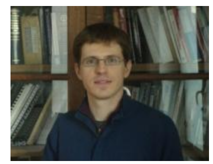
DRIVING THE SPIN EXCITATIONS IN $BiFeO_3$ FROM SPIRAL TO CANTED STATE USING PRESSURE

J. Buhot, C. Toulouse, M.-A. Méasson, M. Cazayous, Y. Gallais, A. Sacuto





Laboratoire Matériaux et Phénomènes Quantiques, UMR 7162 CNRS, Université Paris Diderot - Paris 7, France

Collaborations:

Dawei Wang
Electronic Materials Research Laboratory, Xi'an Jiaotong University, Xi'an (CHINA)

L. Bellaiche
Physics Department, University of Arkansas, Fayetteville (USA)

R. de Sousa
Department of Physics and Astronomy, University of Victoria, Victoria, B.C., V8W 3P6, Canada

D. Colson
Service de Physique de l'Etat Condensée, DSM/IRAMIS/SPEC, CEA Saclay, F-91191 Gif-sur-Yvette, France

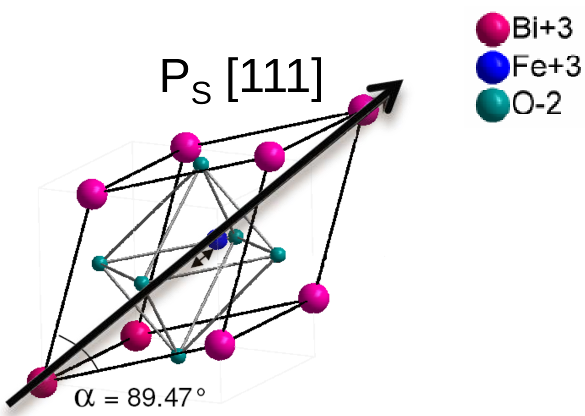
BFO: The most studied multiferroic compound

Ferroelectric < T_c = 1100K

Ferroelectric single domain crystal

✓ Very large polarization

P_S~ 100 μC/cm²

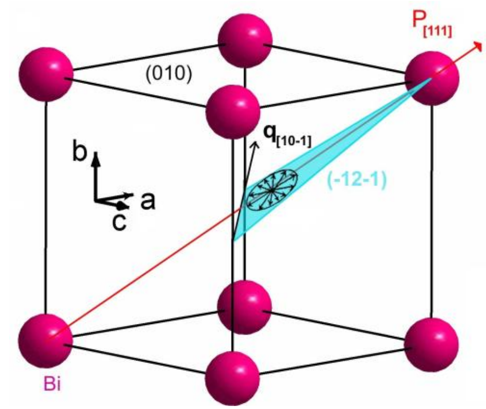


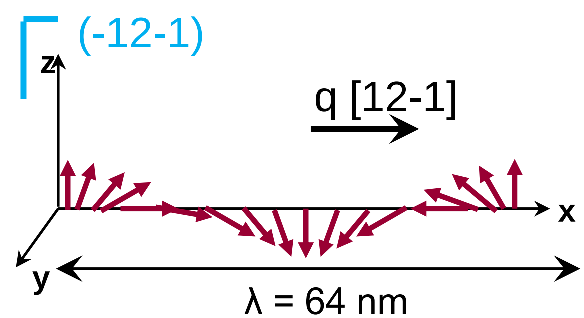
Pseudo cubic structure

G type antiferromagnetic < T_N = 640K

Antiferromagnetic single domain crystal

✓ One spin rotation plane (-12-1) containing P and q : one cycloid



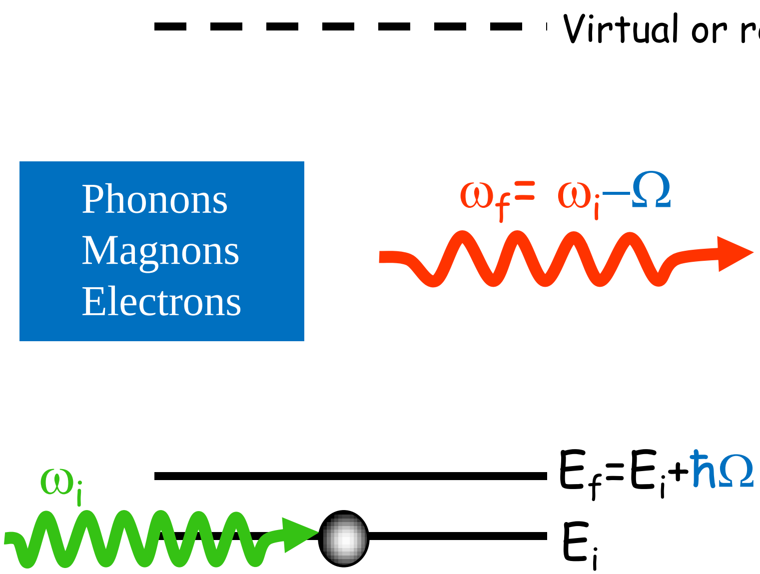


Incommensurate cycloid

Inelastic light scattering

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

Stokes Process

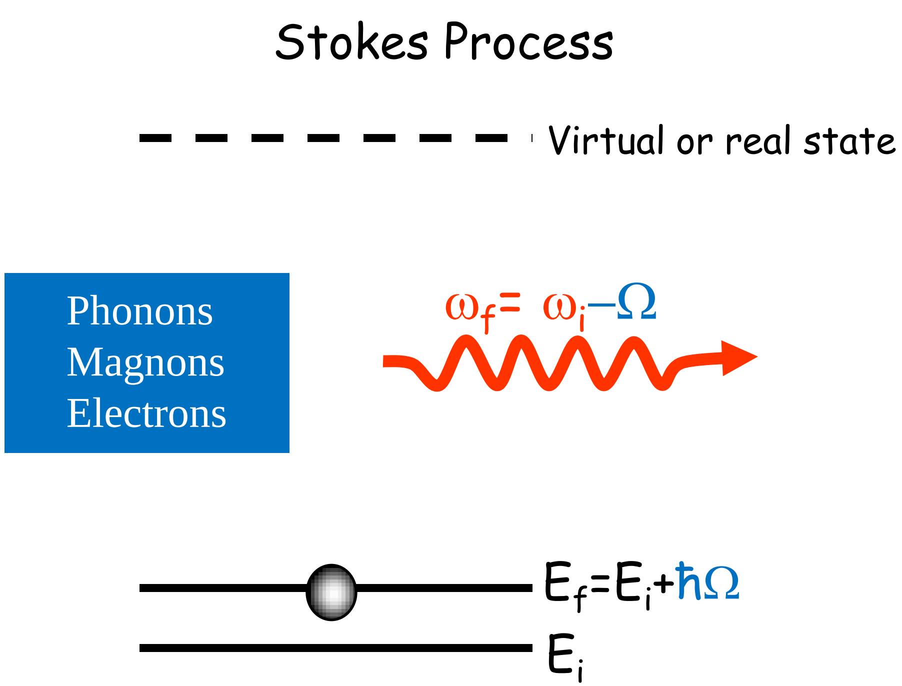


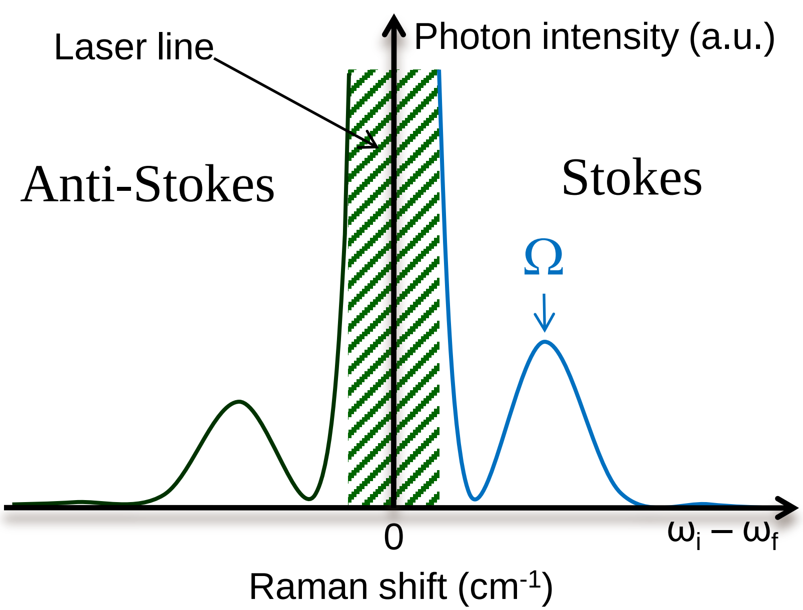
Inelastic light scattering

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

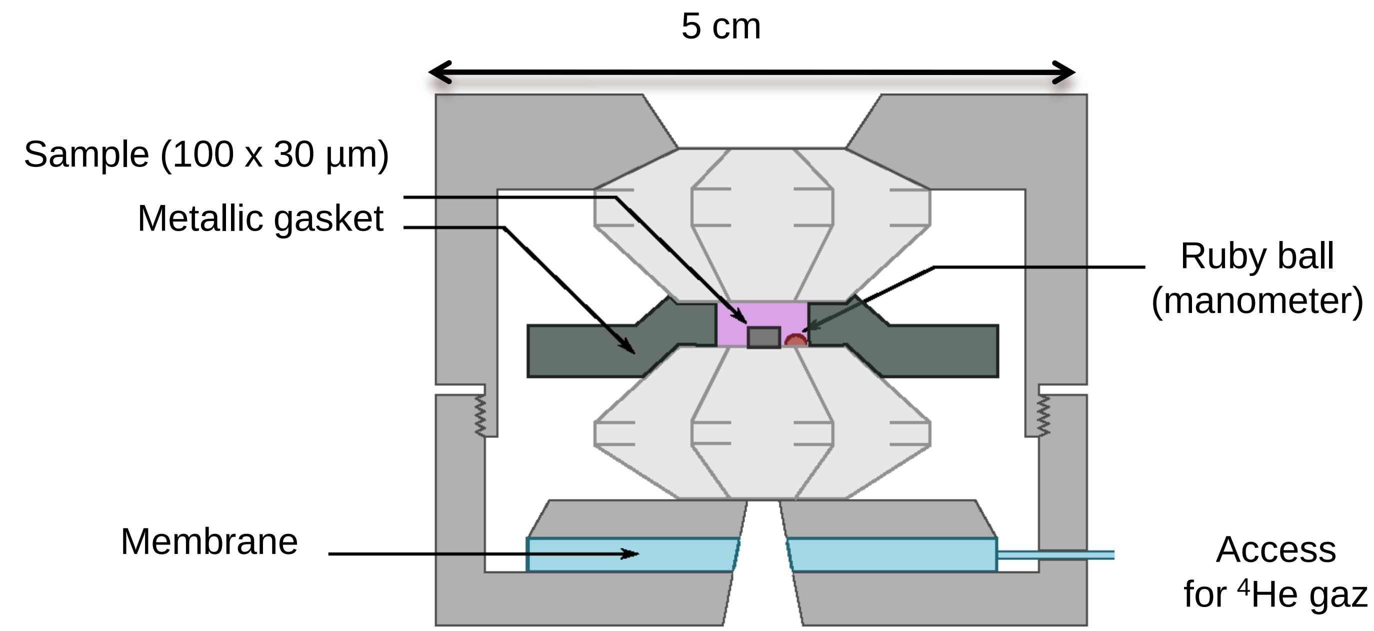
$\mathbf{q} = \mathbf{k}_i - \mathbf{k}_s$

