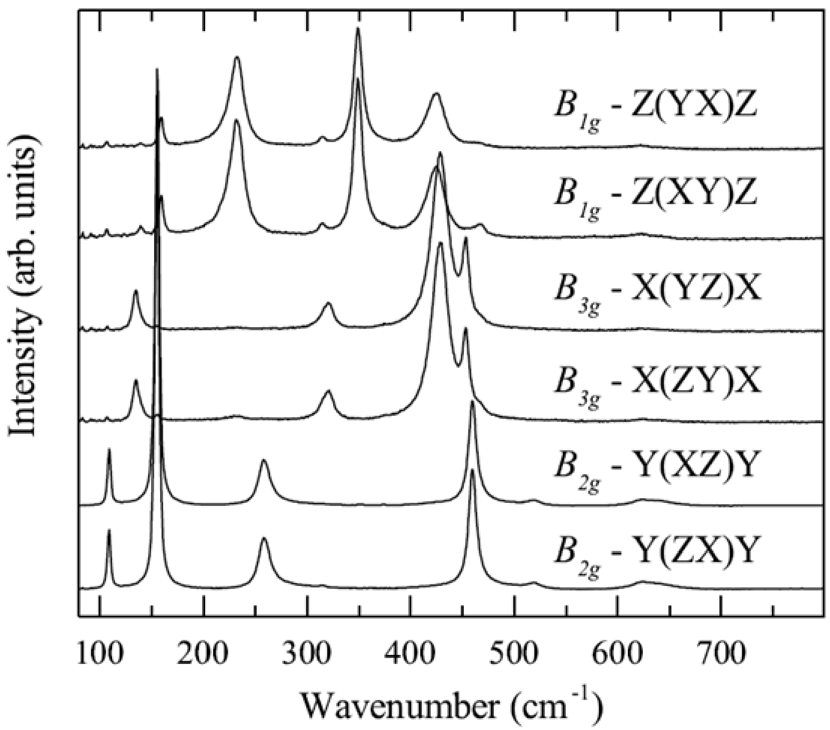
$$\begin{bmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$
B_{1g}

$$\begin{bmatrix} 0 & 0 & e \\ 0 & 0 & 0 \\ e & 0 & 0 \end{bmatrix}$$
B_{2g}

$$\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & f \\ 0 & f & 0 \end{bmatrix}$$
B_{3g}

General principles



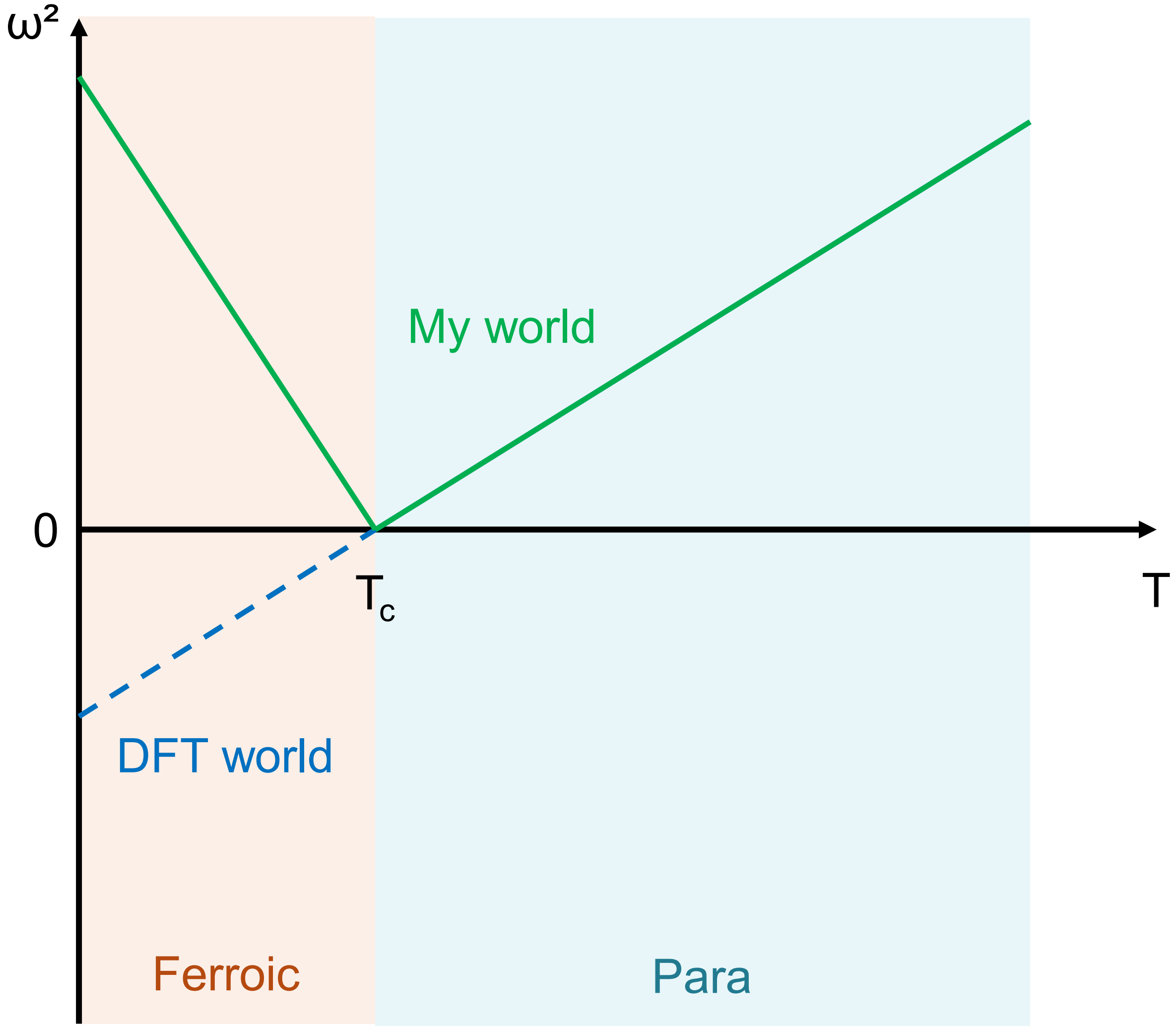


M. V. Abrashev et al., Phys. Rev. B 65, 184301 (2002)

The (experimental) soft mode story I

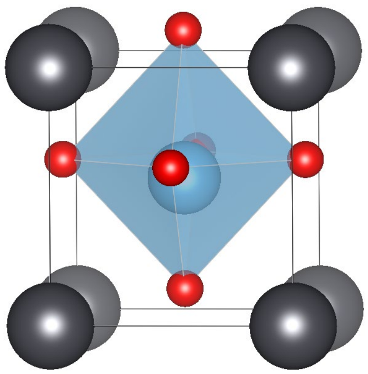
Imaginary frequencies really?

The soft mode story

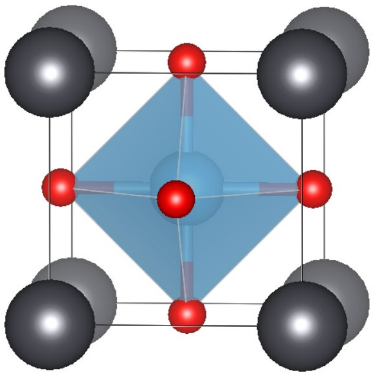


The soft mode story: $PbTiO_3$

Typical example: **$PbTiO_3$**



T_c = 760 K



Ferroelectric phase
P4mm

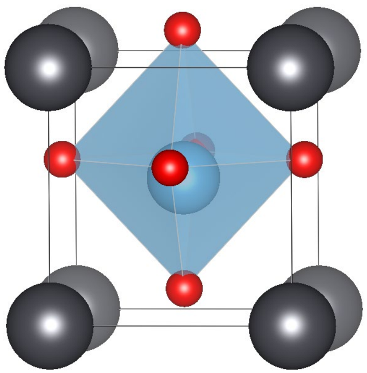
Paraelectric phase
Pm-3m

Phonon modes:

$3(A_1 + E) + (B_1 + E)$ ← $3T_{1u} + T_{2u}$

The soft mode story: $PbTiO_3$

Typical example: **$PbTiO_3$**



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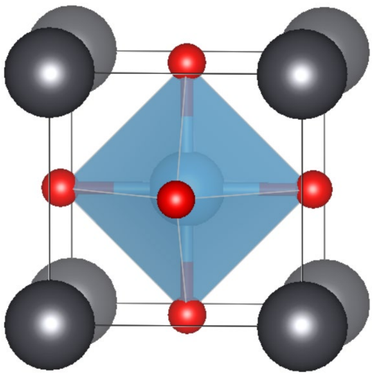
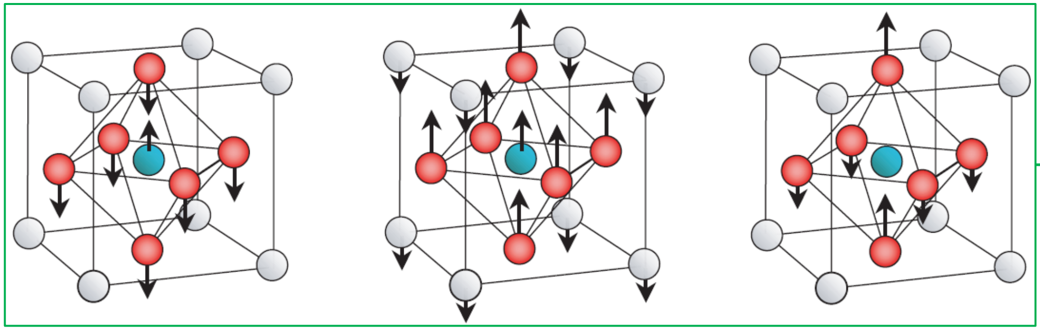


Ferroelectric phase
P4mm

Paraelectric phase
Pm-3m



$3T_{1u}$ + T_{2u}

The soft mode story: $PbTiO_3$

Measuring the phonon modes in $PbTiO_3$

m-3m	4m.m
A_{1g}	**A_1**
A_{1u}	A_2
A_{2g}	B_1
A_{2u}	B_2
E_g	**A_1** + B_1
E_u	$A_2 + B_2$
T_{1g}	A_2 + **E**
T_{1u}	**A_1** + **E**
T_{2g}	B_2 + **E**
T_{2u}	B_1 + **E**

bold IR Active Modes

Raman Active Modes

Hyper-Raman Active Modes

Raman and Hyper-Raman Active Modes

	Below T_c	Above T_c
Infrared	OK	OK-ish
Raman	OK	KO
Hyper-Raman	KO	OK

The soft mode story: $PbTiO_3$

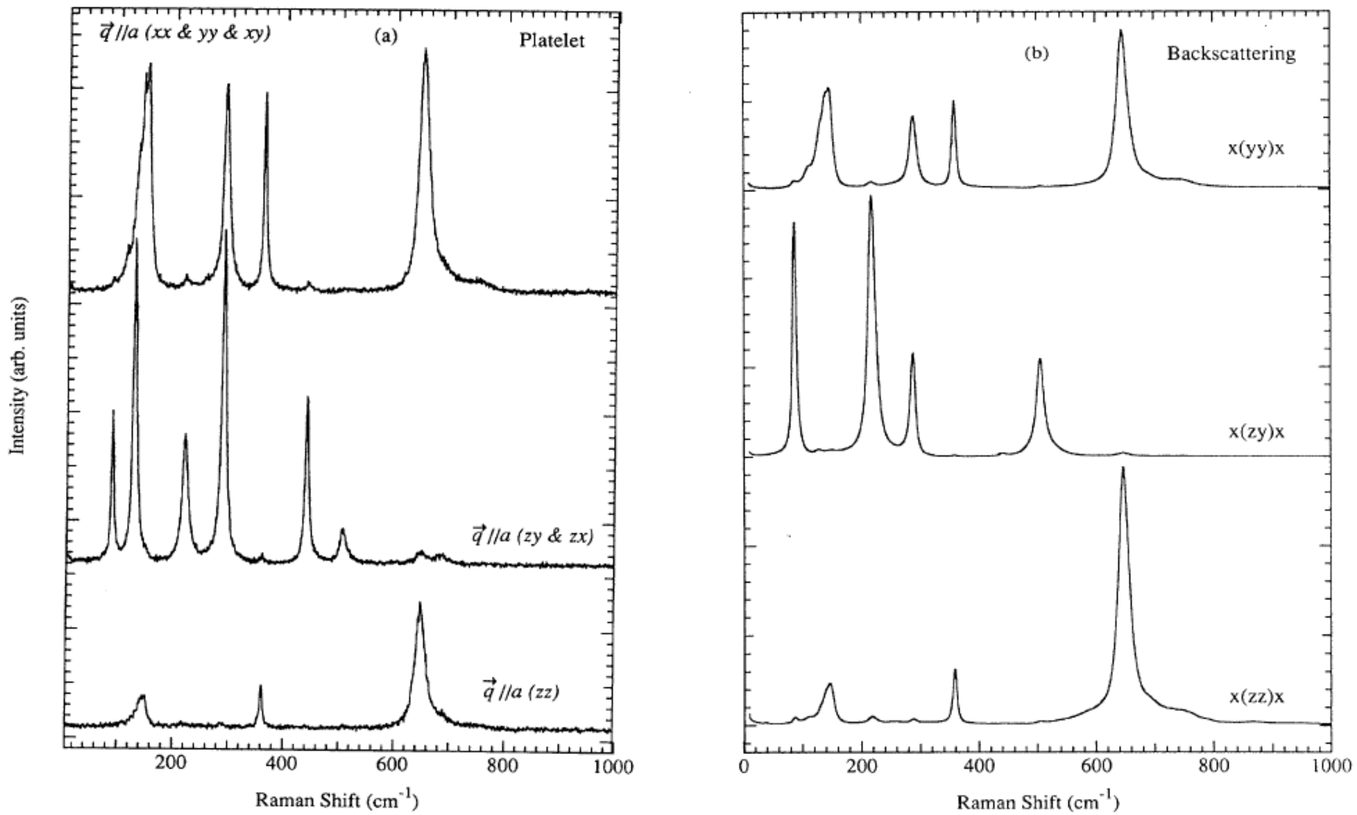
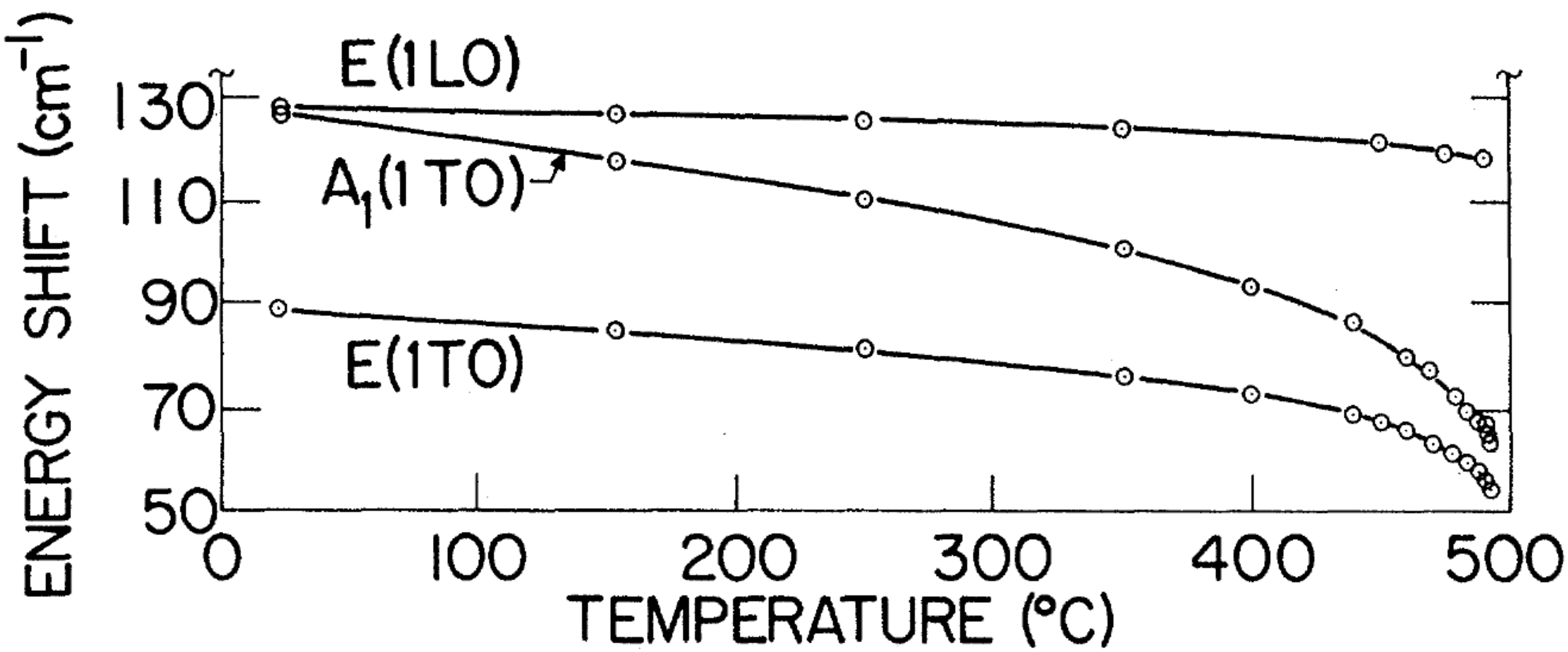


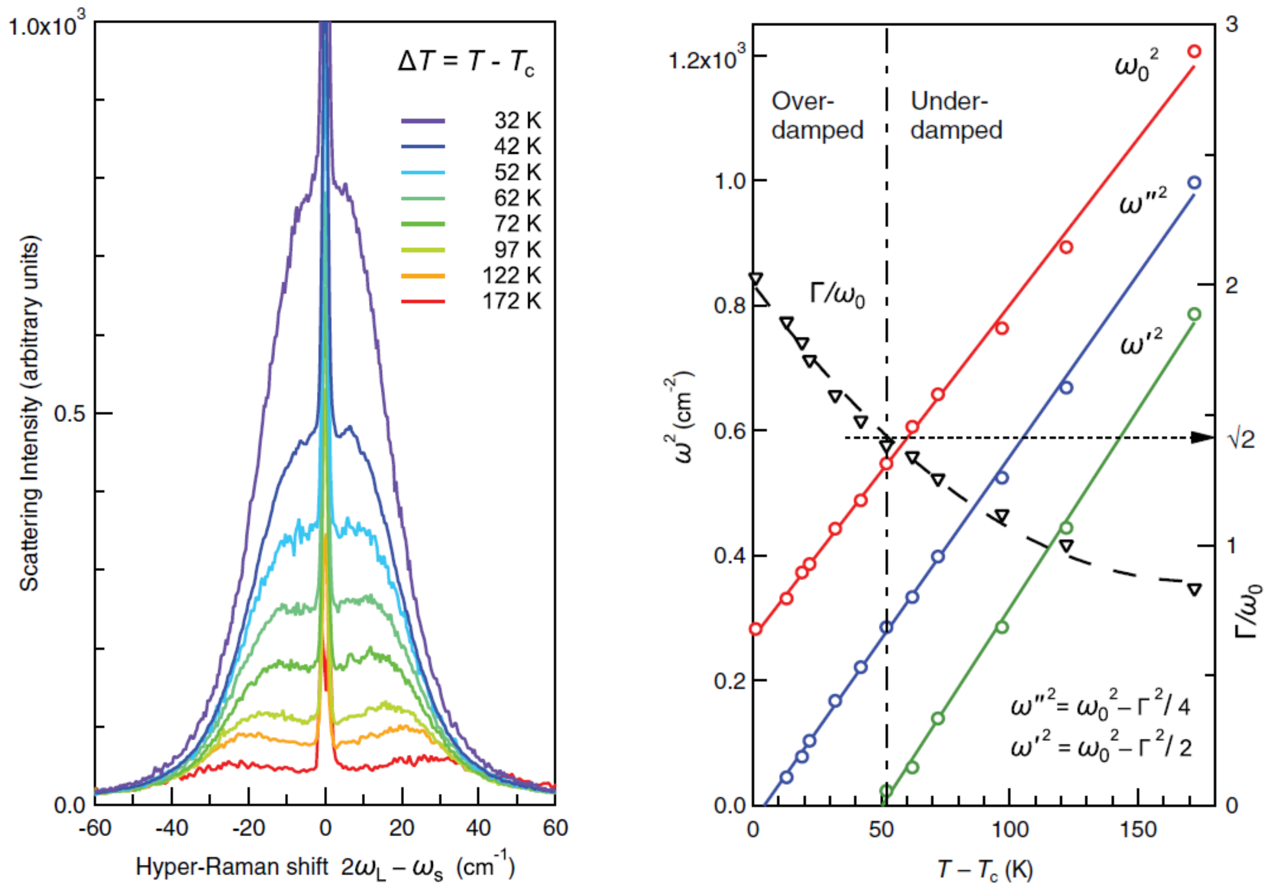
FIG. 1. Polarized Raman spectra of single-domain single-crystal $PbTiO_3$ at 300 K in (a) platelet and (b) 180° backscattering. The Raman selection rules are strictly obeyed. The bottom curves show the three A_1(TO) phonons. The middle curves show the four E(TO) modes, and the platelet $\mathbf{q}\|\mathbf{x}$ $(zx)+(zy)$ polarization curve also shows the four E(LO) modes. The top curve shows the B_1-symmetry component of the silent phonon in addition to the three A_1(TO) phonons.

The soft mode story: $PbTiO_3$



D. Burns and J. Scott, Phys. Rev. Lett. 25, 167 (1970)

The soft mode story: $PbTiO_3$



J. Hlinka, B. Hehlen, A. Kania and I. Gregora, Phys. Rev. B 87, 064101 (2013)

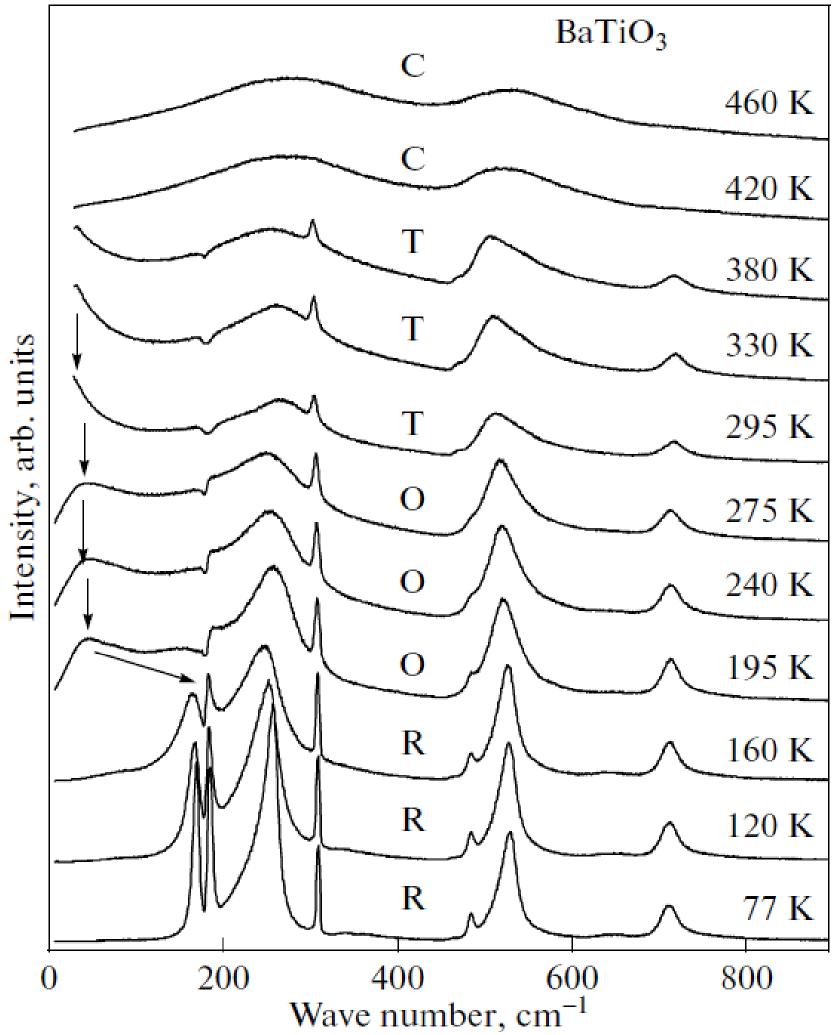
The soft mode story: $BaTiO_3$

$BaTiO_3$

- Cubic-tetragonal transition
- Symmetry identical to $PbTiO_3$

- Non-standard peak shapes
- Coupling mechanisms
- Spectrum does not vanish at T_c

$BaTiO_3$ ceramics



Yuzyuk, Phys. Solid state 54, 1026 (2012)

The soft mode story: $BaTiO_3$

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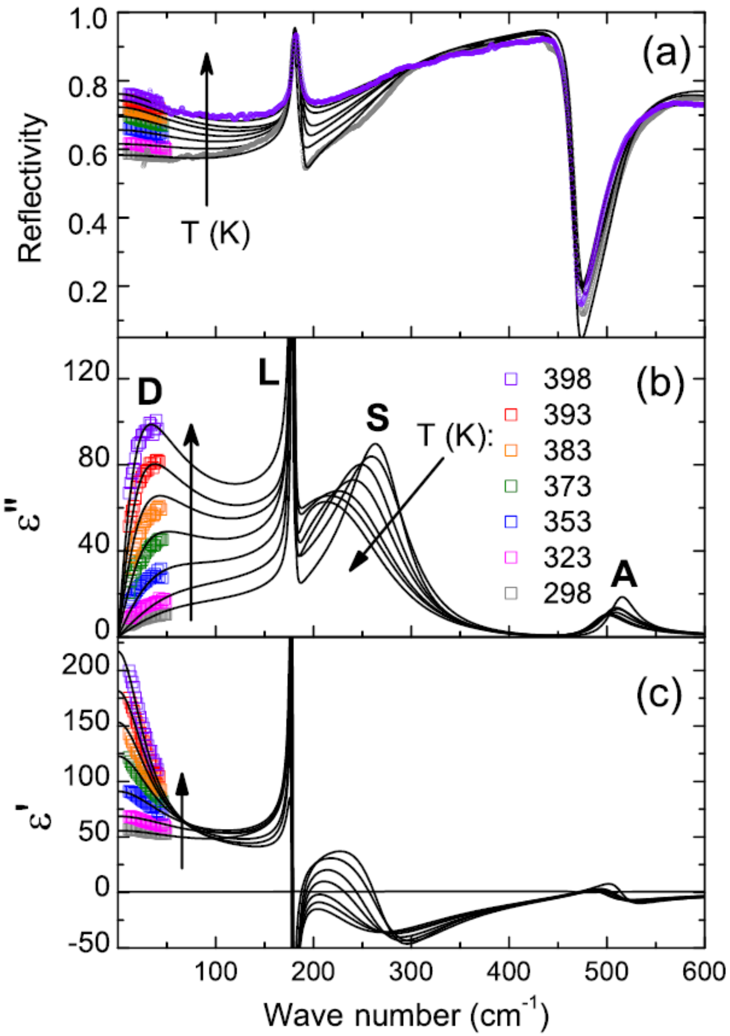


Soft mode in $BaTiO_3$ from FTIR + THz

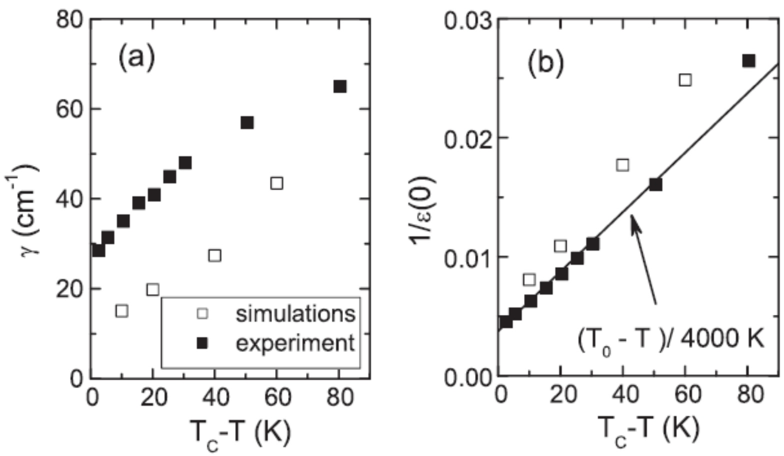


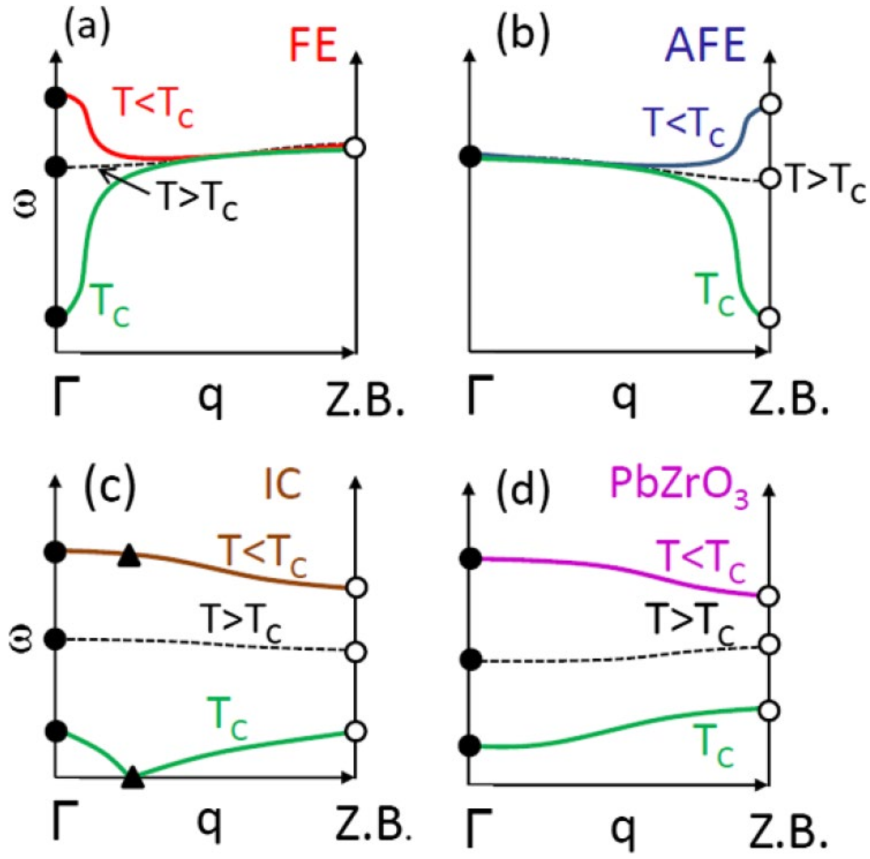
FIG. 2. Temperature dependence of (a) Debye mode frequency and (b) inverse static permittivity. Full symbols are from the THz experiment, open symbols are derived from MD simulations described in the text.