$\mathbf{q} << 1/a$: zone center probe

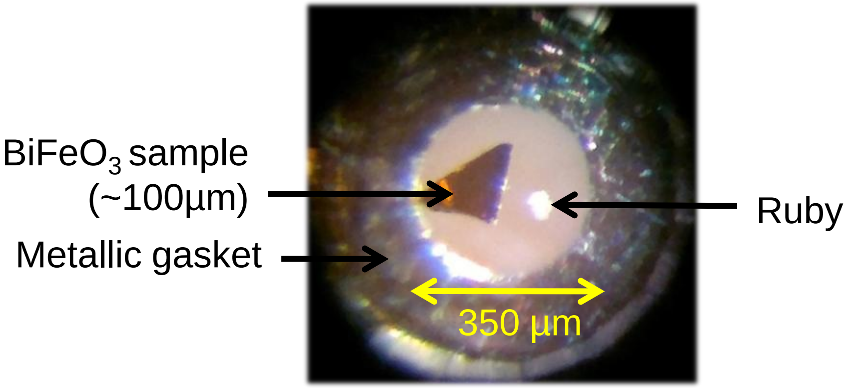




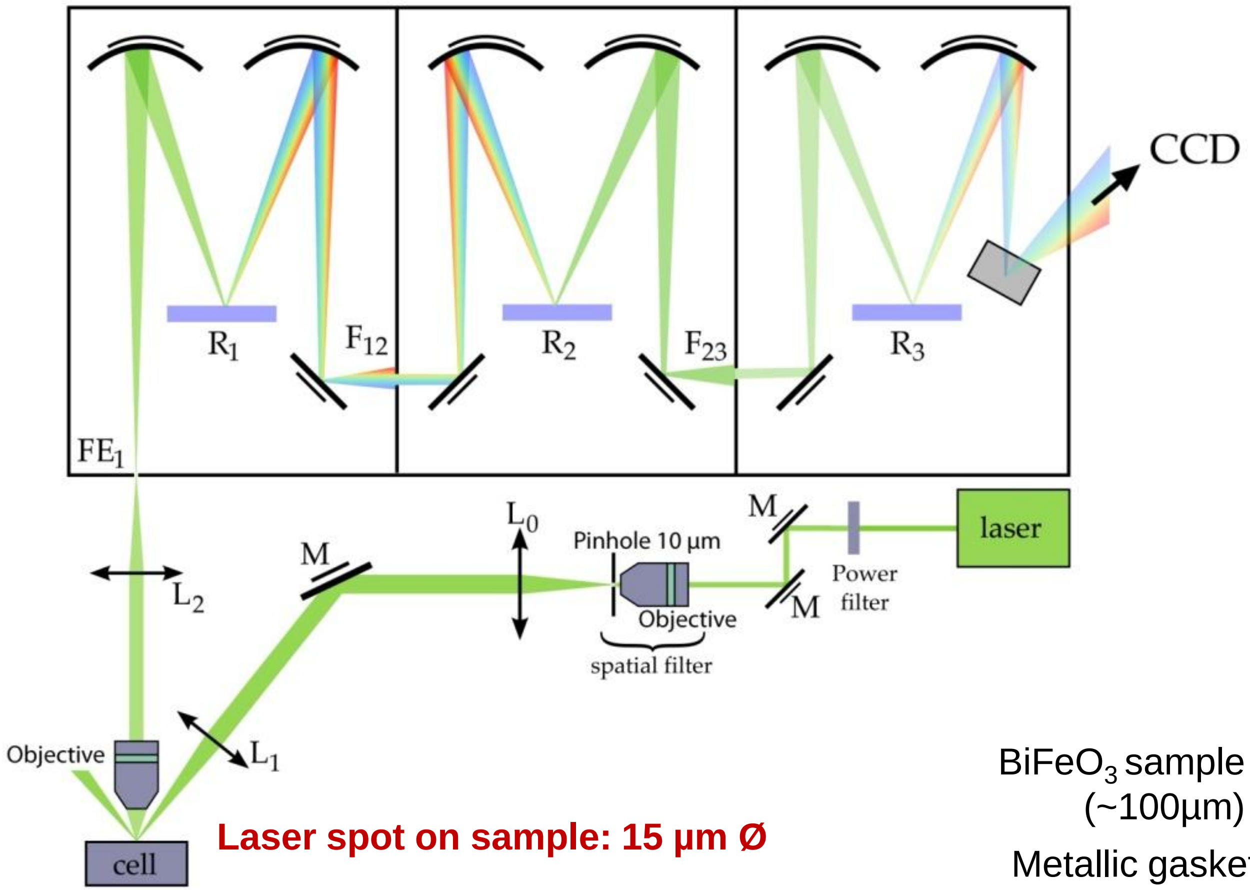
Experimental set up of Raman Spectroscopy under high pressure



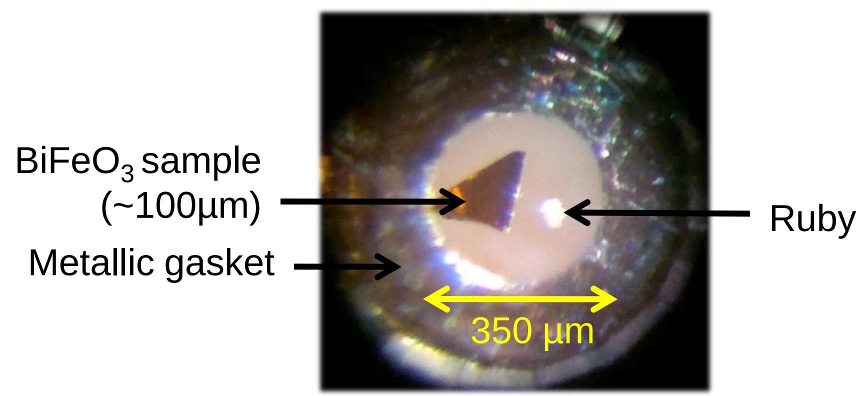
- ✓ Up to 20 Gpa
- ✓ Load with argon gas or helium gas (good hydrostaticity)
- ✓ Diamond anvil cell with membrane: in-situ change of pressure
- ✓Synthetic diamond with Boelher design (large numerical aperture 85°) and low impurities (low Raman signal from diamond)



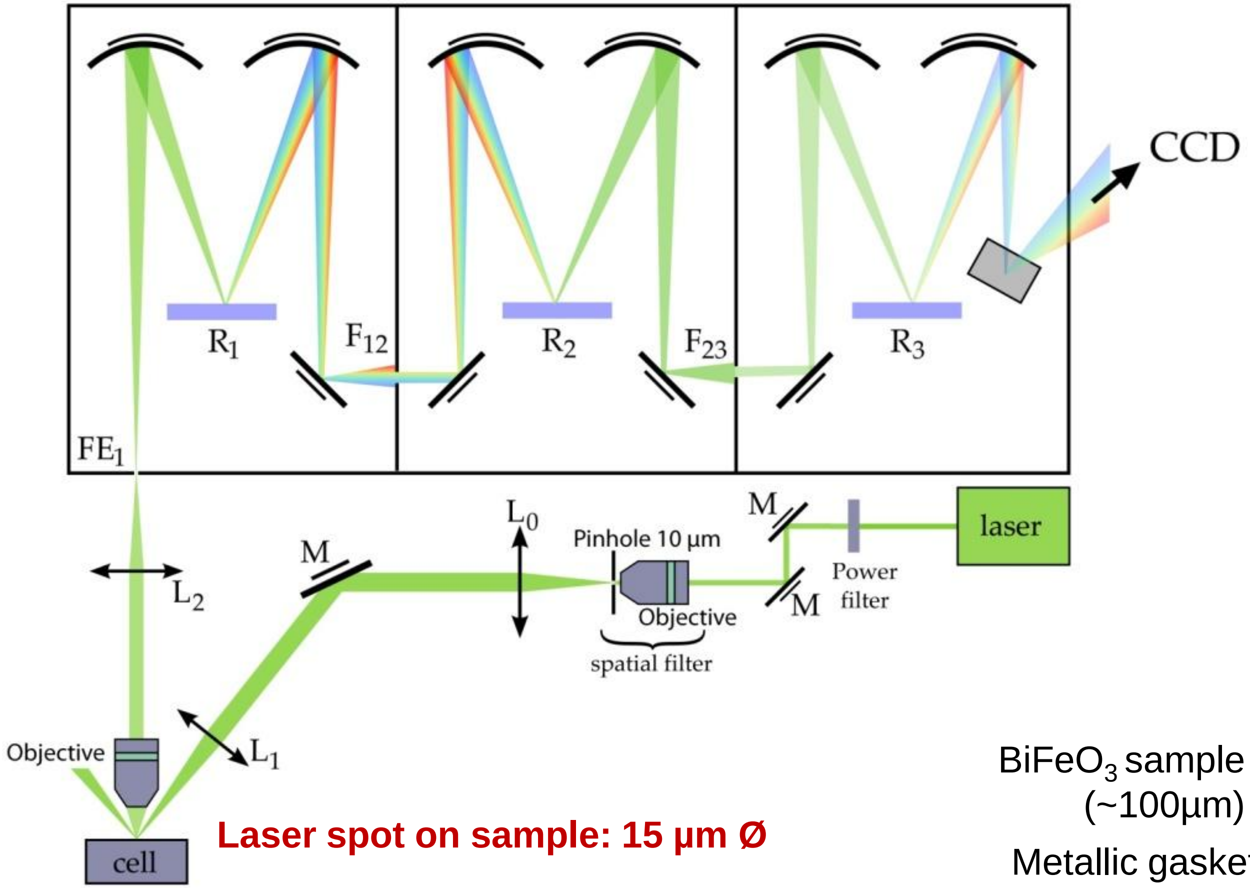
Experimental set up of Raman Spectroscopy under high pressure