Coexistence of soft mode and relaxation
Mixed displacive and order-disorder character

Hlinka et al., Phys. Rev. Lett. 101, 167402 (2008)

The soft mode story

Is there such a thing as a antiferroelectric (or antipolar) soft mode?



Hlinka *et al.*, Phys. Rev. Letters **112**, 197601 (2014)

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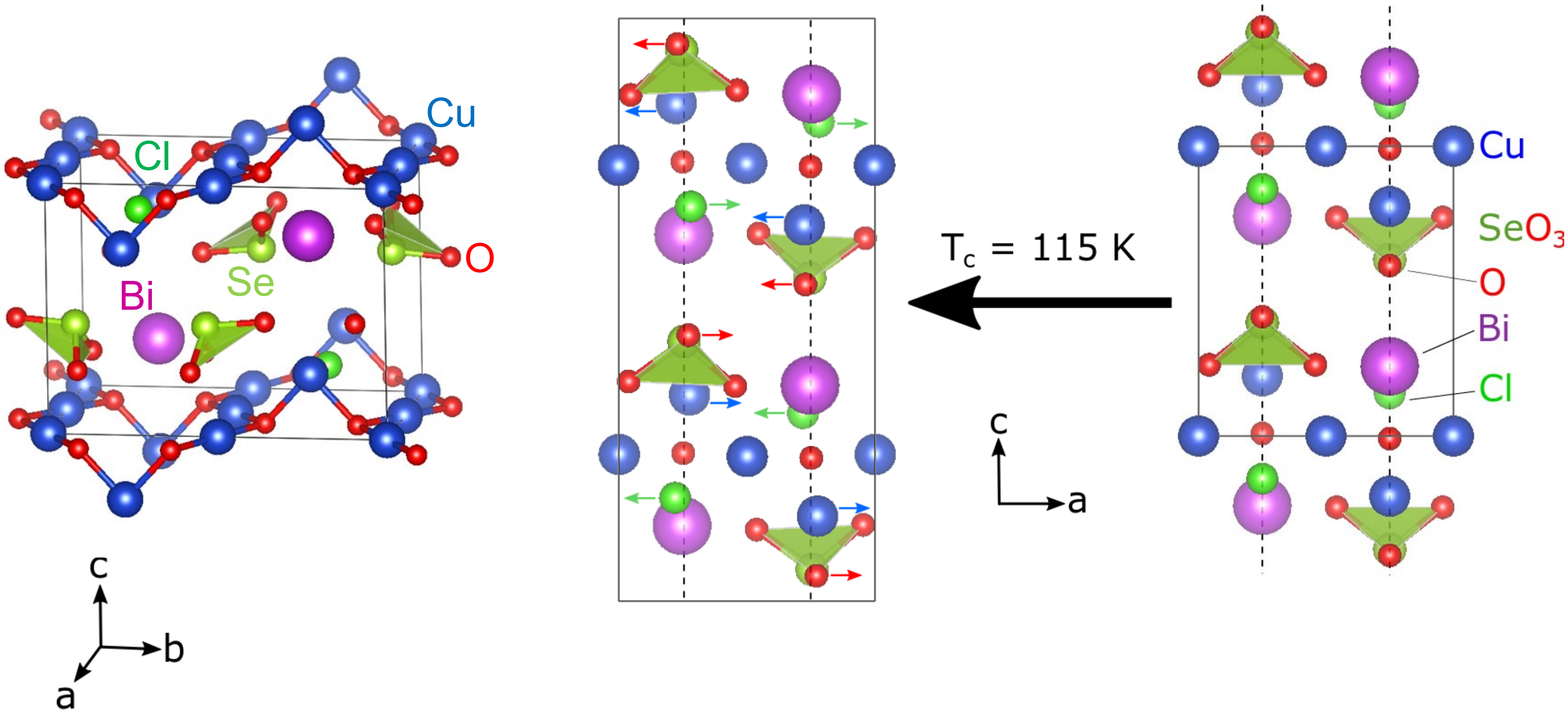
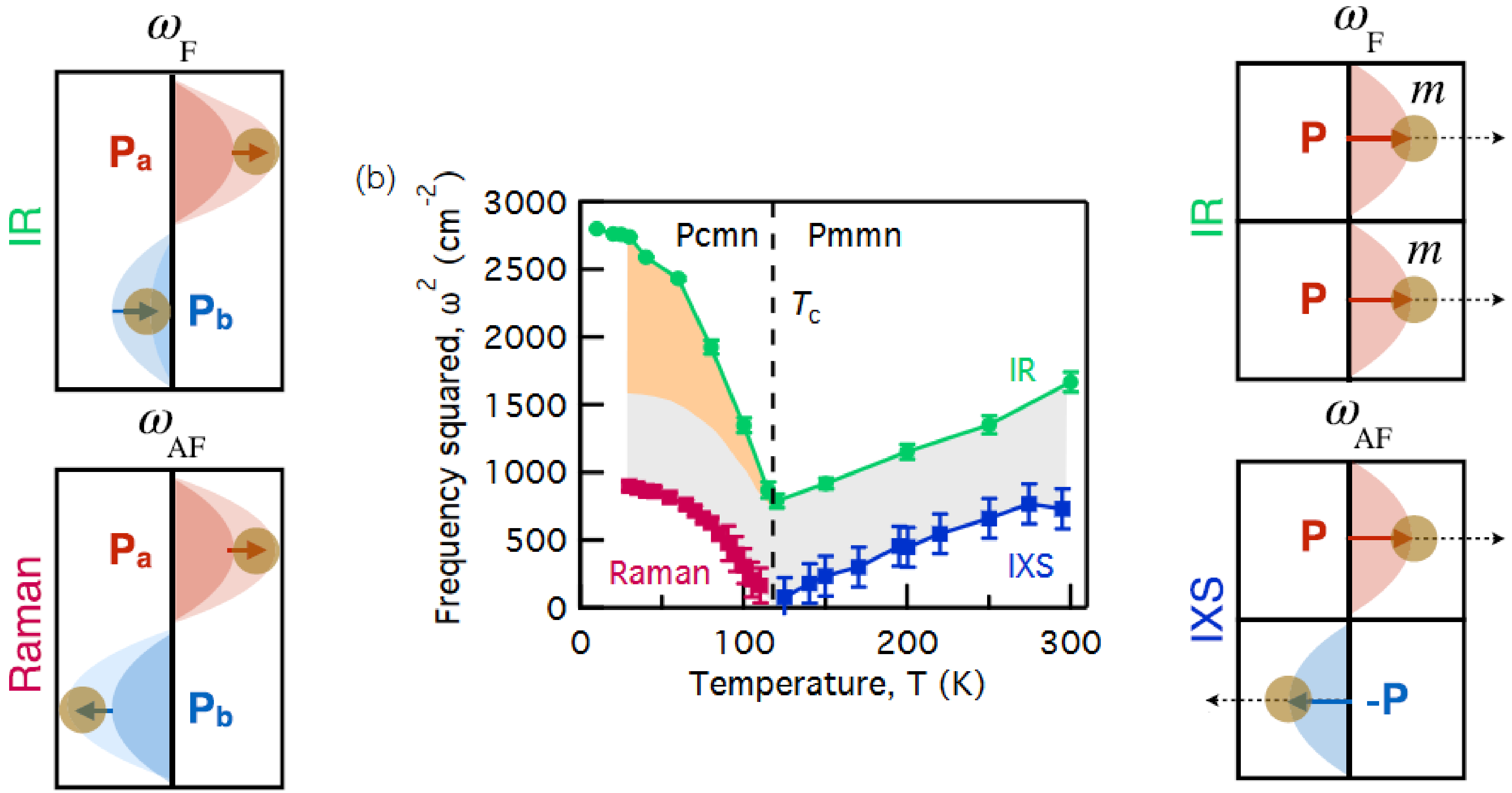


Constable et al., Phys. Rev. Research **5**, L012036 (2023)

The soft mode story



Constable et al., Phys. Rev. Research **5**, L012036 (2023)

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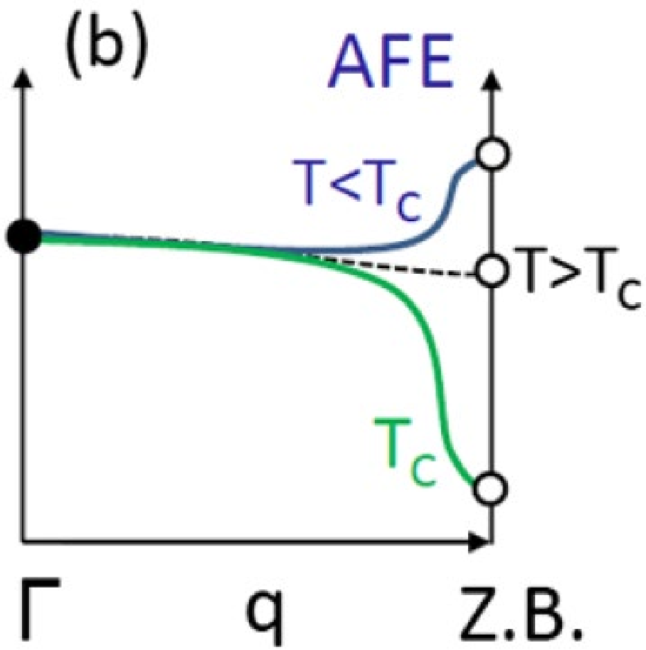
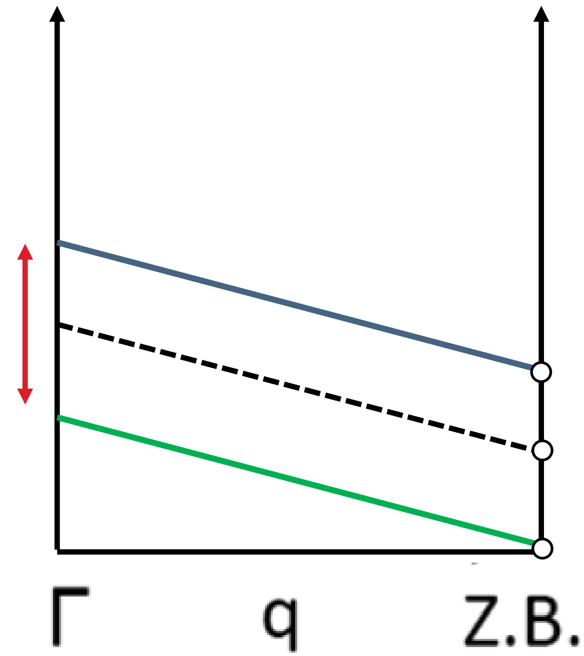