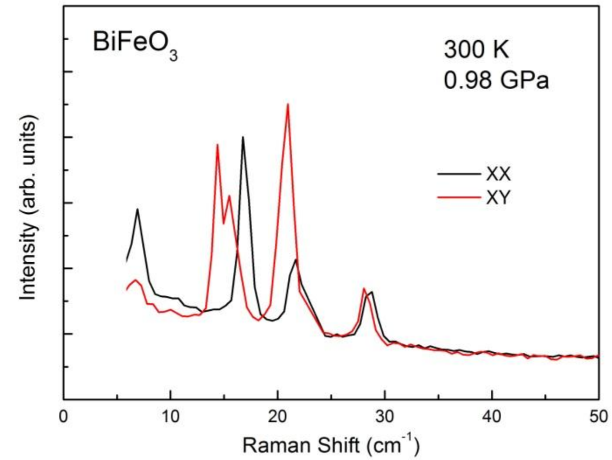


Laser spot on sample: 15 µm Ø

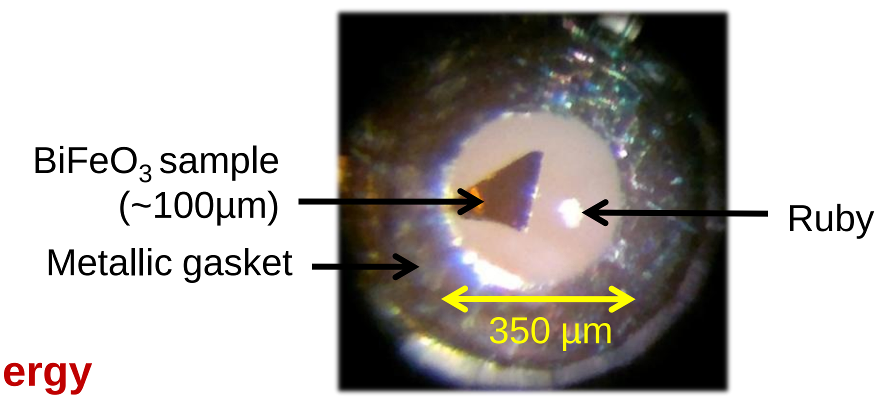


Experimental set up of Raman Spectroscopy under high pressure





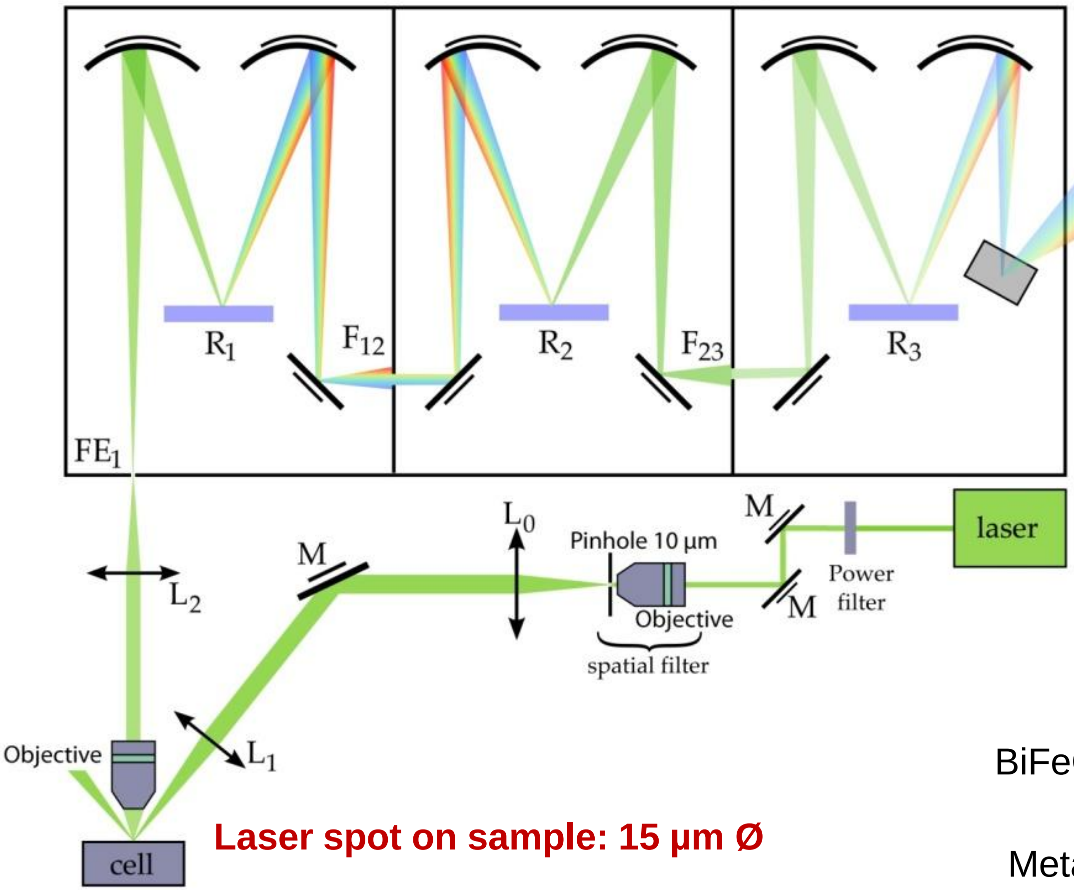
Laser spot on sample: 15 µm Ø

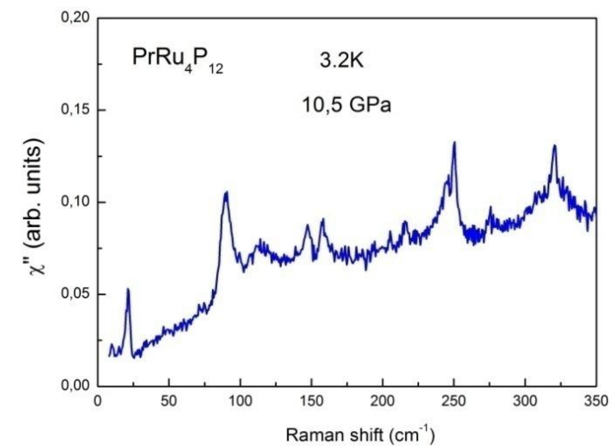


For the first time, possibility to study low energy excitations under pressure (down to 5 cm^{-1}~0.6 meV)

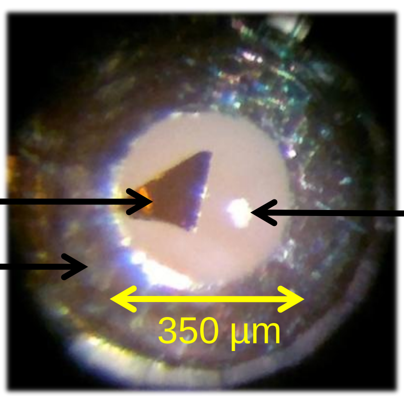
Experimental set up of Raman Spectroscopy under high pressure

At low temperature (down to 3K)





Laser spot on sample: 15 µm Ø



$BiFeO_3$ sample (~100µm)

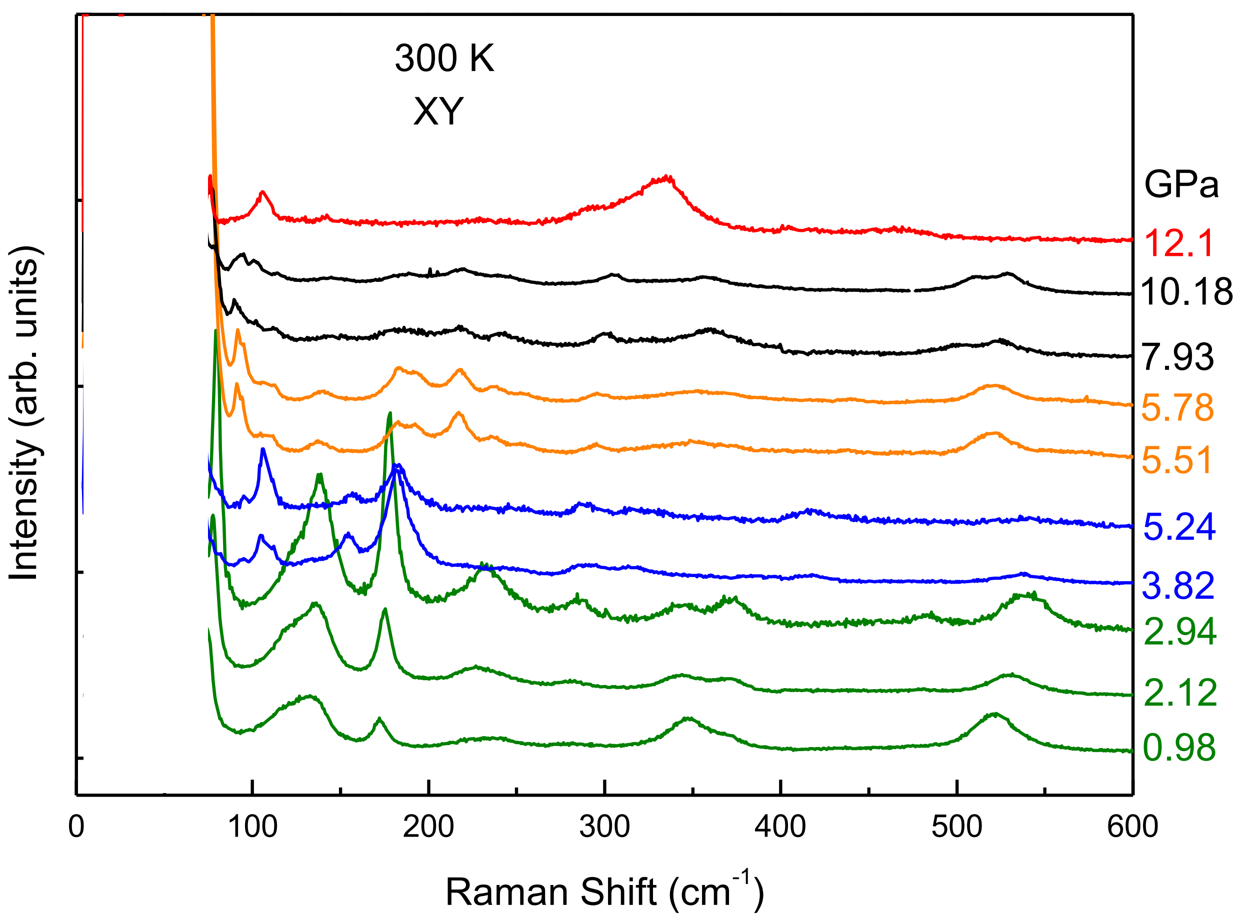
Metallic gasket

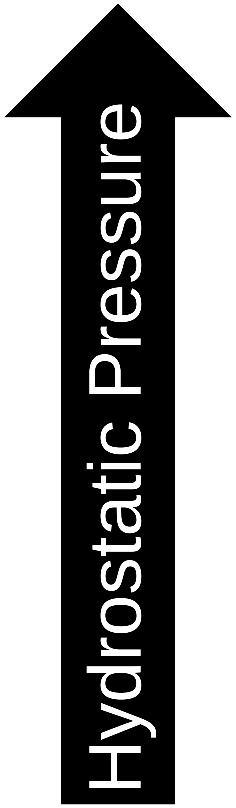
Ruby

For the first time, possibility to study low energy excitations under pressure (down to 5 cm^{-1}~0.6 meV)

Phonon modes under pressure in $BiFeO_3$

✓ Four structural transitions around 3, 5, 8 and 11 GPa, respectively, from R3c to Pmna through three phases.

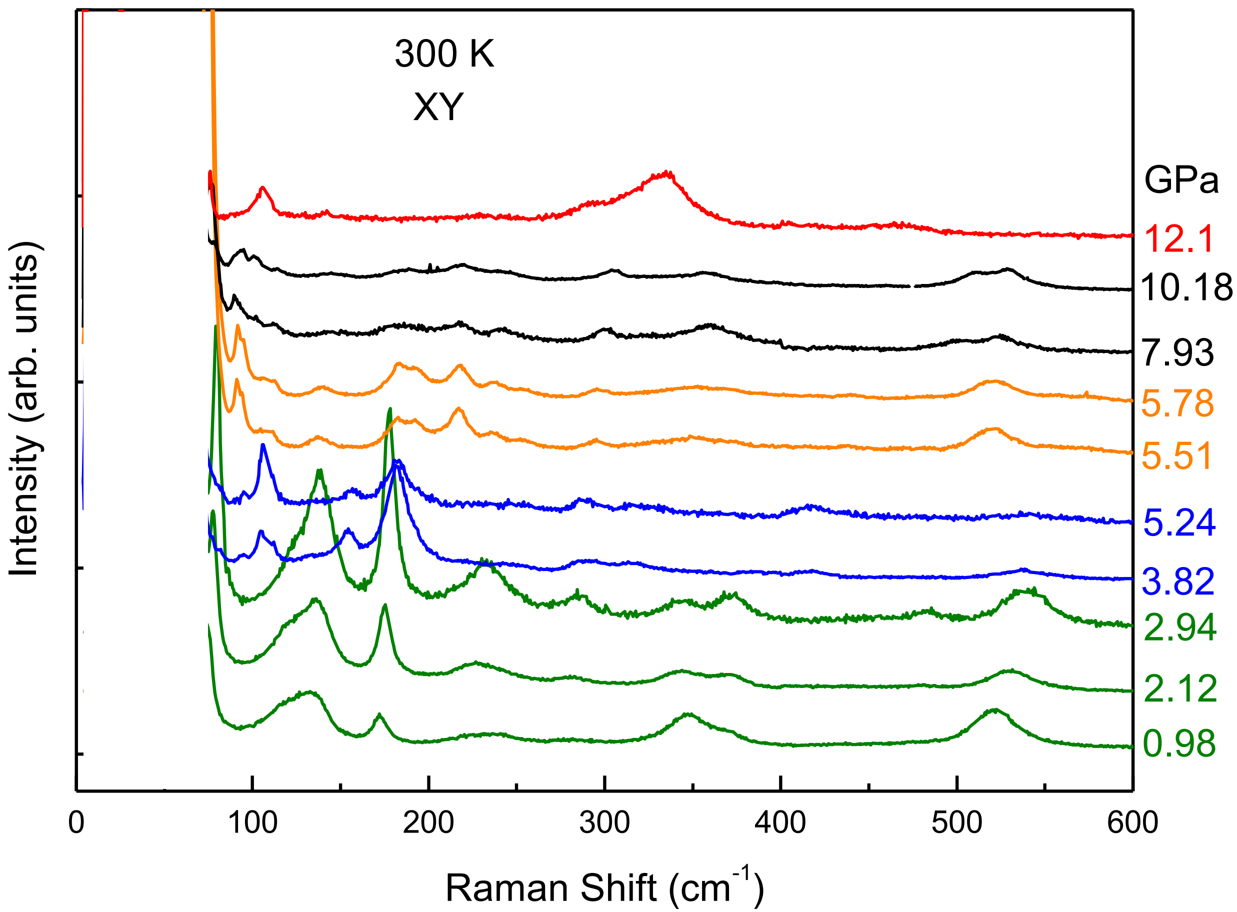


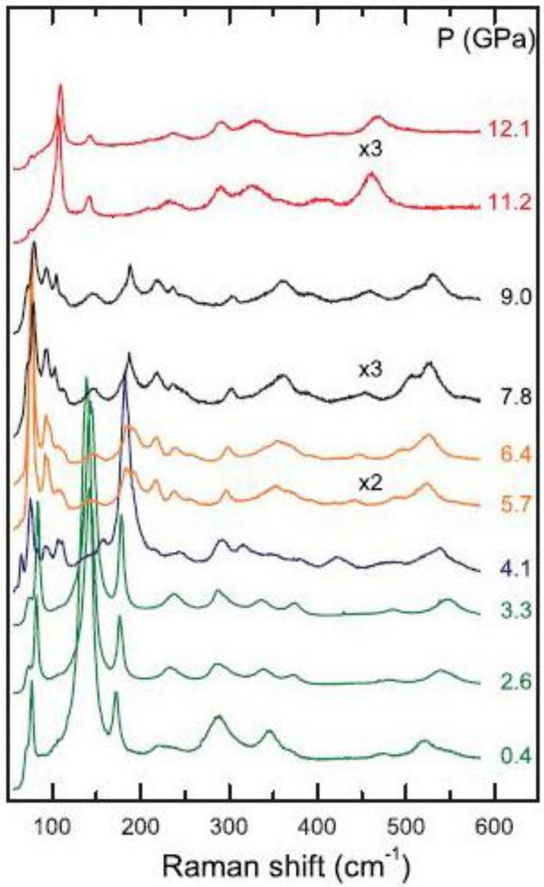


Phonon modes under pressure in $BiFeO_3$

✓ Four structural transitions around 3, 5, 8 and 11 GPa, respectively, from R3c to Pmna through three phases.