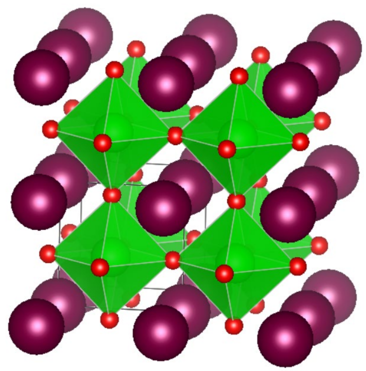


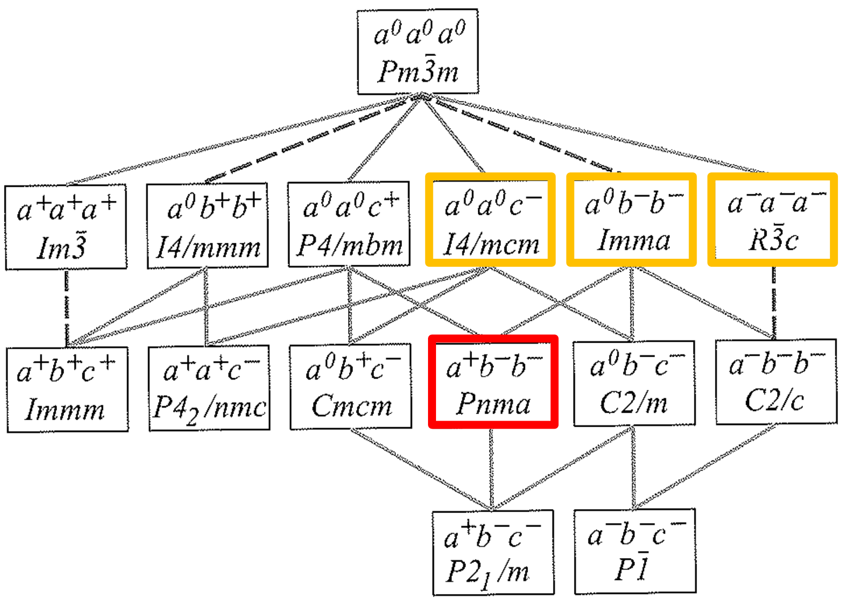
To be continued…

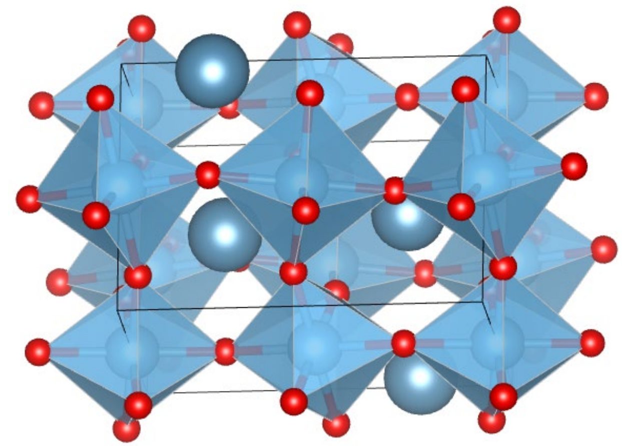
The (experimental) soft mode story II

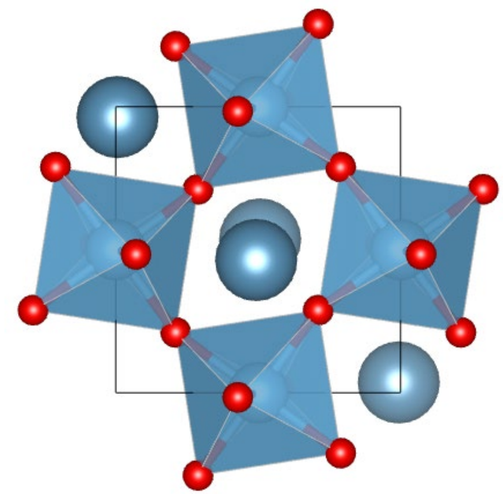
Tilts, tilts, tilts…

The soft mode story



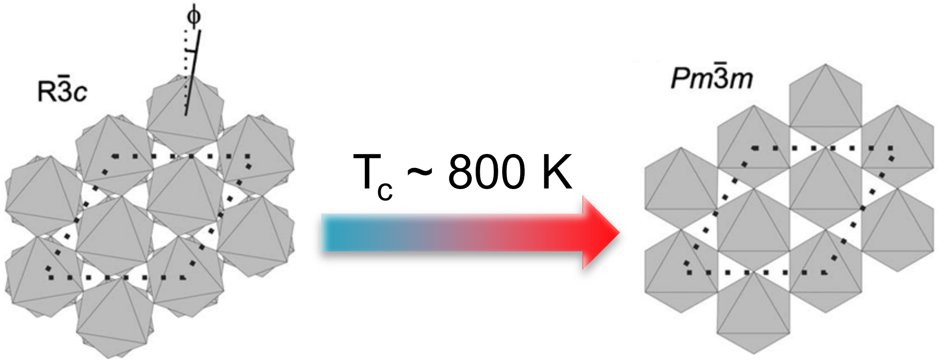


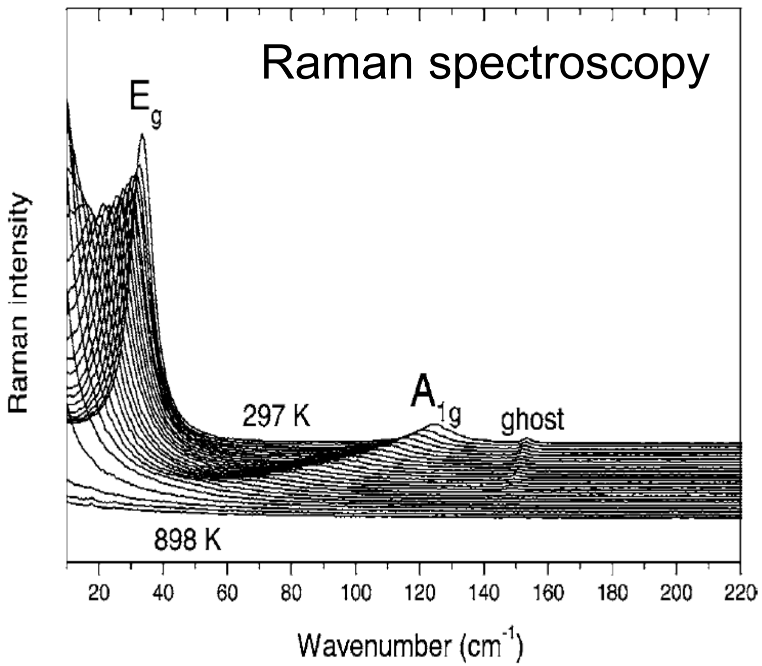


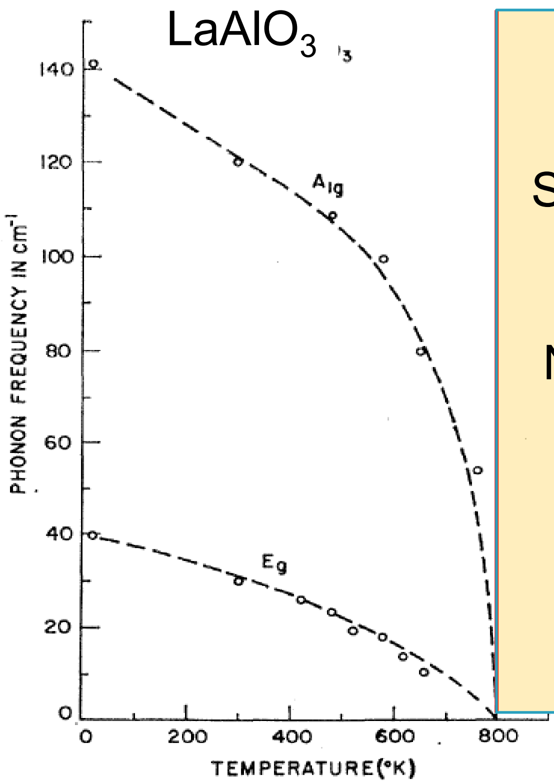


Carpenter & Howard, Acta Cryst. B65, 134 (2009).

The soft mode story







Soft mode not a Γ

Neutrons or X-ray needed!

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

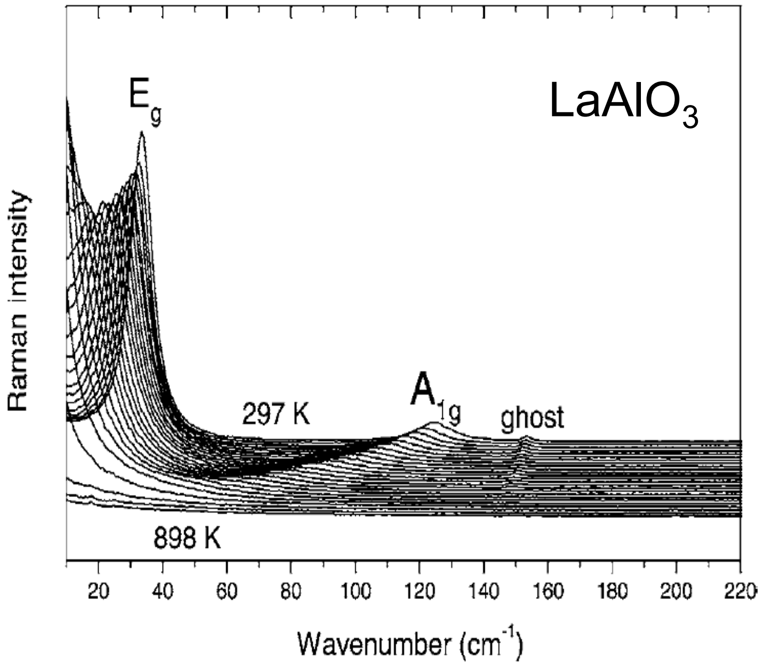
« Cochran's law »

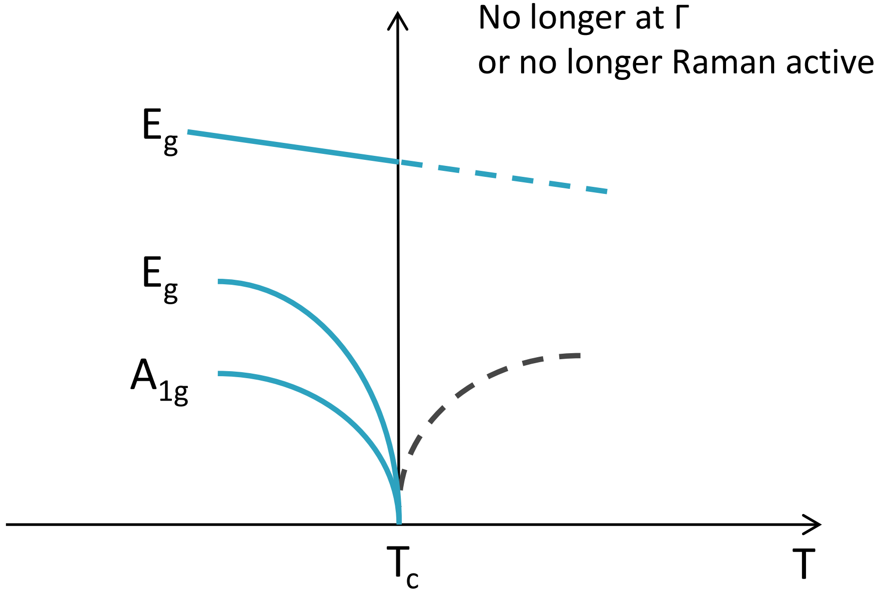
P. A. Fleury et al., Phys. Rev. Lett. 21, 16 (1968); Scott, Phys. Rev. 183, 823 (1969); Hayward et al., Phys. Rev. B 72, 054110 (2005)

The soft mode story

In the rhombohedral phase:

Raman spectroscopy



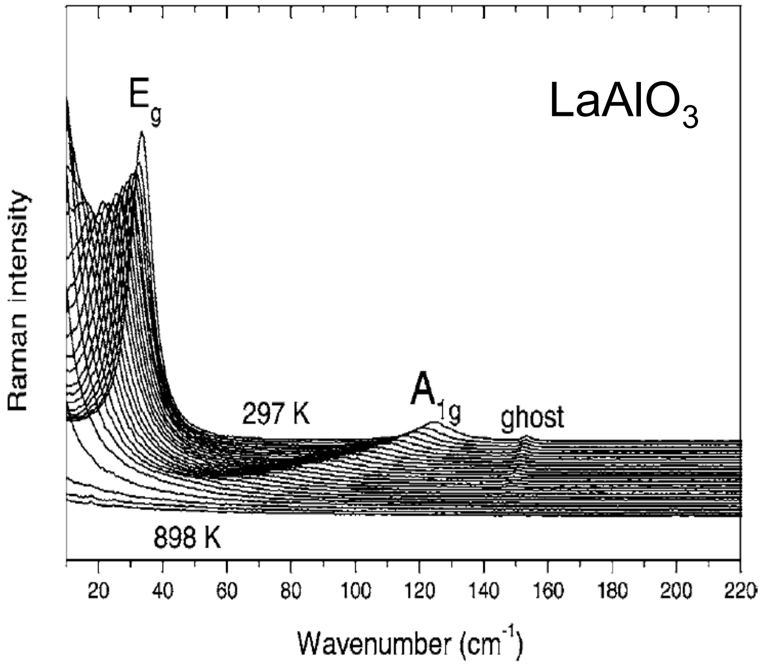


P. A. Fleury et al., Phys. Rev. Lett. 21, 16 (1968); Scott, Phys. Rev. 183, 823 (1969); Hayward et al., Phys. Rev. B 72, 054110 (2005)

The soft mode story

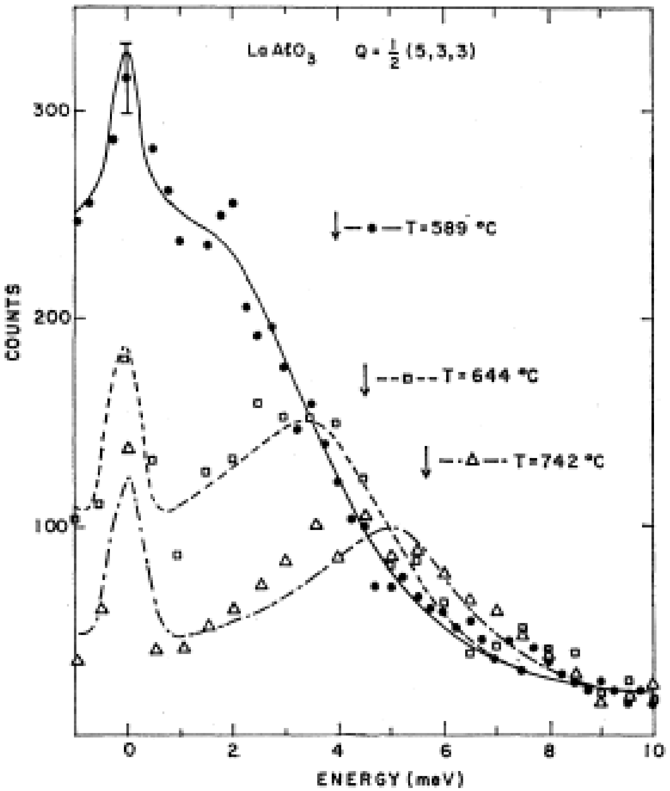
In the rhombohedral phase:

Raman spectroscopy



In the cubic phase:

Inelastic neutron scattering

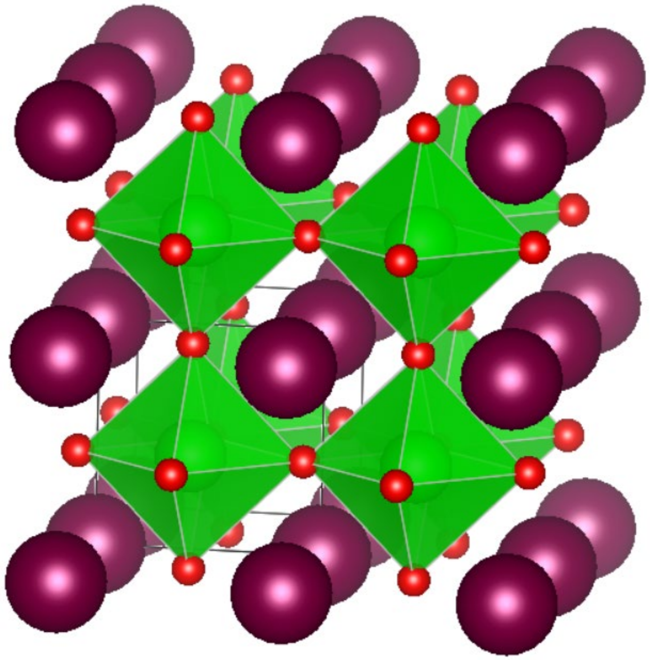


Axe et al., Phys. Rev. **183**, 820 (1969)

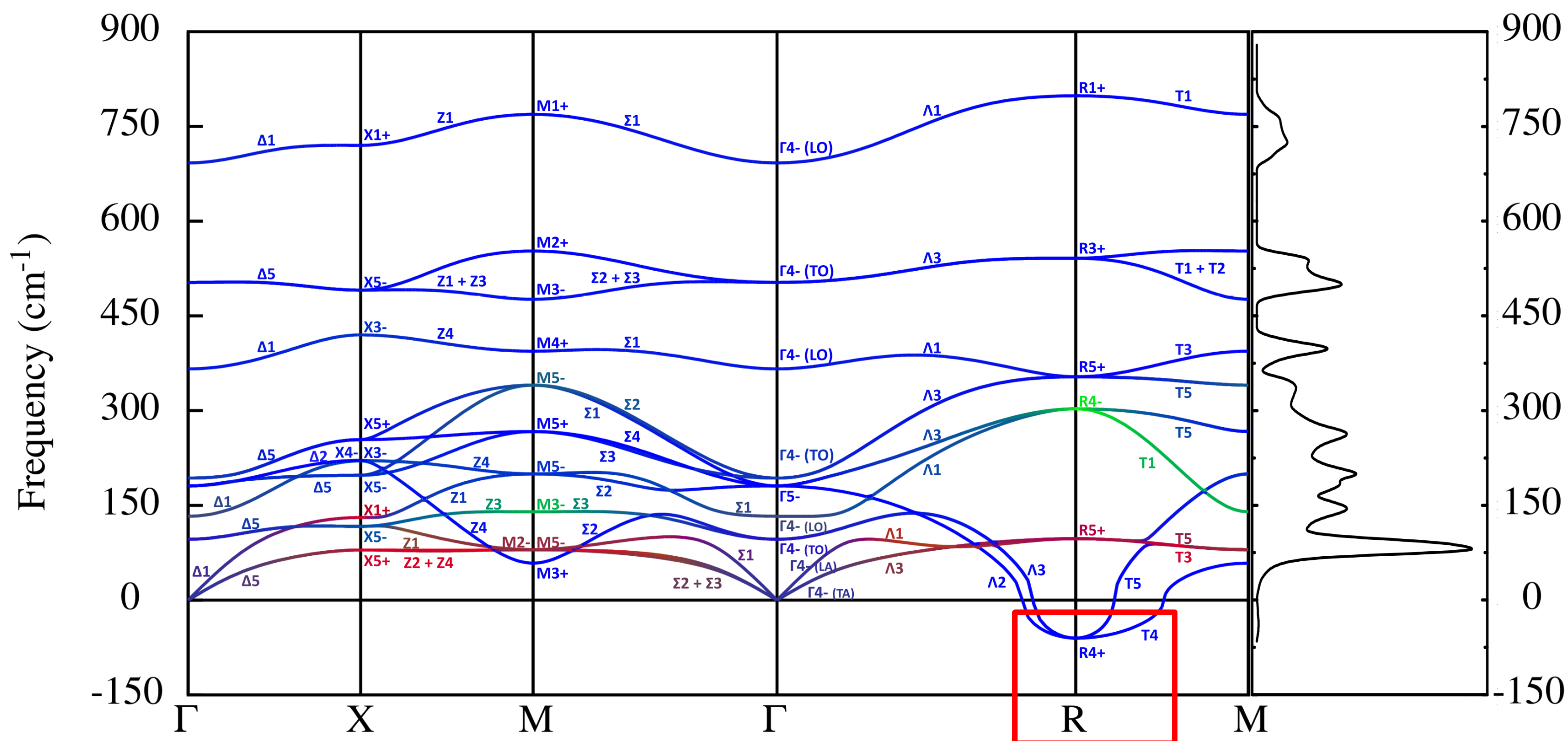
The soft mode story – $BaZrO_3$

$BaZrO_3$

- Tolerance factor ~ 1
- Cubic Pm-3m at all temperatures
- Melting point ~ 2600 ºC
- Single crystals now available!



The soft mode story – $BaZrO_3$

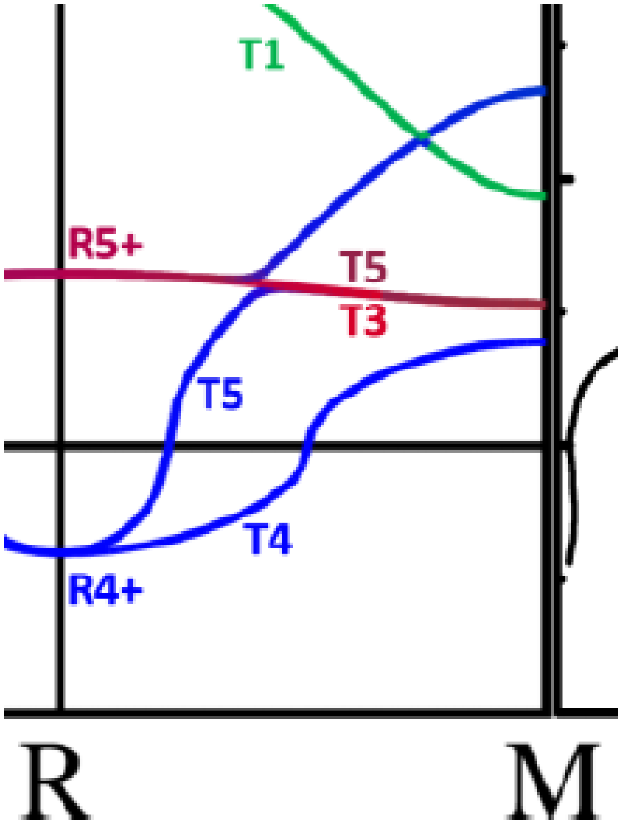


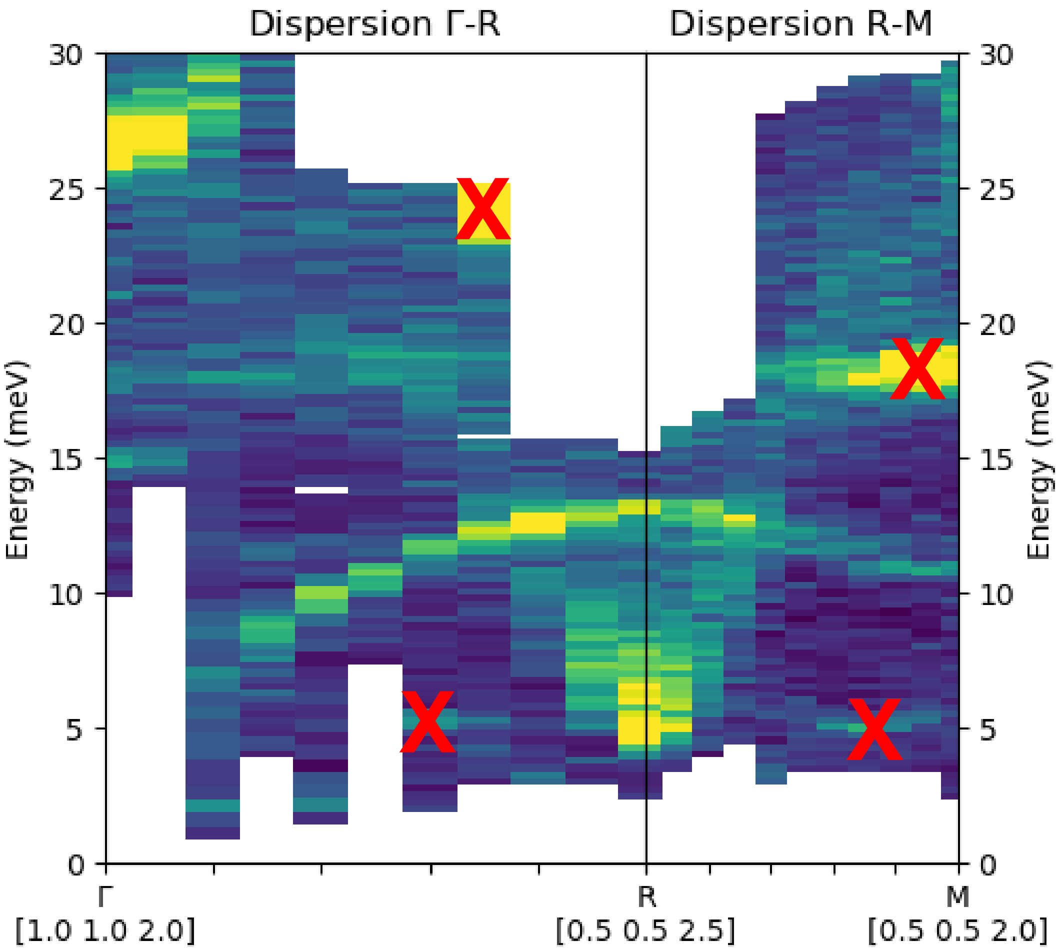
Octahedra tilt mode

- Unstable phonon mode at the R point
- Structure of the ground state?
- Tilts at the local scale?

Toulouse et al., Phys. Rev. B 100, 134102 (2019)

The soft mode story – $BaZrO_3$





The soft mode story – $BaZrO_3$

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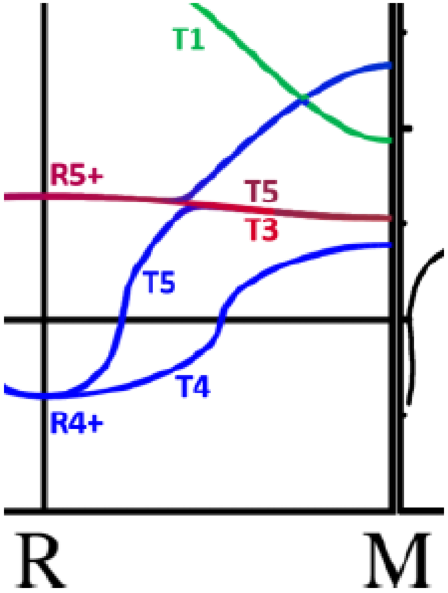
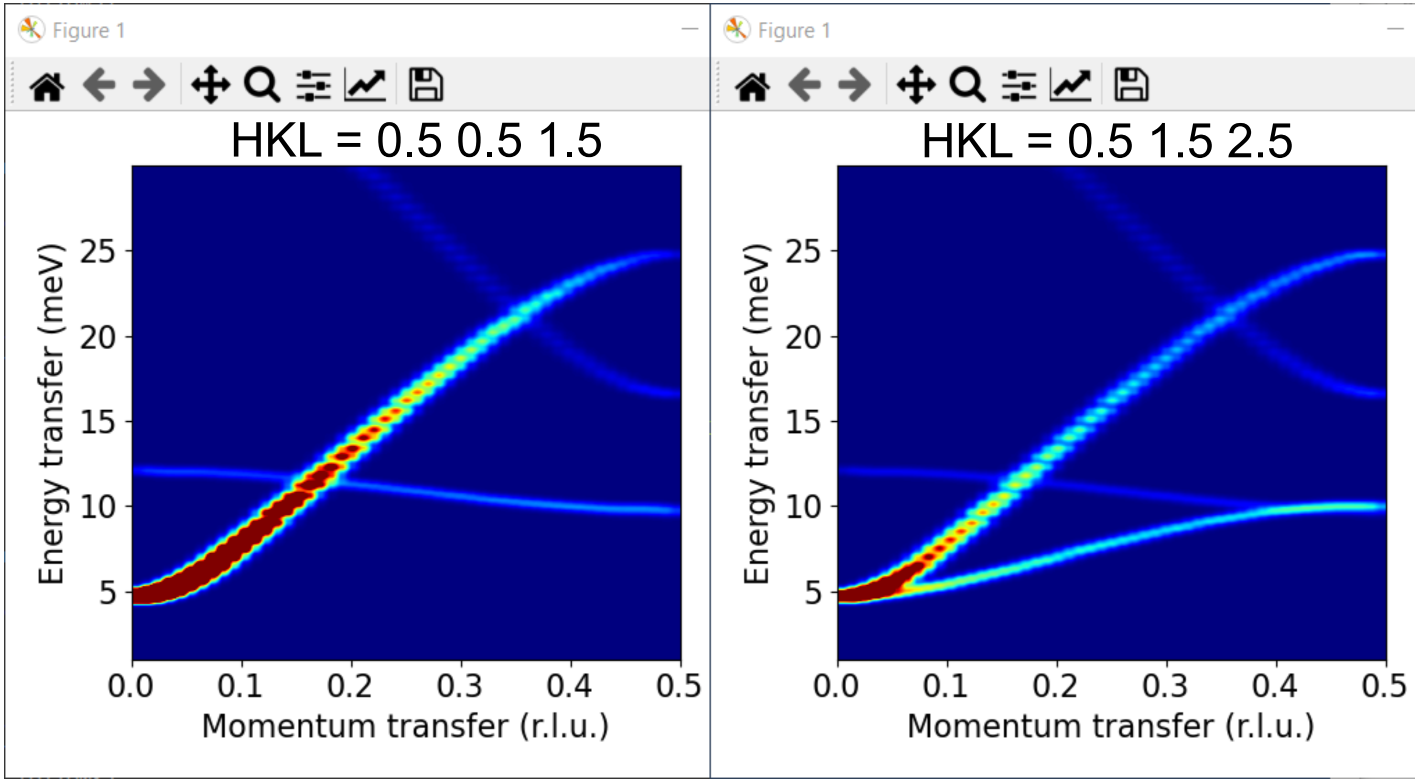
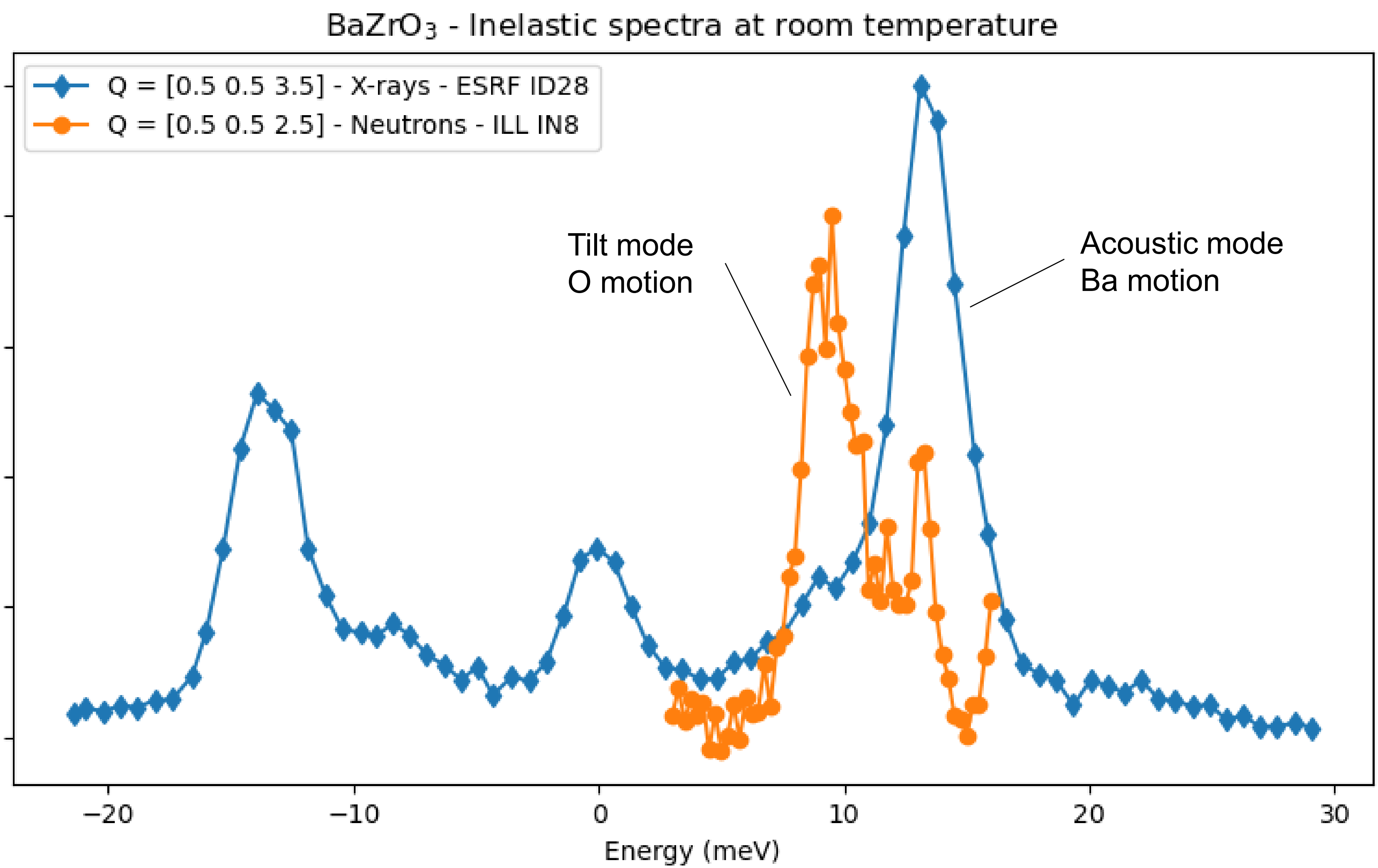
Selection rules in inelastic neutron scattering



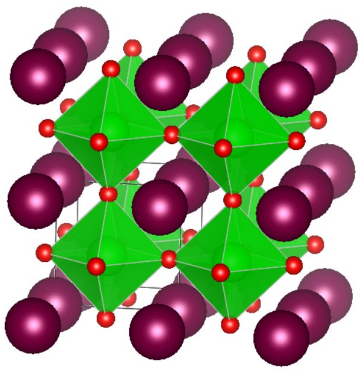


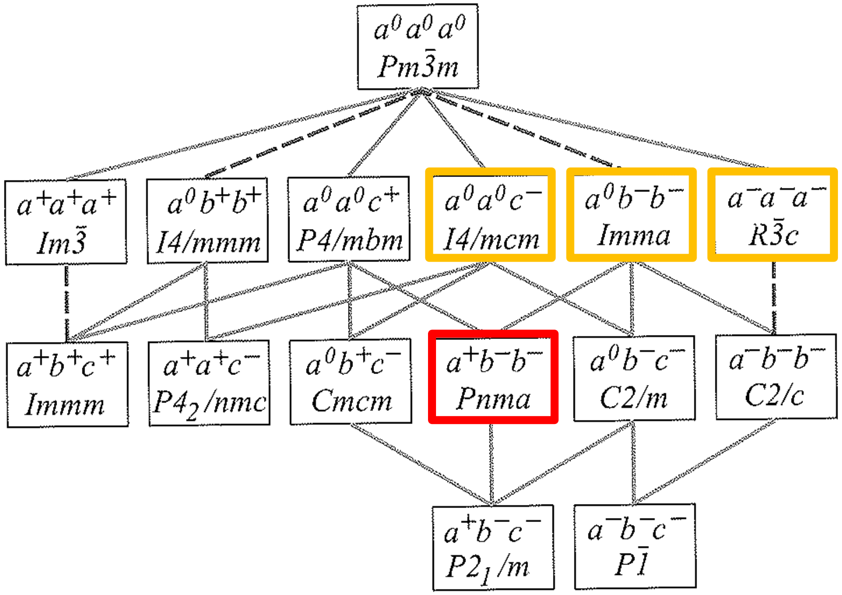
Special thanks to Binayak Mukherjee

The soft mode story – $BaZrO_3$



The soft mode story

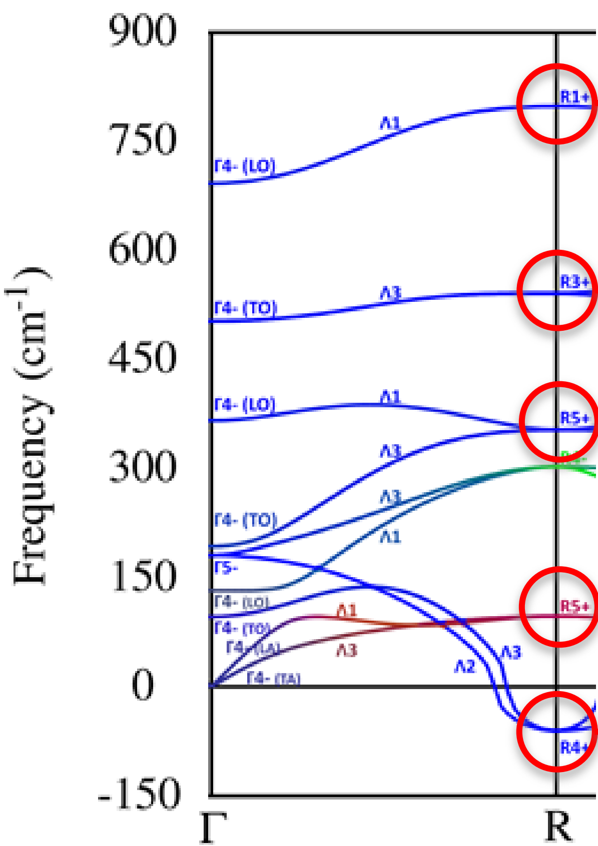




Carpenter & Howard, Acta Cryst. B65, 134 (2009).