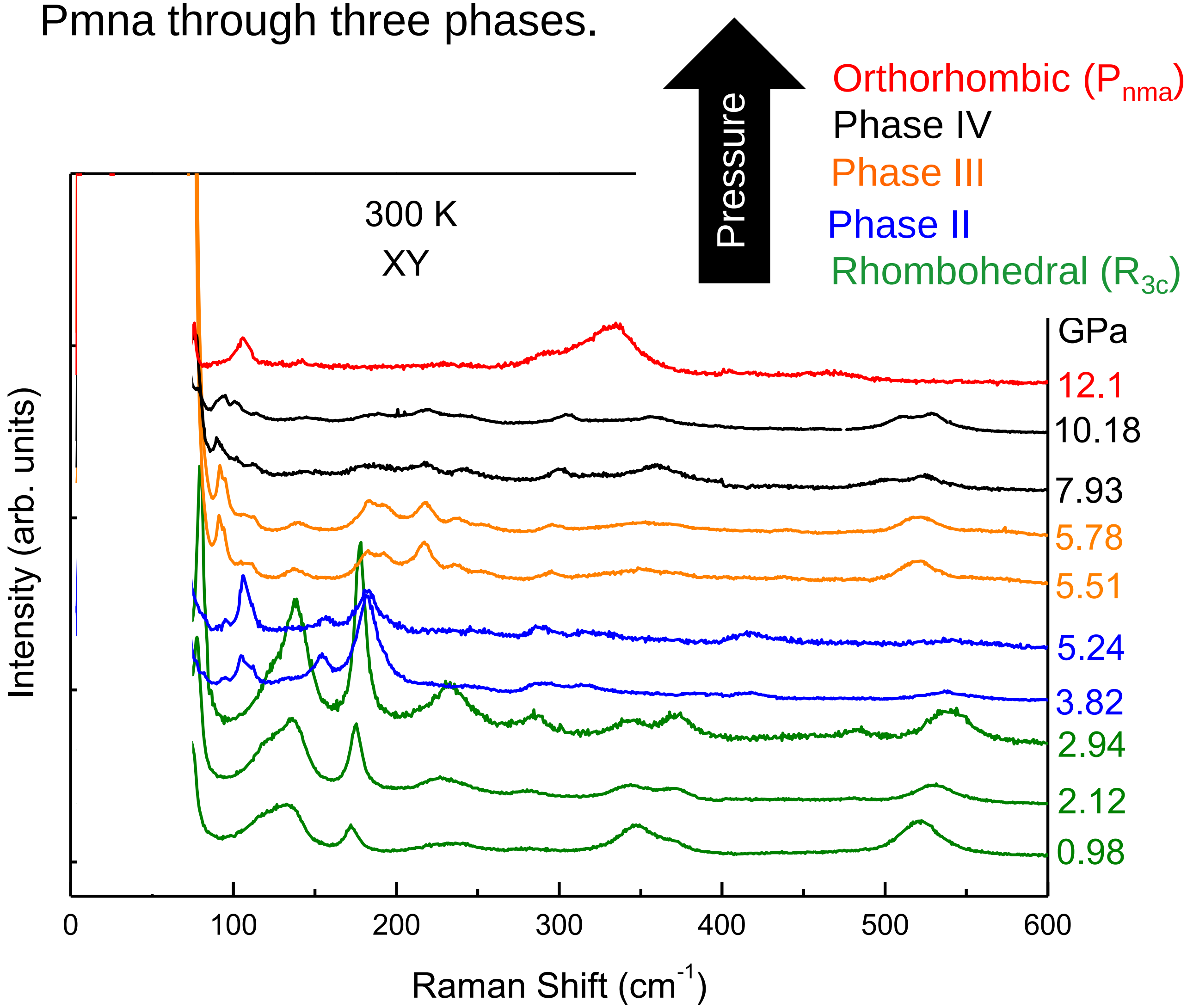
Guennou *et al.* PRB 2011



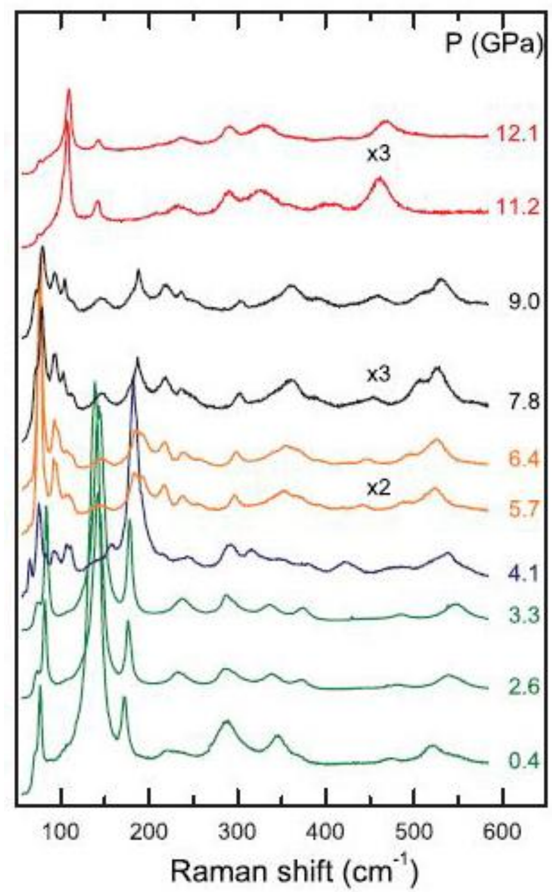


Phonon modes under pressure in $BiFeO_3$

✓ Four structural transitions around 3, 5, 8 and 11 GPa, respectively, from R3c to Pmna through three phases.