The soft mode story – $BaZrO_3$

Symmetry analysis:



I4/mcm	Imma	R-3c
7 Raman modes	12 Raman modes	5 Raman modes
	B_{3g}	
B_{1g}	$B_{1g} + B_{3g}$	E_g
$B_{2g} + E_g$	$A_g + B_{2g} + B_{3g}$	E_g
$B_{2g} + E_g$	$A_g + B_{2g} + B_{3g}$	E_g
$A_{1g} + E_g$	$A_g + B_{1g} + B_{2g}$	$A_{1g} + E_g$

Very small splitting + twinning close to the transition!

The soft mode story – $BaZrO_3$

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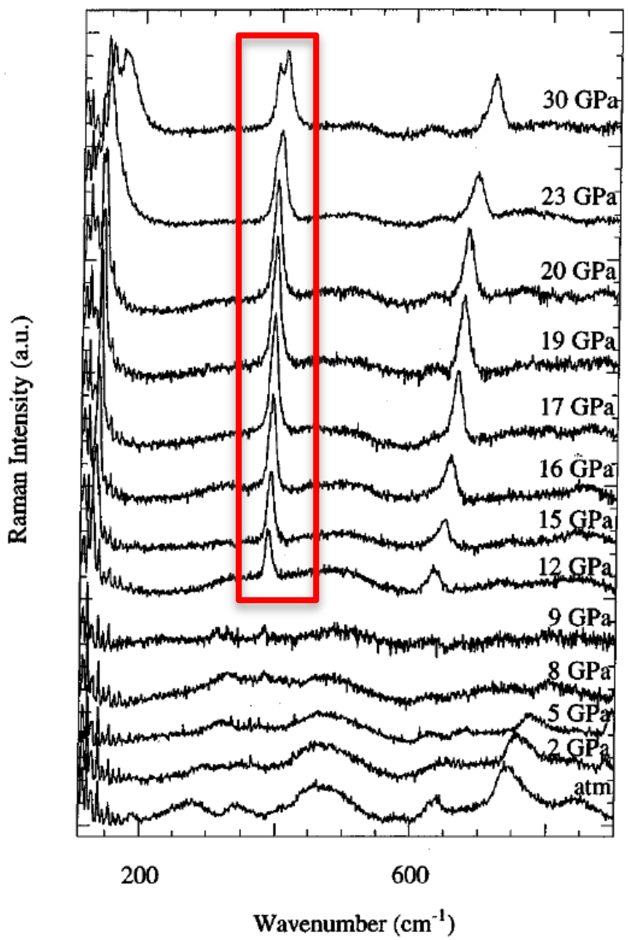
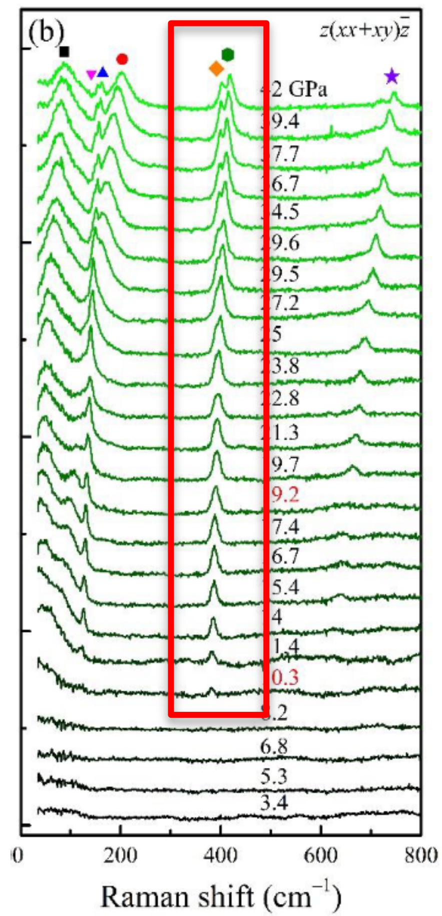
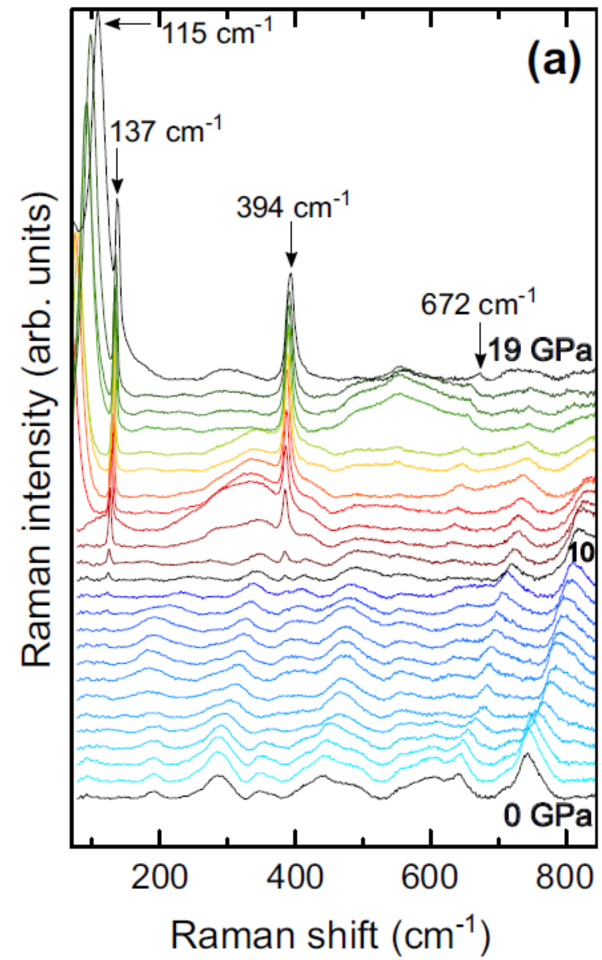
High-pressure Raman spectroscopy







Chemarin *et al.*, J. Solid State Chem. 149, 298 (2000); Gim et al., Materials 15, 4286 (2022); This work.

Thin and ultrathin films

Is there such as thing as « too small for Raman »?

Thin and ultrathin films

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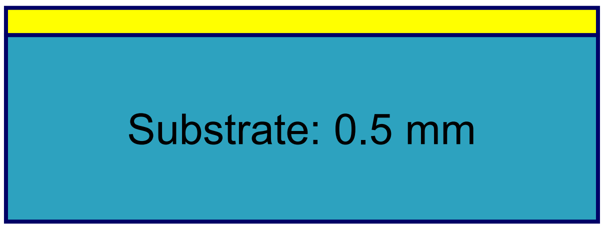
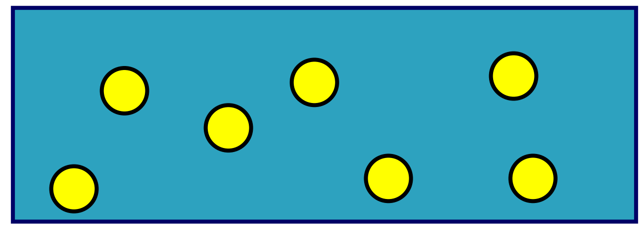
Is there a limiting thickness or size?

Thin film on a substrate

$0.4 \text{ nm} < t < 100 \text{ nm}$ and more



Nanoparticles in a matrix



- Very small sample volume → very low Raman intensity
- Very large substrate/matrix volume → very strong background signal

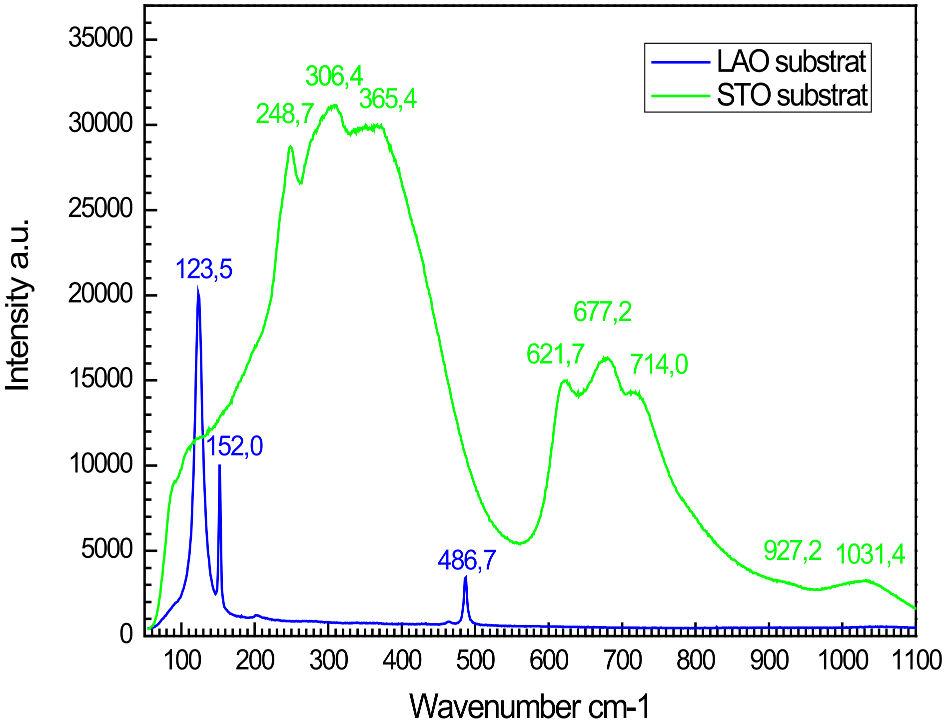
No general answer! It depens on:

➔ Excitation wavelength
➔ Sample absorption
➔ Enhancement mechanisms

Thin and ultrathin films

« Thin » film

0.4 nm < t < 100 nm and more



« Good » substrates: LAO, Pt, Au…

« Bad » substrates: STO, Glass…

Thin and ultrathin films

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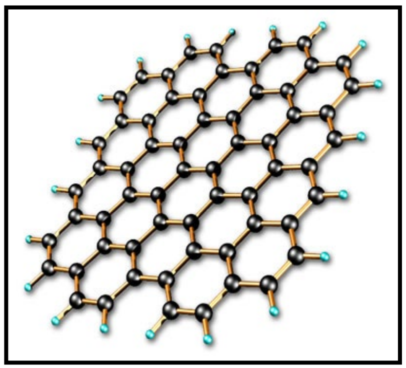
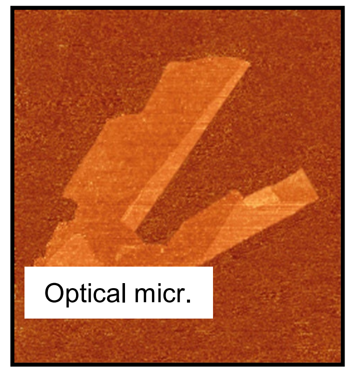
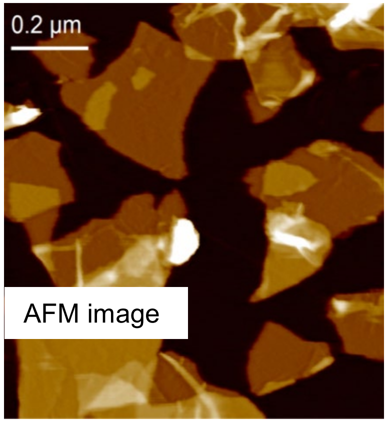
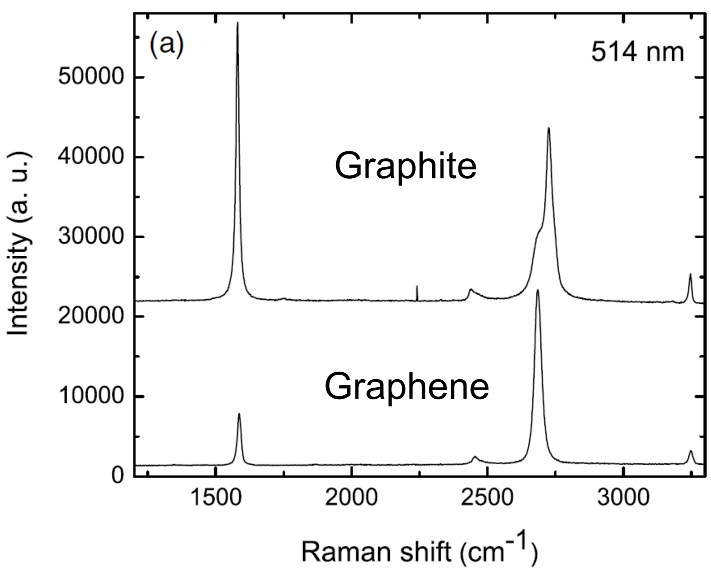
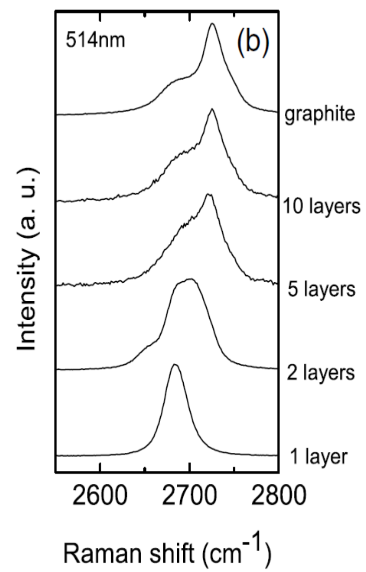
Counting graphene sheets