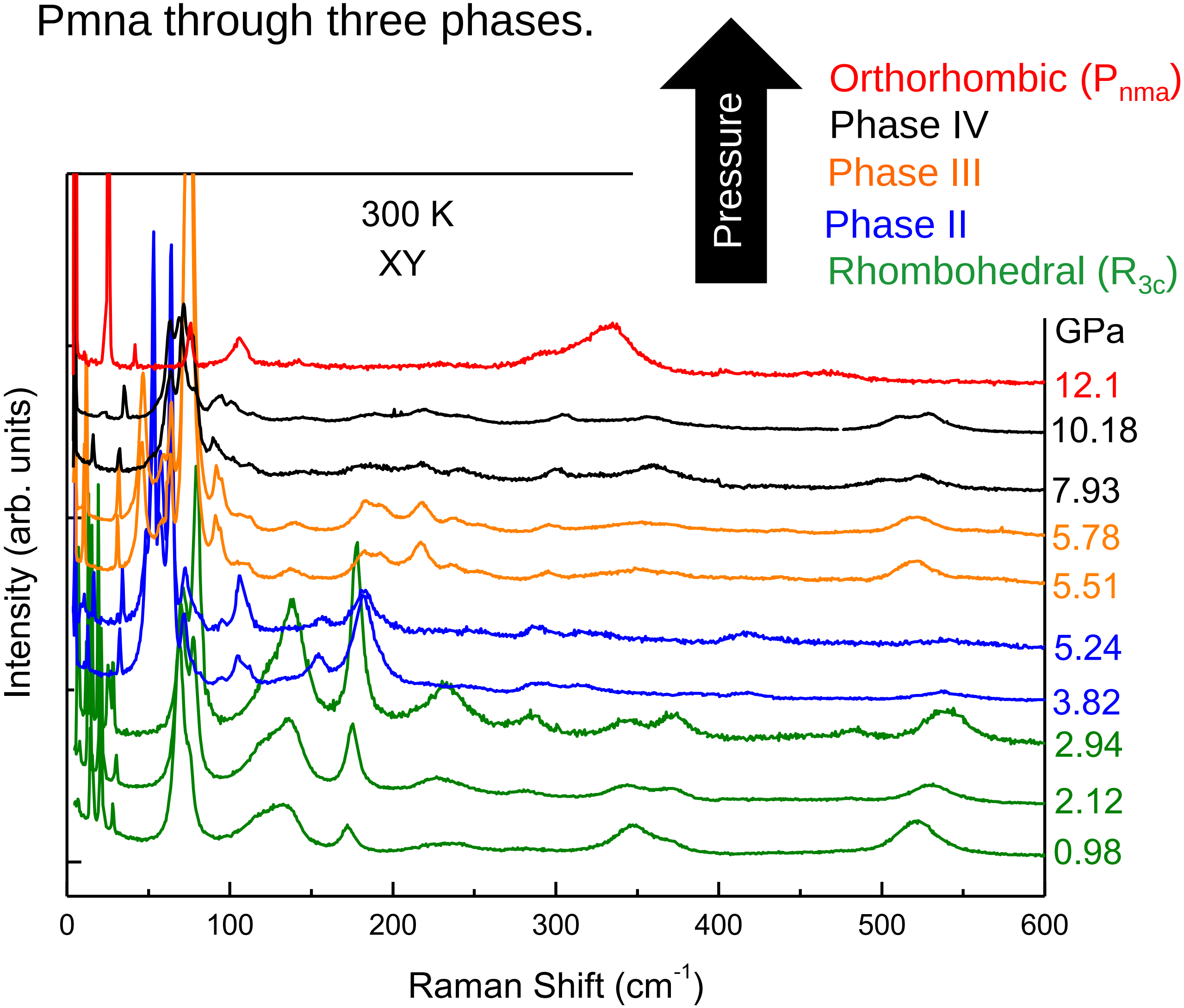


Guennou *et al.* PRB 2011

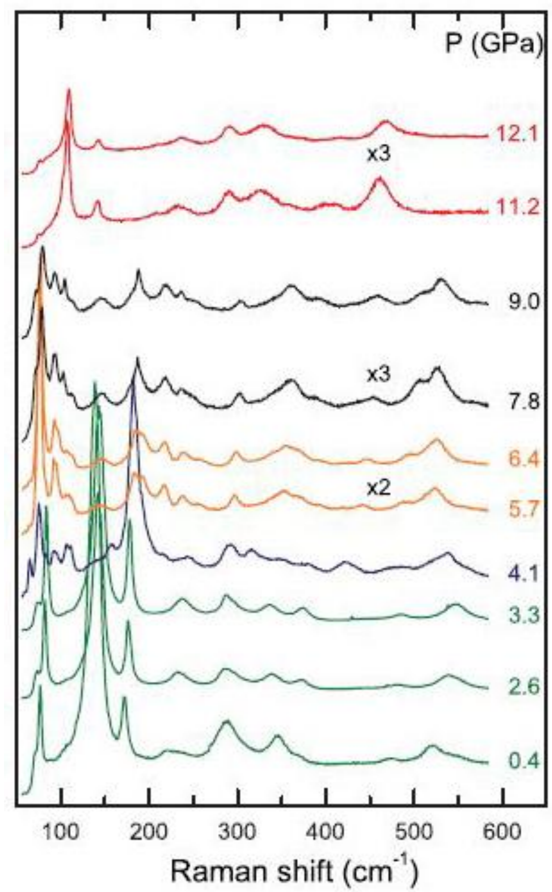


Phonon modes under pressure in $BiFeO_3$

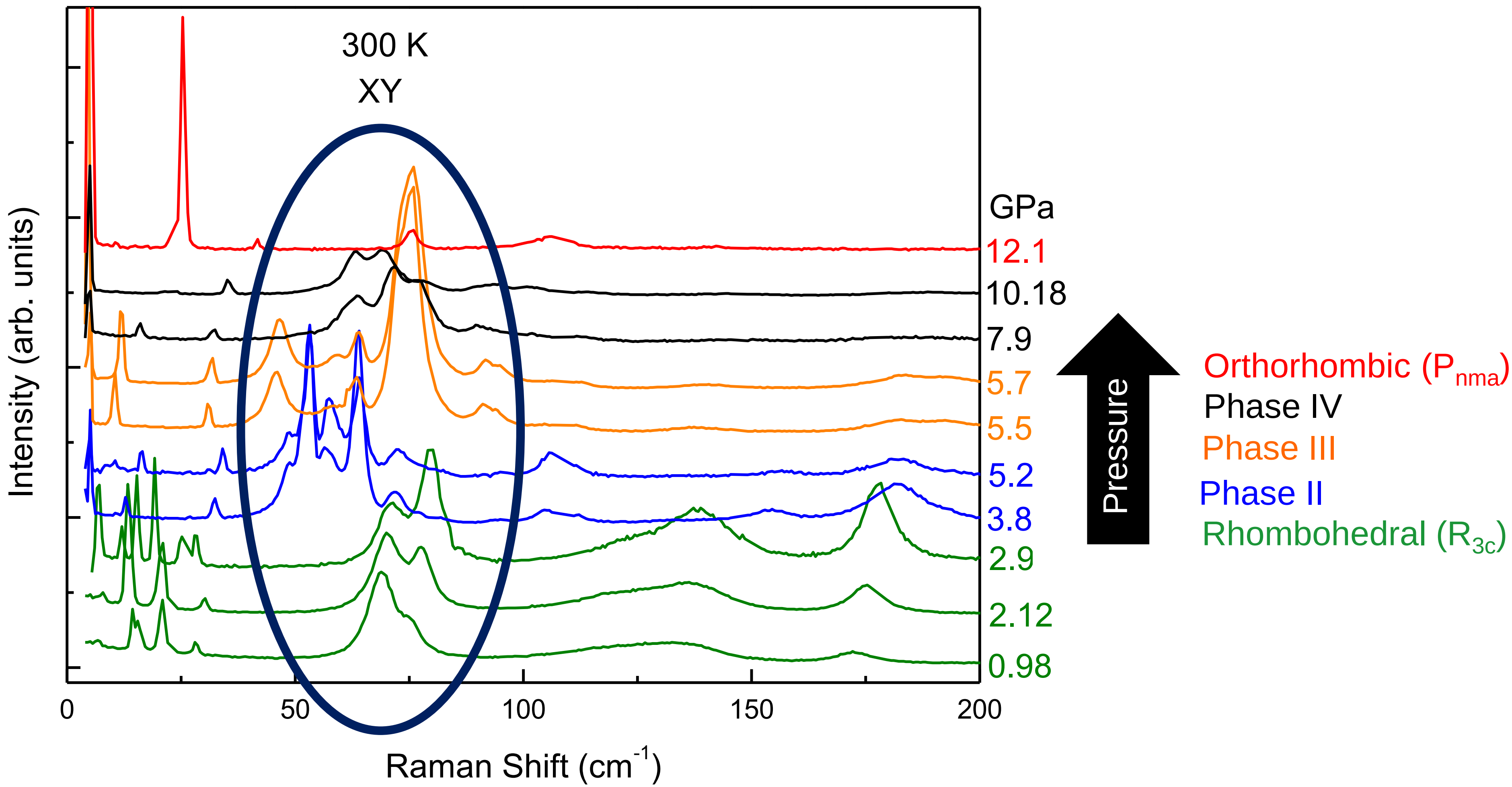
✓ Four structural transitions around 3, 5, 8 and 11 GPa, respectively, from R3c to Pmna through three phases.



Guennou *et al.* PRB 2011

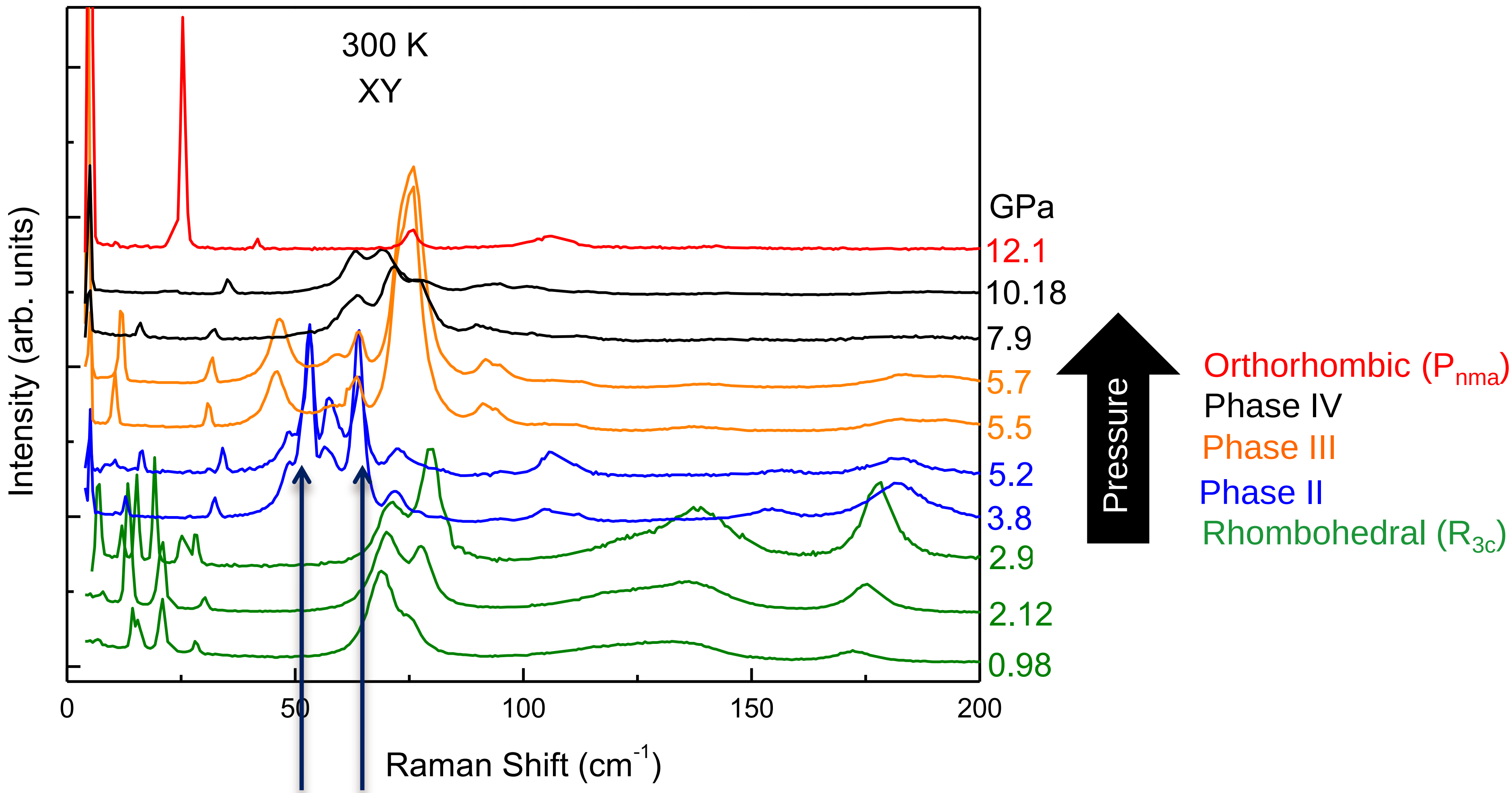


Phonon modes under pressure in $BiFeO_3$



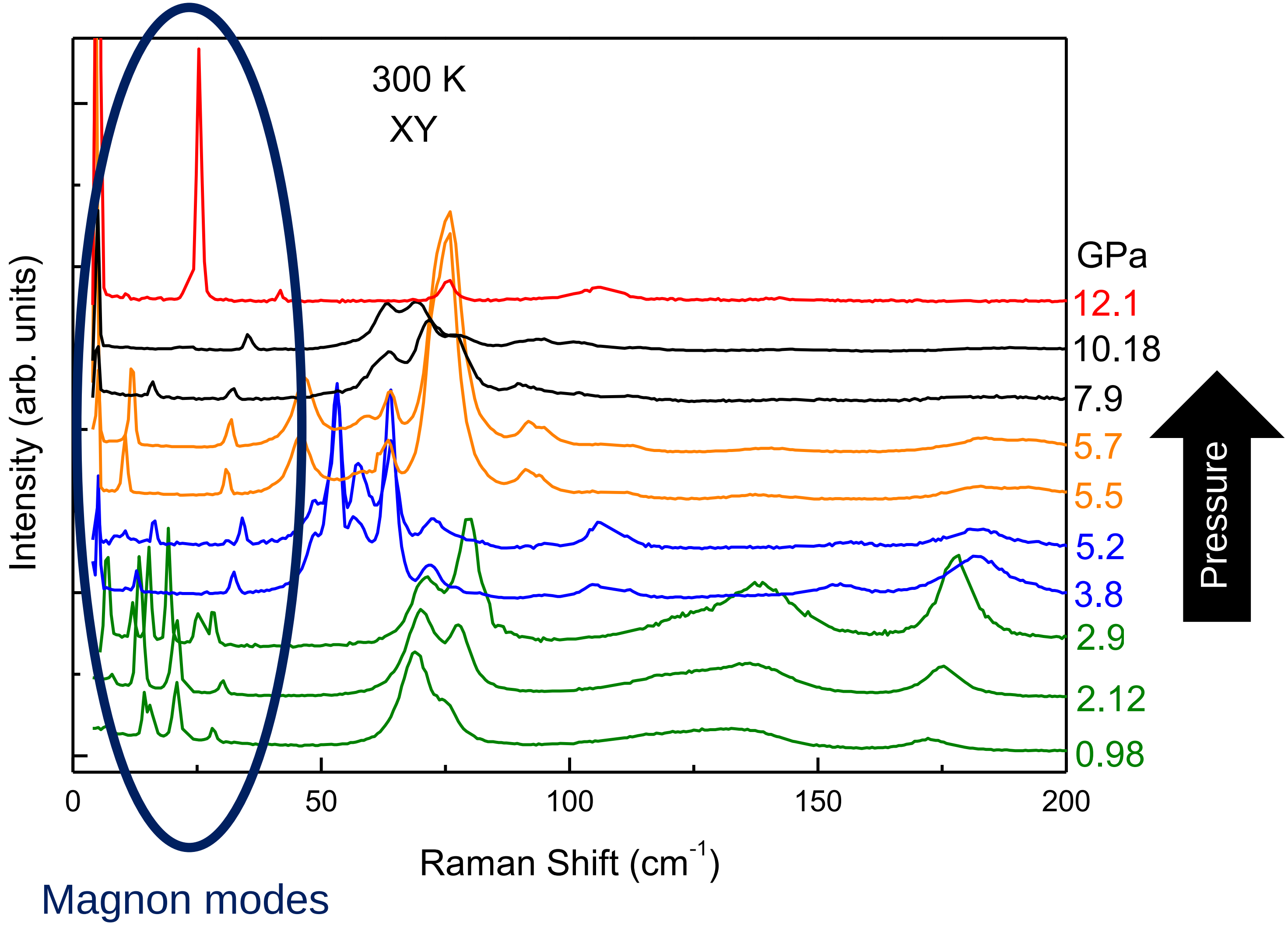
New phonon modes are observed

Phonon modes under pressure in $BiFeO_3$



Narrow peaks in Phase II → tilt of oxygen octahedra

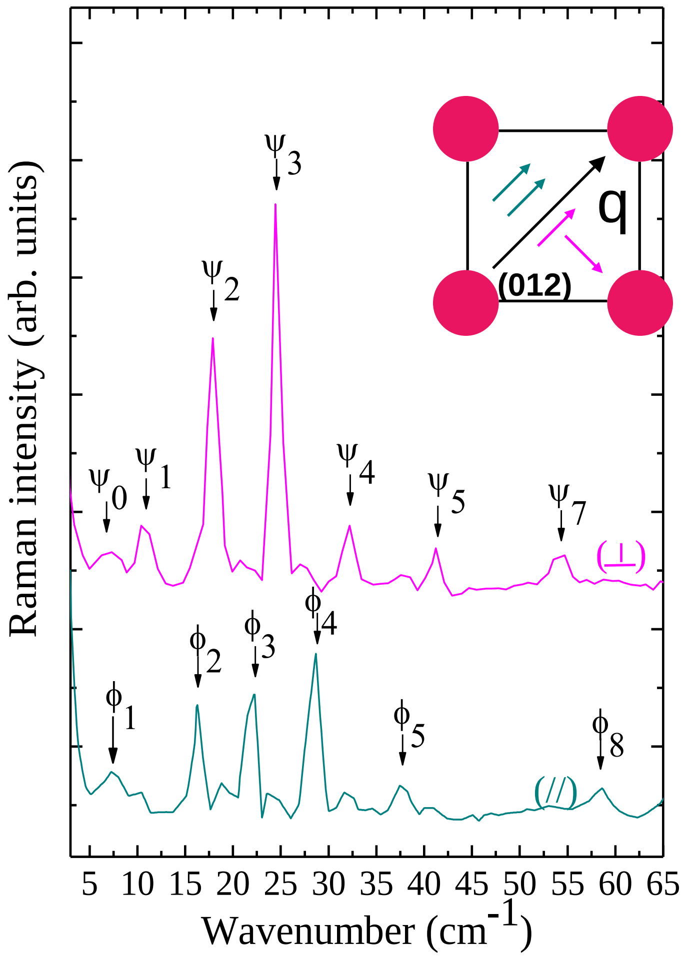
Phonon modes under pressure in $BiFeO_3$

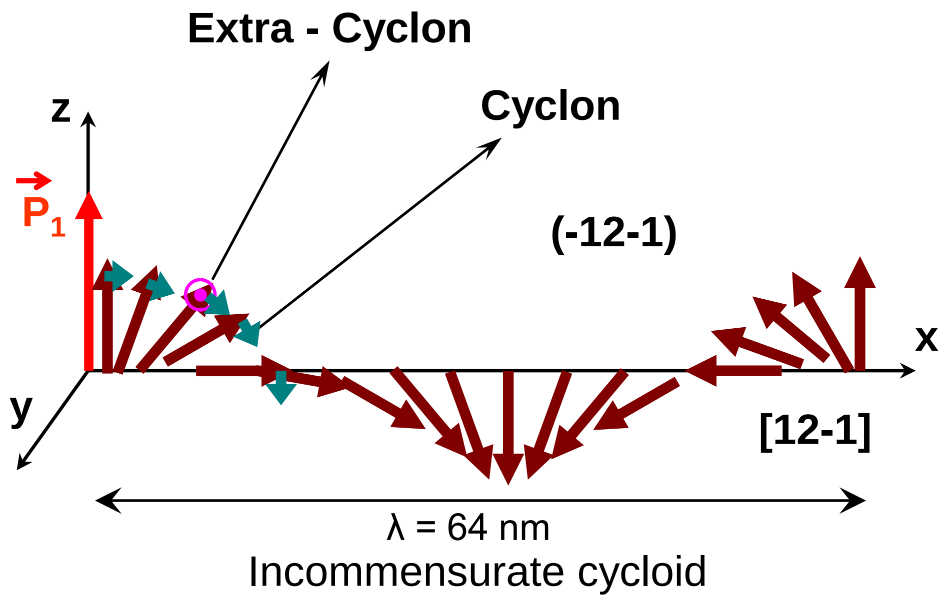


Orthorhombic (P_{nma})
Phase IV
Phase III
Phase II
Rhombohedral (R_{3c})

Magnon modes at ambient pressure in $BiFeO_3$: a fingerprint of the cycloid

Cazayous *et al.* PRL 2008
De Sousa *et al.* PRB 2008



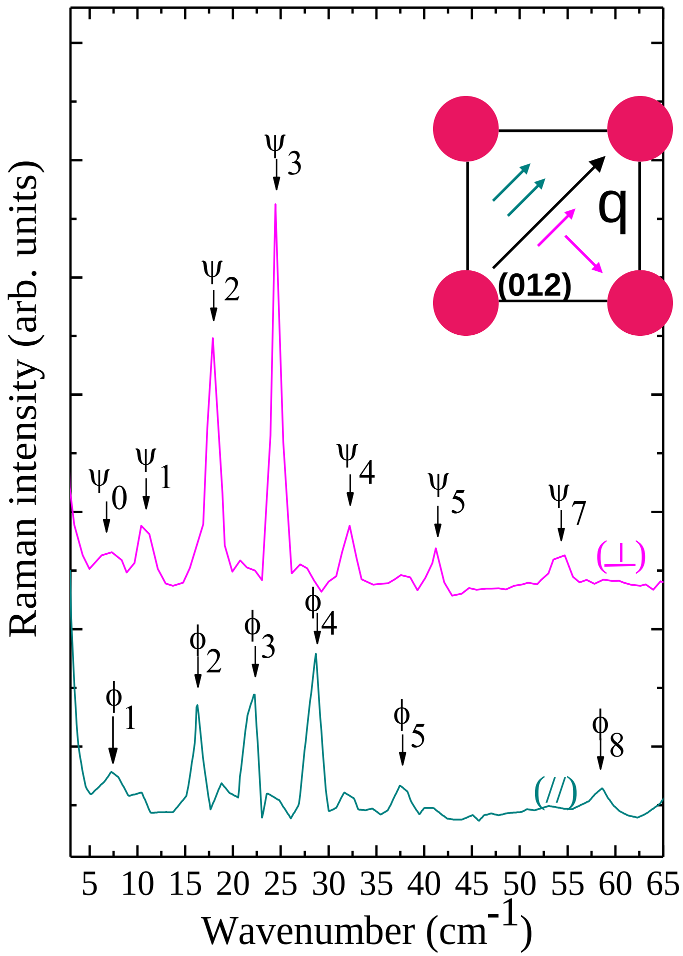


✓ Two modes of spin excitations Φ_n and Ψ_n

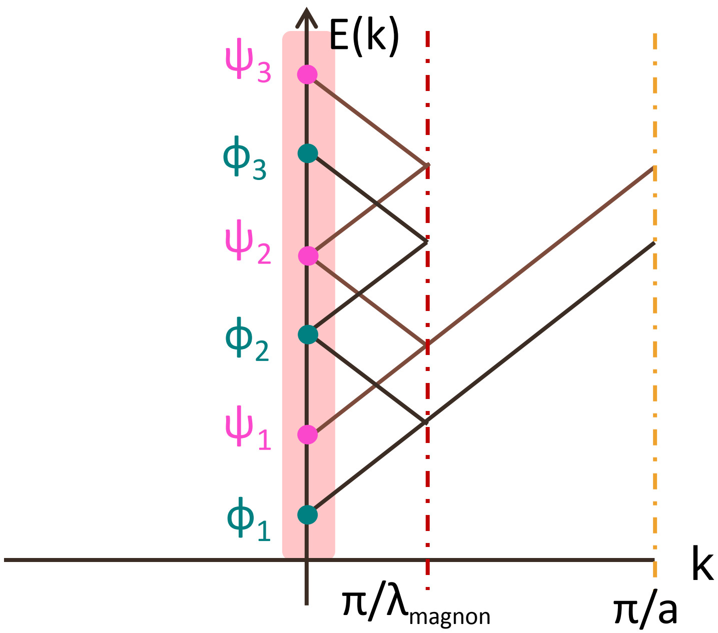
Φ_n : in-plane mode
Ψ_n : extra-plane

Magnon modes at ambient pressure in $BiFeO_3$: a fingerprint of the cycloid

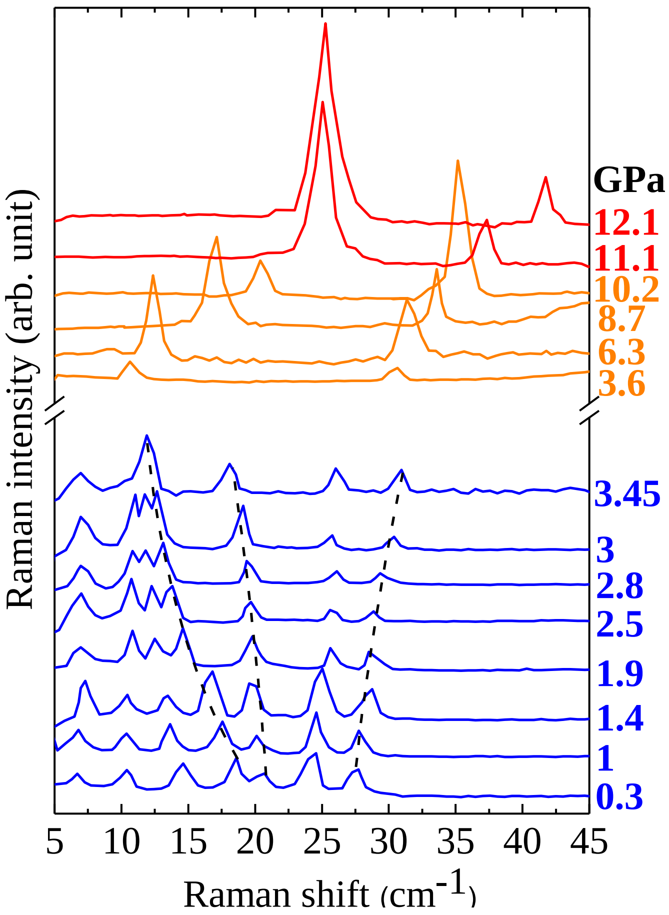
Cazayous *et al.* PRL 2008
De Sousa *et al.* PRB 2008