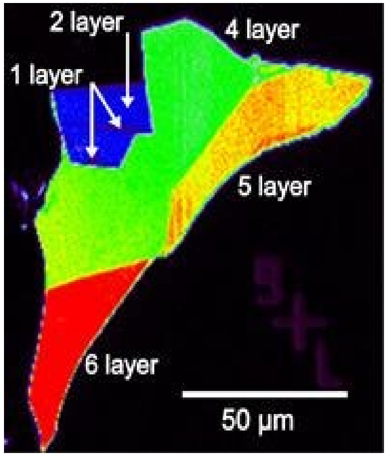








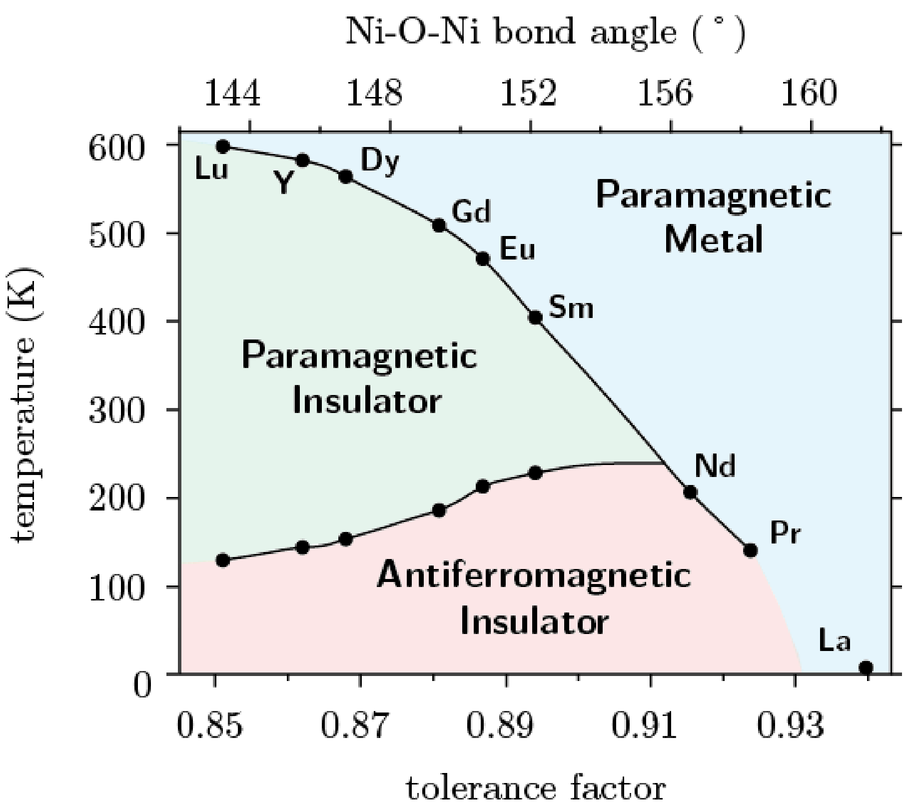




A. C. Ferrari, et al., Phys. Rev. Lett. 97, 187401 (2006)

Thin and ultrathin films

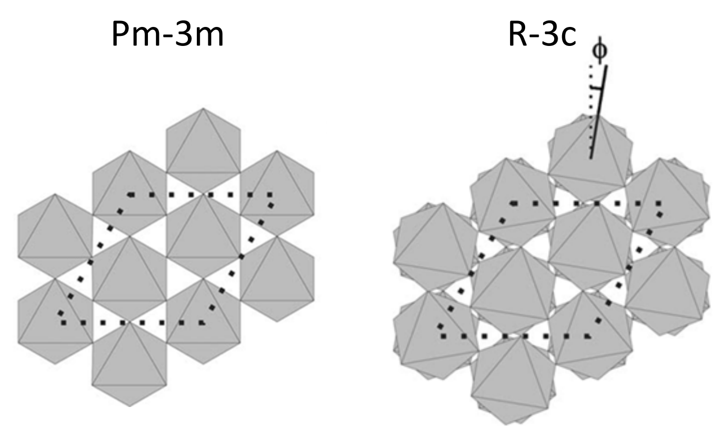
Rare Earth Nickelates $RNiO_3$



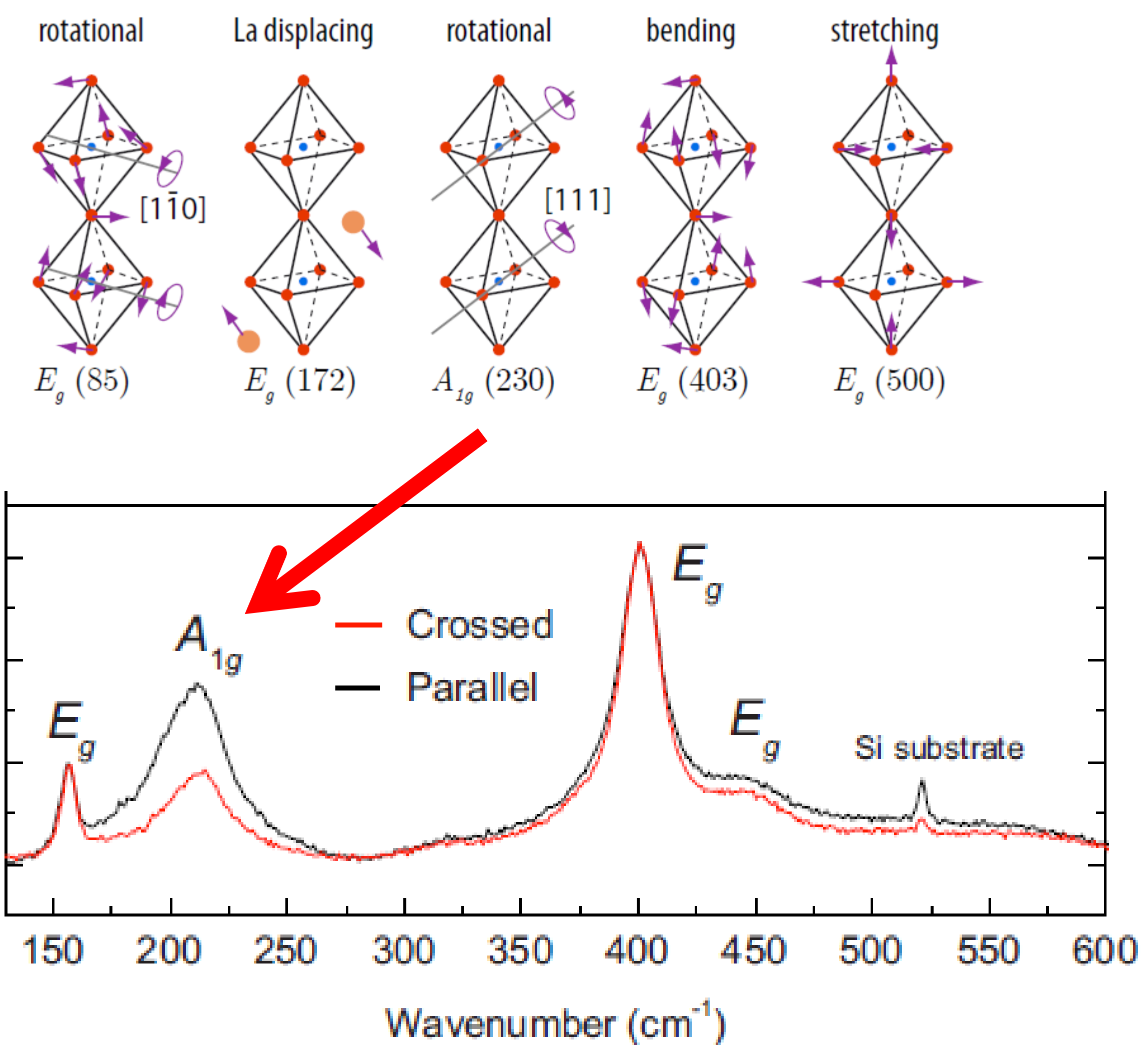
$LaNiO_3$

- "Model" tilt structure
- R3c
- $a^-a^-a^-$ tilt
- transition to cubic @ high T

Metallic & paramagnetic at all T

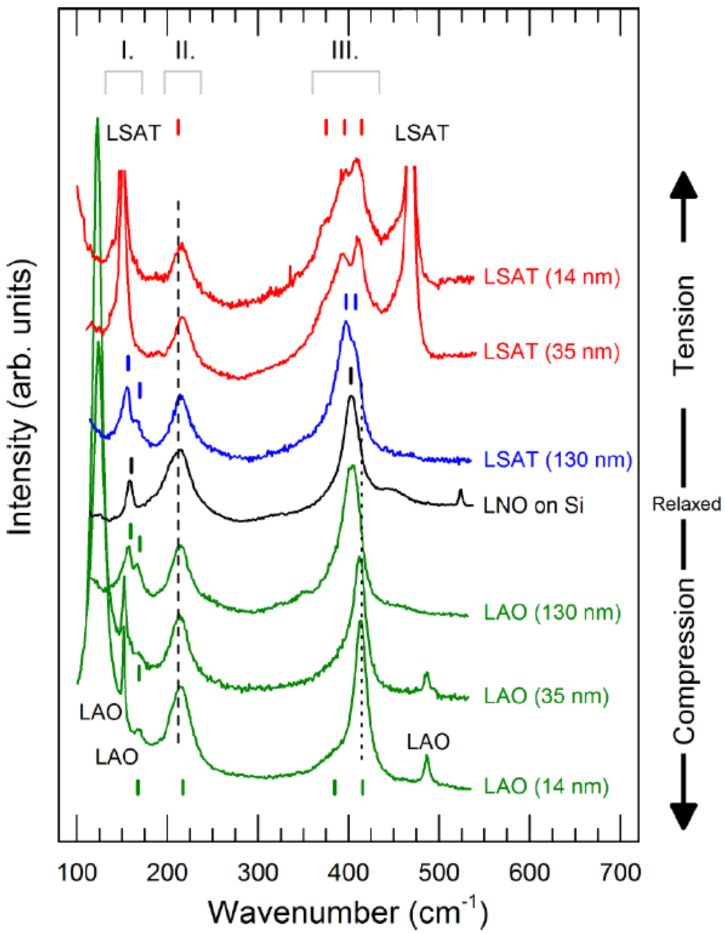


Thin and ultrathin films

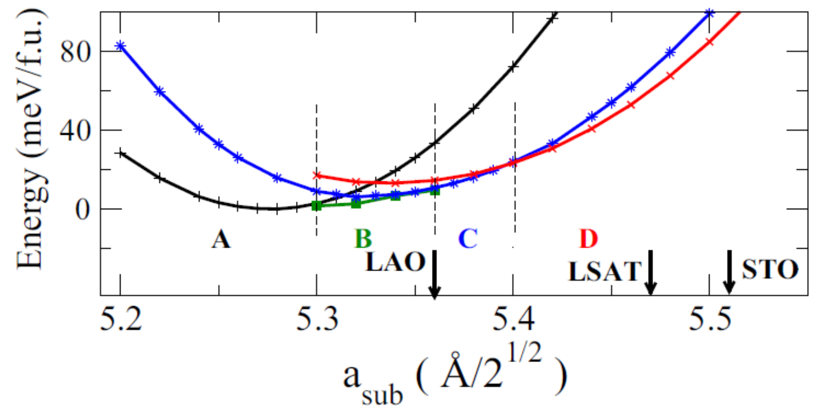


N. Chaban et al., Appl. Phys. Lett. 97, 031915 (2010)

Thin and ultrathin films



Ab-initio prediction (LDA-VASP)

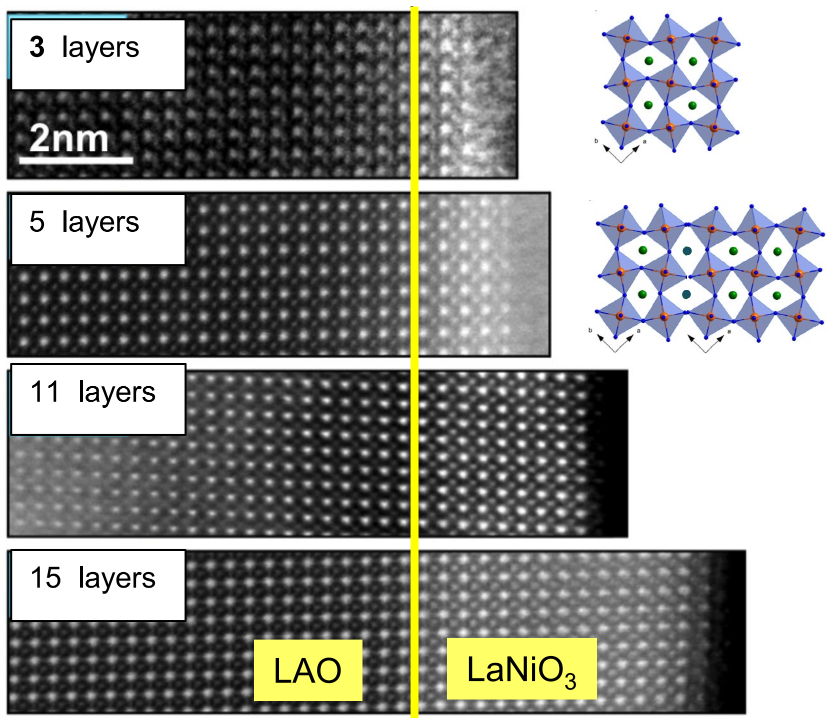


D	*Strong* in-plane tension:	Fmmm	$a^-b^0c^0$
C	*Weak* in-plane tension:	Imma	$a^-a^-b^0$
	Relaxed (bulk):	R-3c	$a^-a^-a^-$
B	In-plane compression:	C2/c	$a^-a^-c^-$
A	*Strong* compression:	I4/mcm	$a^0a^0c^-$

Structure with tilts only
Several others close in energy !

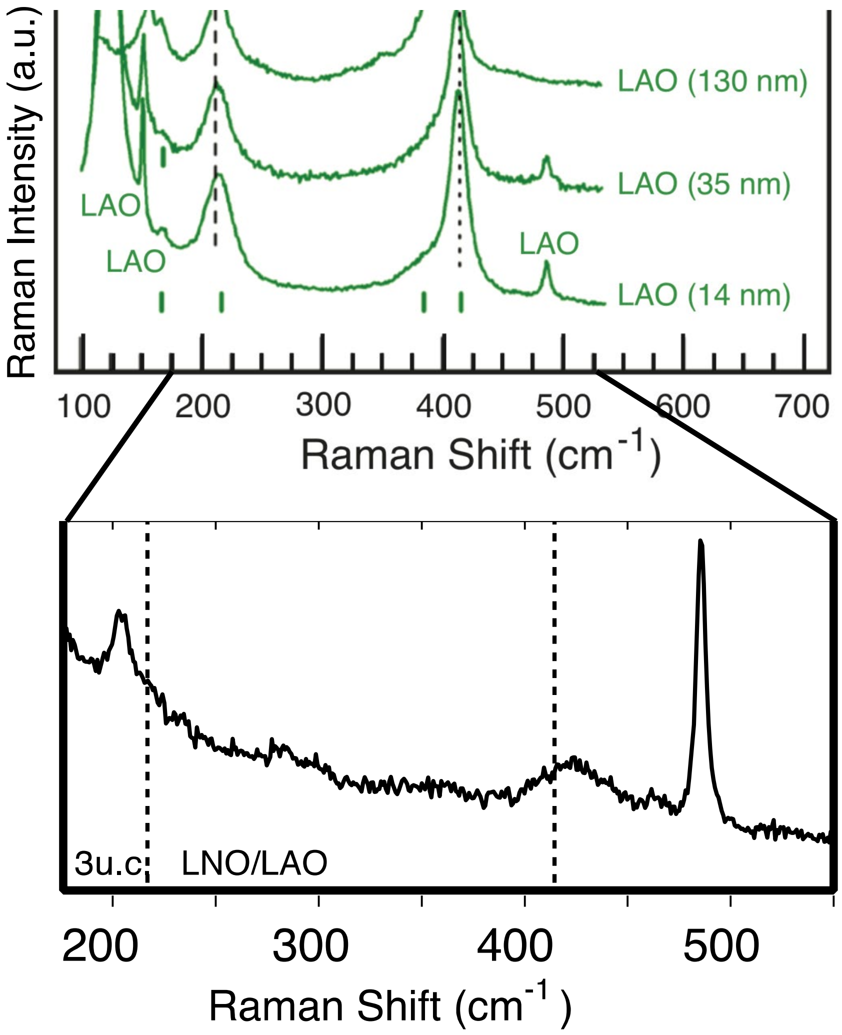
Thin and ultrathin films

What if we go even thinner?



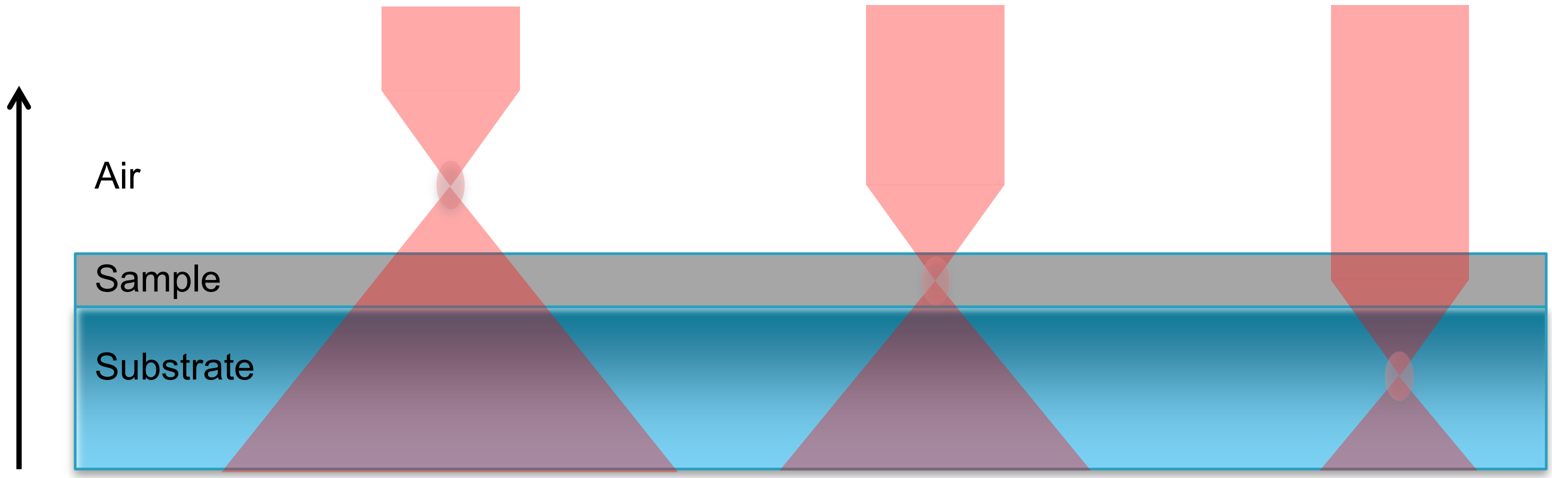
J. Fowlie et al., Adv. Mater., 1605197 (2017)

Thin and ultrathin films

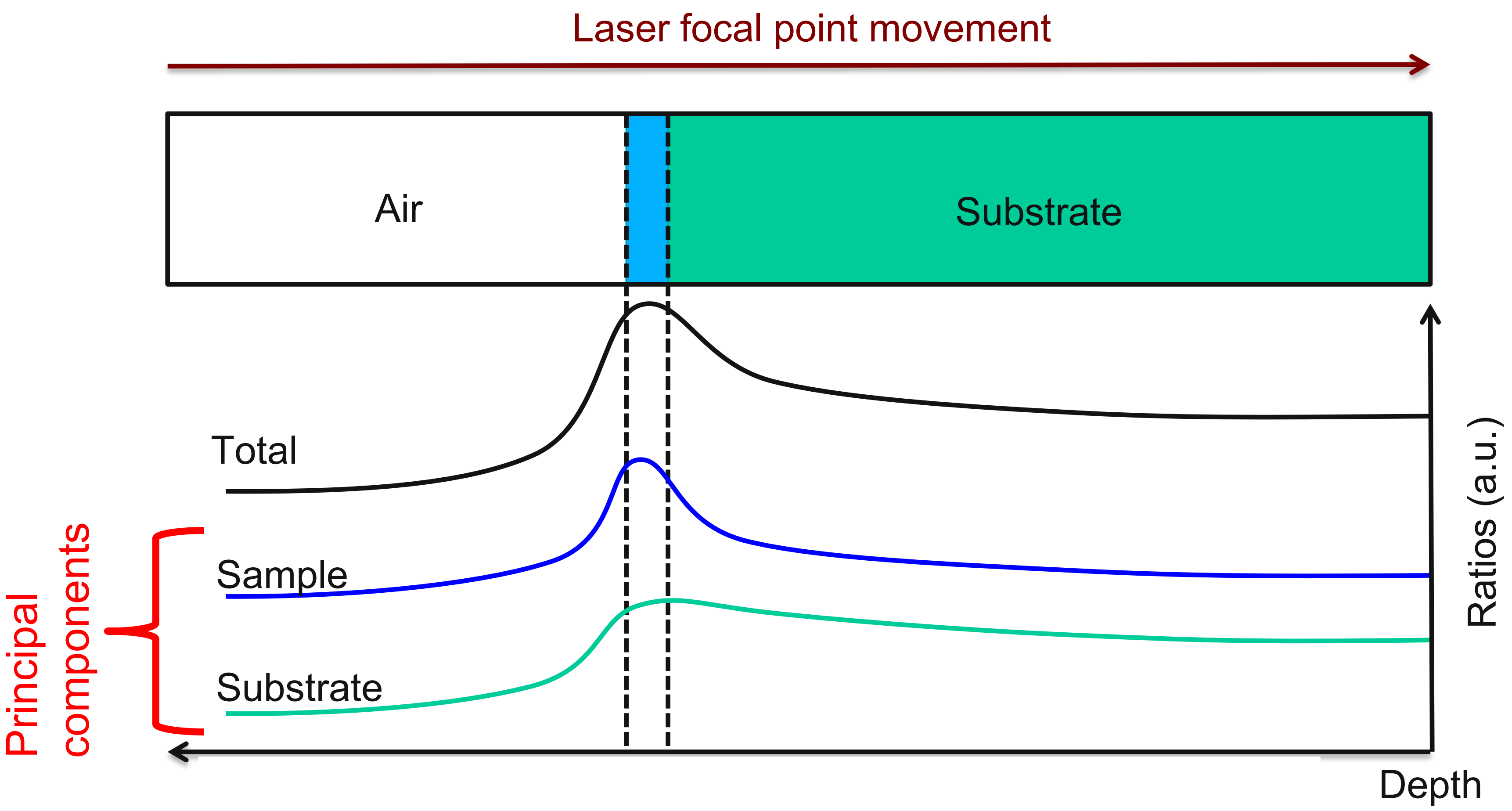


Thin and ultrathin films

The principle of depth profiling



Thin and ultrathin films



Thin and ultrathin films

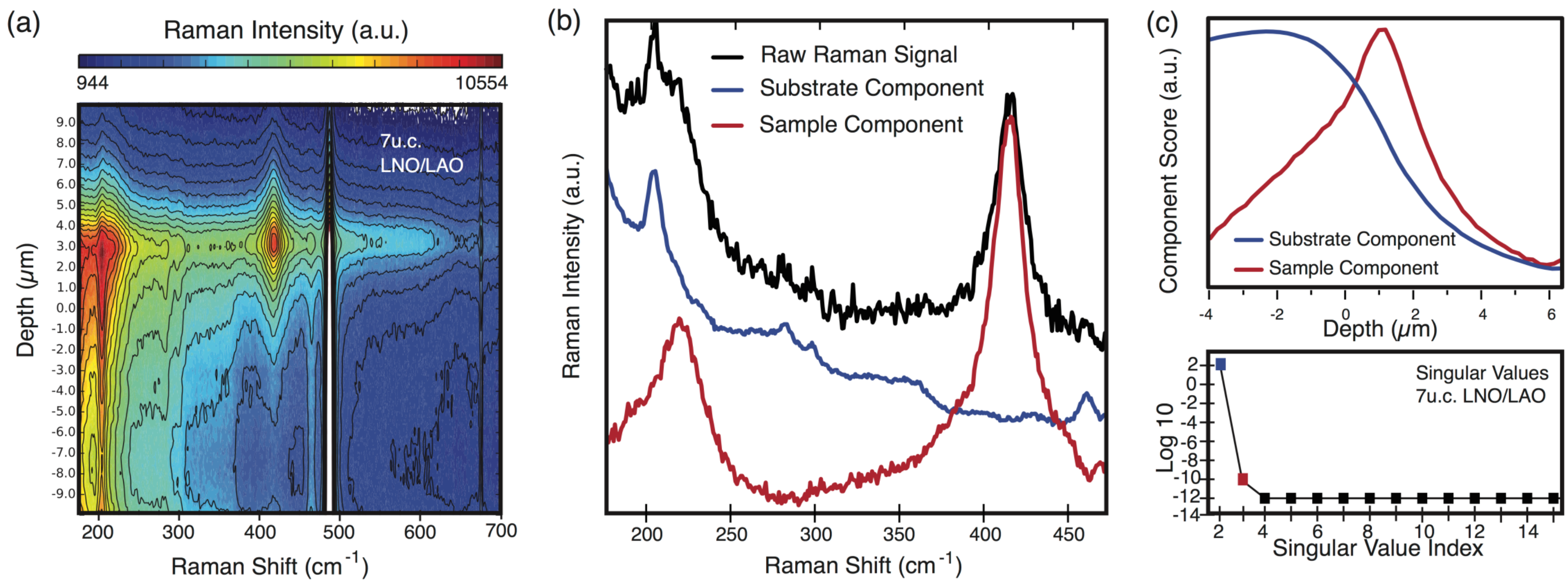
$LaNiO_3$ on $LaAlO_3$

7 pseudo-cubic unit cells (➔ ≈ 2.8 nm)

Scan:

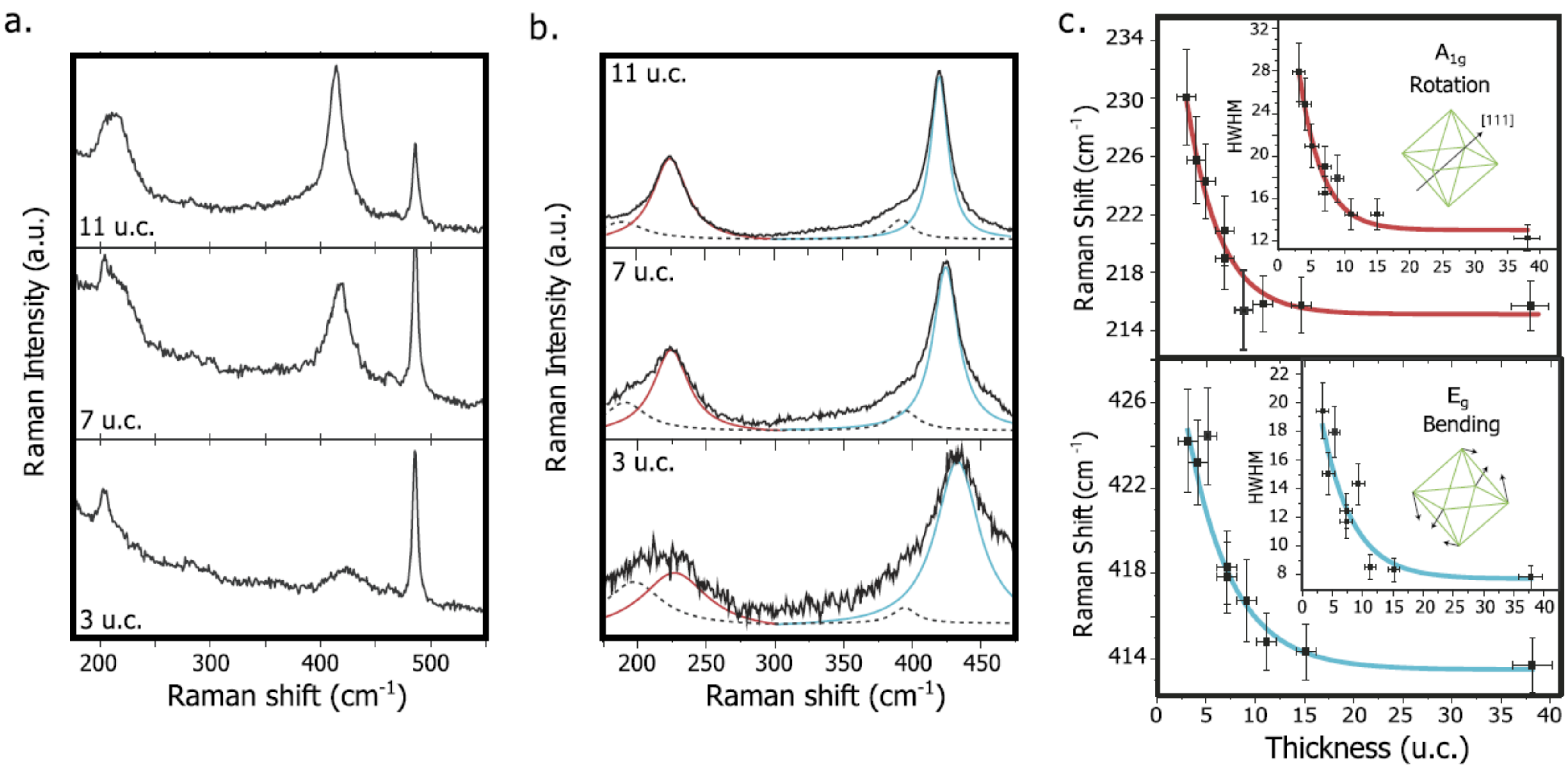
- Range: -10 to 10 µm
- Steps: 0.2 µm

➔ 100 spectra



Schober et al., APL Mater. 8, 061102 (2020)

Thin and ultrathin films



- Octahedra tilts : stable for low thicknesses
- New regime for t < 8 unit cells (3.2 nm)
- Relation with the tilt angle?

Schober et al., APL Mater. 8, 061102 (2020)

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What's next?

- Sensitivity to magnetism
  - Directly by magnons
  - Indirectly by spin-phonon coupling
- Measurements of mixed excitations (electromagnons…)
- Resonant Raman scattering
- …

For further reading

- E. Smith, G. Dent, *Modern Raman Spectroscopy – A practical approach*, Weily, 2005.
  - As the title says, a practical approach, with some experimental details, but more shallow in the theoretical descriptions.
- Yu and Cardona, *Fundamentals of semiconductors* (3rd edition), Springer, 2001.
  - A classical textbook, not centered on Raman spectroscopy, but very useful to get an overview of Raman spectroscopy together with other spectroscopy technique.
- D. Long, *The Raman effect*, Wiley, 2002.
  - Many details on the theoretical treatements, both classical and quantum. Sometimes a bit unconventional in its approaches.
- W. Hayes, R. Loudon, *Scattering of light by crystals*, Dover publications, 1978.
  - Reference textbook on Raman scattering, goes deep in the physics in a very classical and general way. Recommanded for a deep understanding on the details of the physical scattering processes.