✓ Folding of the magnons branches at the Brillouin zone center



Magnon modes under pressure in $BiFeO_3$

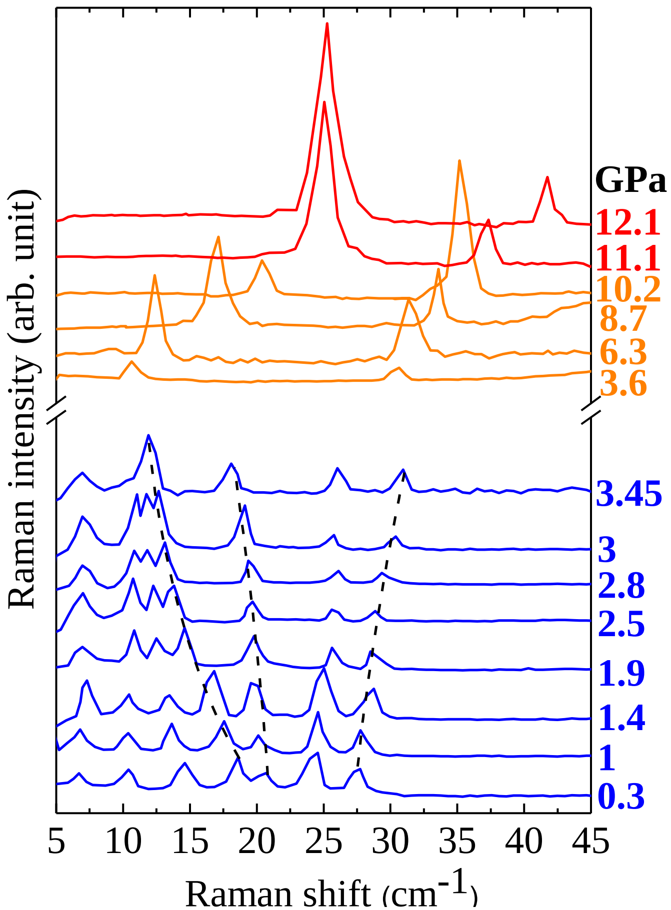


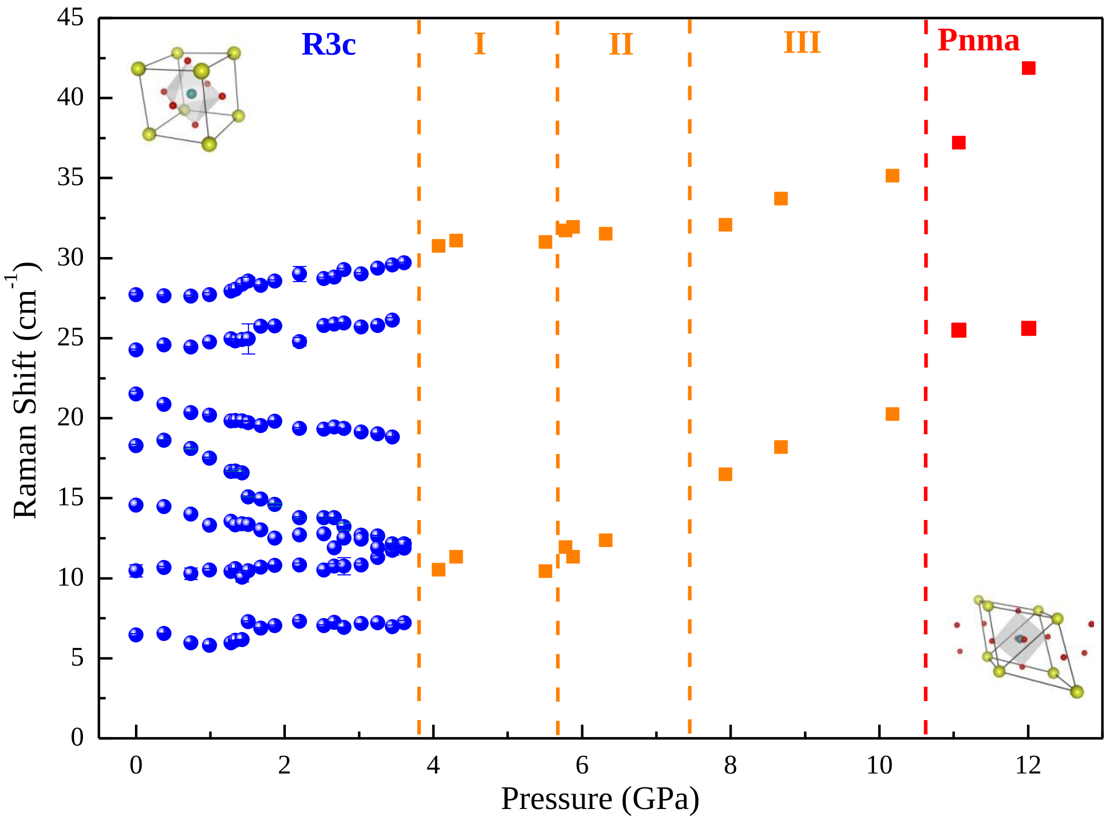
Orthorhombic (P_{nma}) structure

Phases II, III, IV

Rhombohedral (R_{3c}) structure

Magnon modes under pressure in $BiFeO_3$





✓ In R3c phase, shifting of the magnetic excitations

✓ Above 3.5 GPa, after the 1st structural transition, only two magnetic excitations remain.

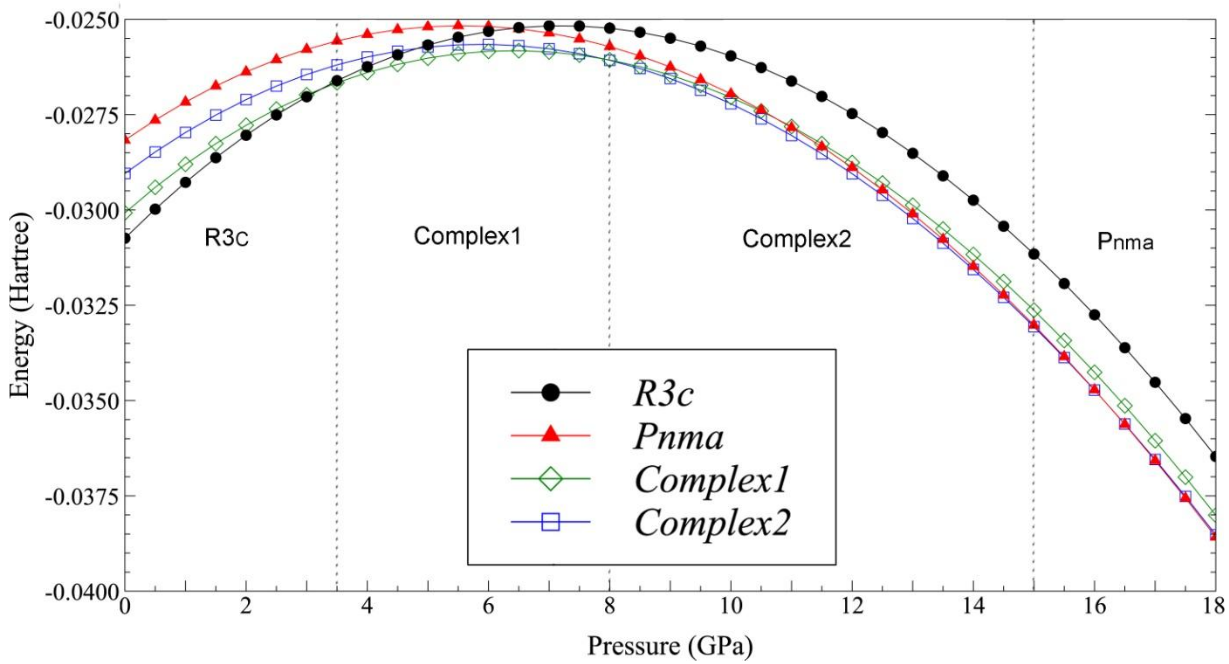
✓ Vanishing of the magnetic cycloid at the first structural transition

→ AF structure (with certainly spin canting)

Theoretical calculations of the structural phases

Derive from: Rahmedov, D., **Wang D.**, Íñiguez, J. & **Bellaiche L.**, Phys. Rev. Lett. 129, 037207 (2012)

✓ Energies of each phase calculated with an effective Hamiltonian scheme. (Ferroelectricity, oxygen octahedra tilting, strain, magnetic moment and their mutual couplings)



Three structural phase transitions:

- At 3.5GPa, R3c → Complex1
- At 8GPa, Complex1 → Complex2 (Complex oxygen octahedra tiltings)
- At 15GPa, Complex2 → Pnma

Theoretical calculations of the magnetic structure

Derive from: Rahmedov, D., **Wang D.**, Íñiguez, J. & **Bellaiche L.**, Phys. Rev. Lett. 129, 037207 (2012)

✓ Spin-current model describing the electric and magnetic dipole interactions:

$$E_{\text{E-M}} = \sum_{i,j} C\,(\mathbf{u}_i \times \mathbf{e}_{ij}) \cdot (\mathbf{m}_i \times \mathbf{m}_j)$$

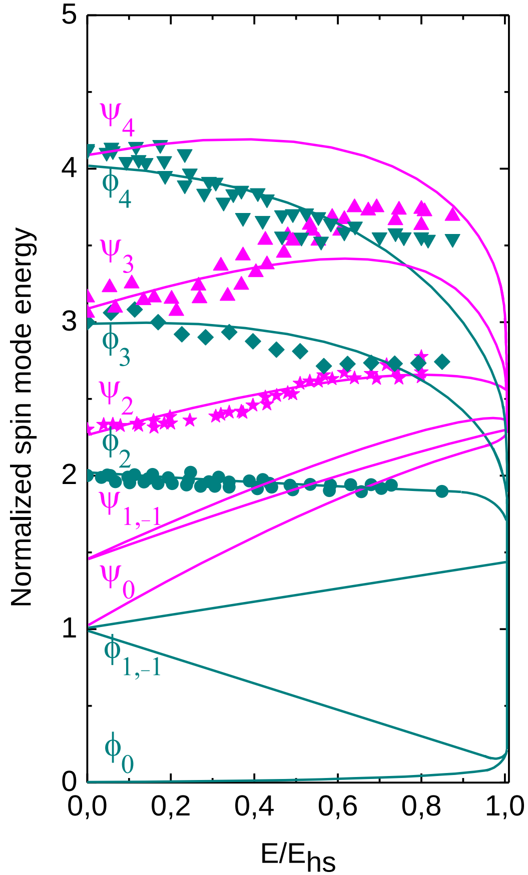
i runs over all the Fe sites
j runs over the second-nearest neighbours (12 sites) of the site i
C is the coupling coefficient
u_i and m_i represent the electric and magnetic dipoles
e_{ij} is a vector along the direction connecting site i and j

- Cycloid vanishing is expected at the first structural transition
- AF structure with spin canted is expected in Complex 1 and 2
- Cycloid is forbidden in Pnma phase (non-polar phase)

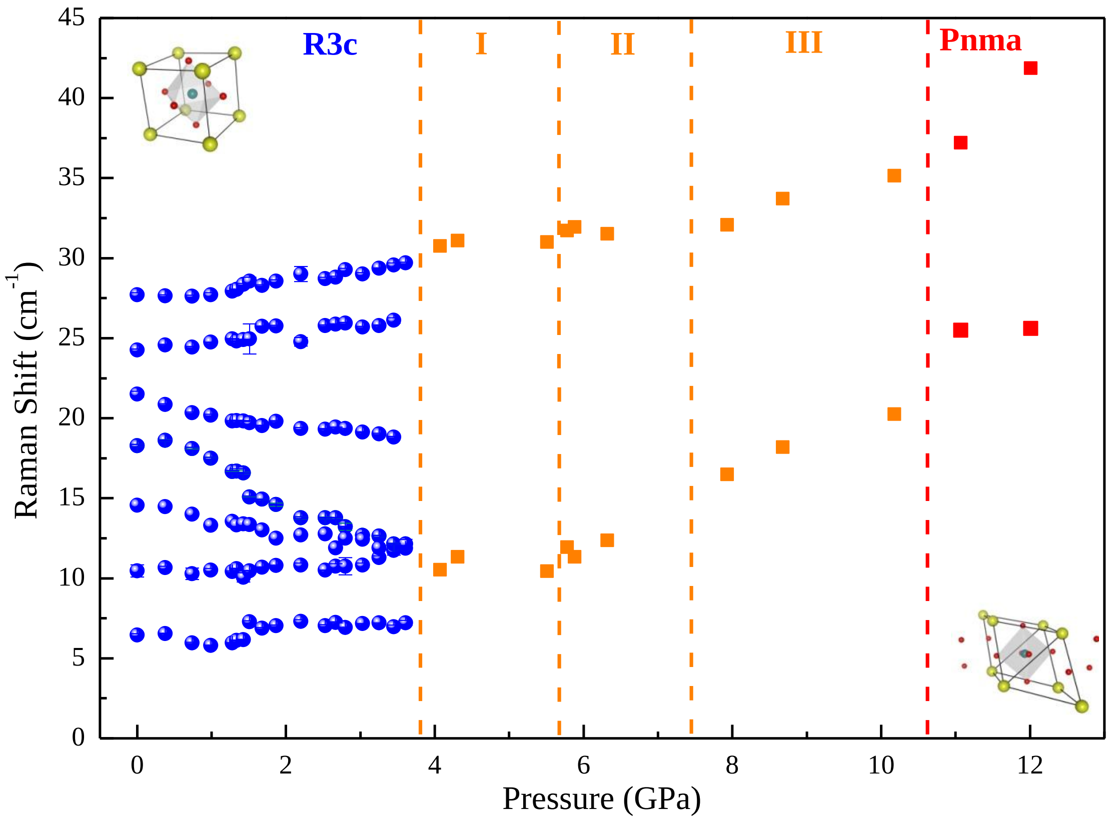
- At the first structural transition, the average electric dipole changes from [111] to approximately [012] for Complex1 and decrease in magnitude.

Magnon modes under pressure in $BiFeO_3$

✓Shift of the magnetic excitations vs electric field : can be interpreted using the Landau free-energy model.



With E_{hs}=160 kV/cm

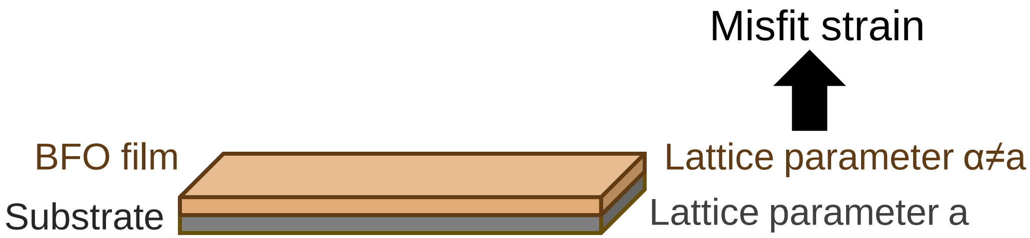


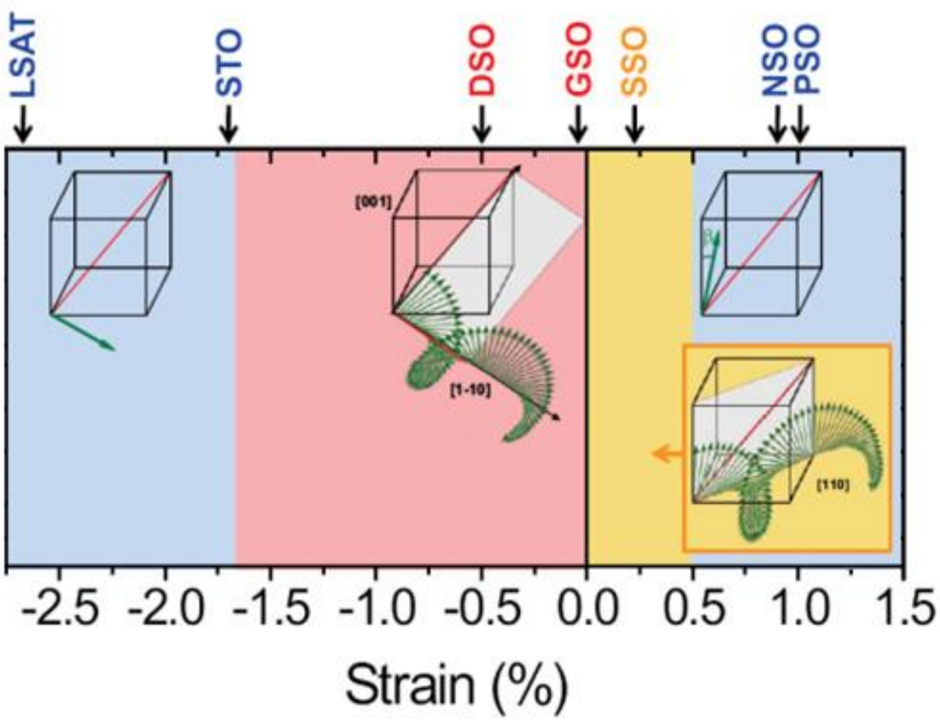
R. De Sousa and M. Cazayous, Phys. Rev. Lett. (2013)

Magnetoelectric mechanism under hydrostatic pressure?

Ongoing analysis

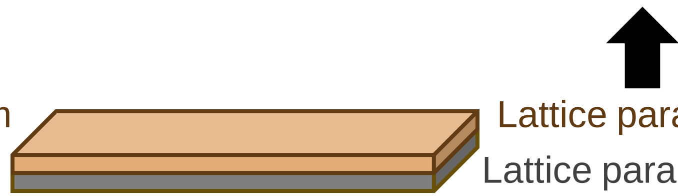
Comparison with thin films

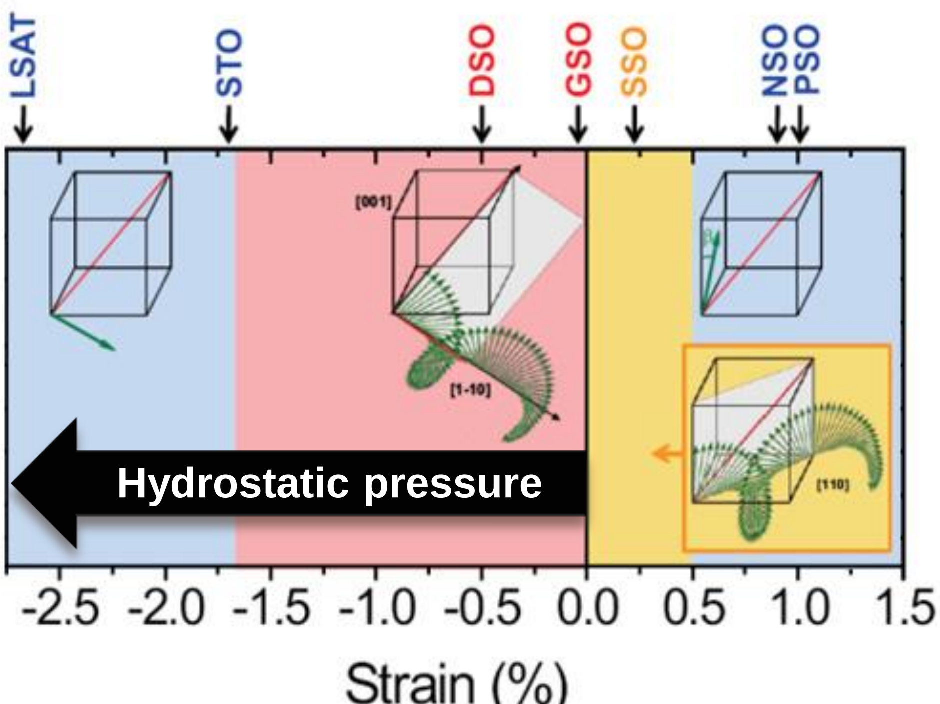




D. Sando et al., Nat. Mater. 12, 641–646,(2013)

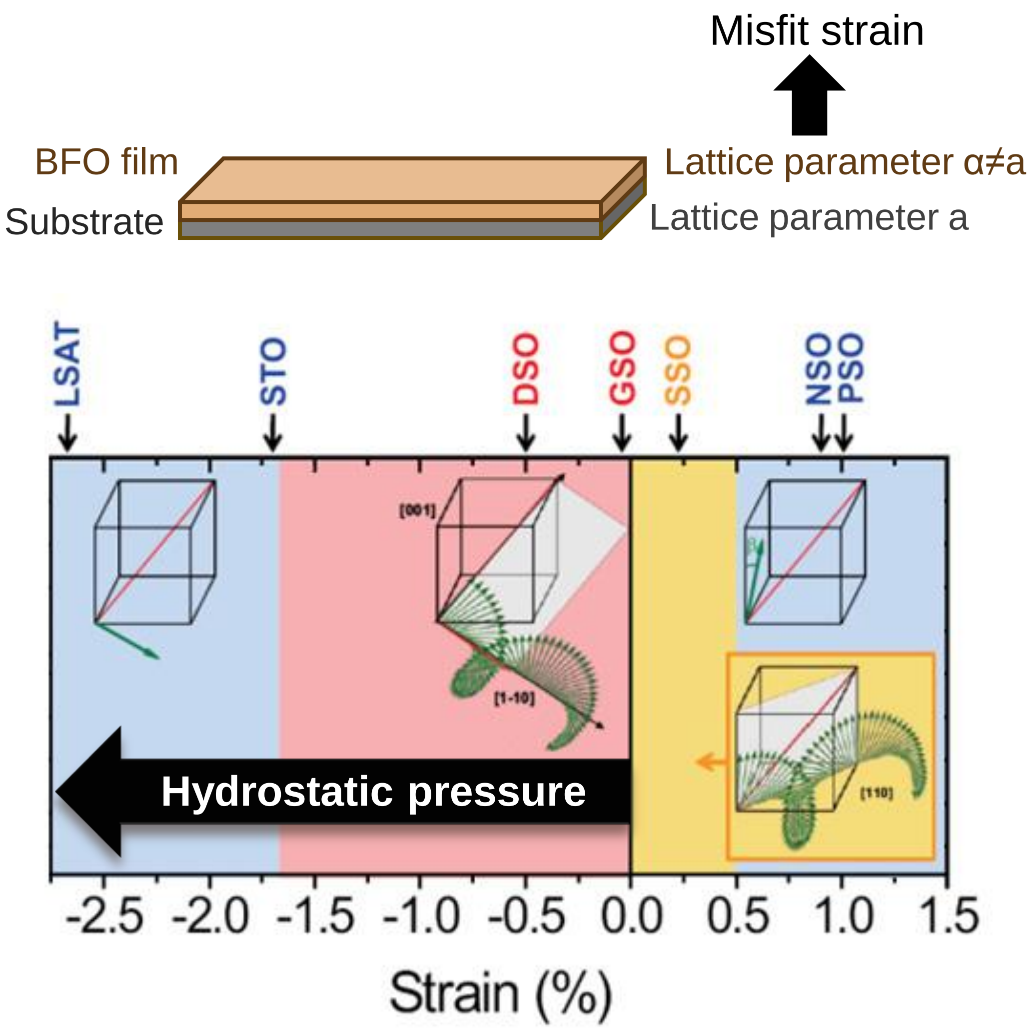
Comparison with thin films



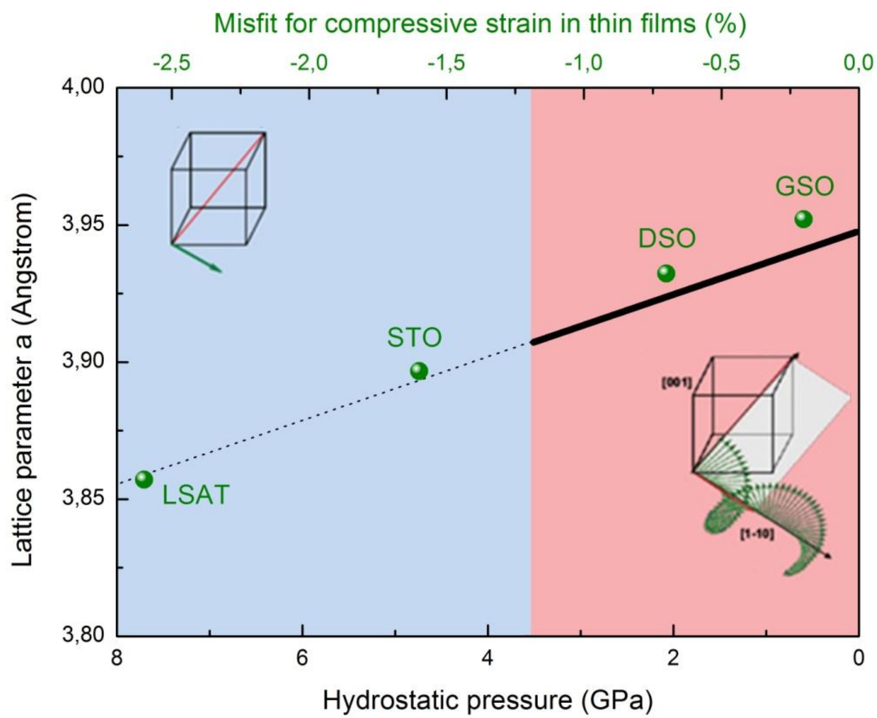


D. Sando et al., Nat. Mater. 12, 641–646,(2013)

Comparison with thin films

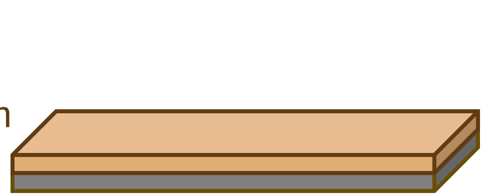


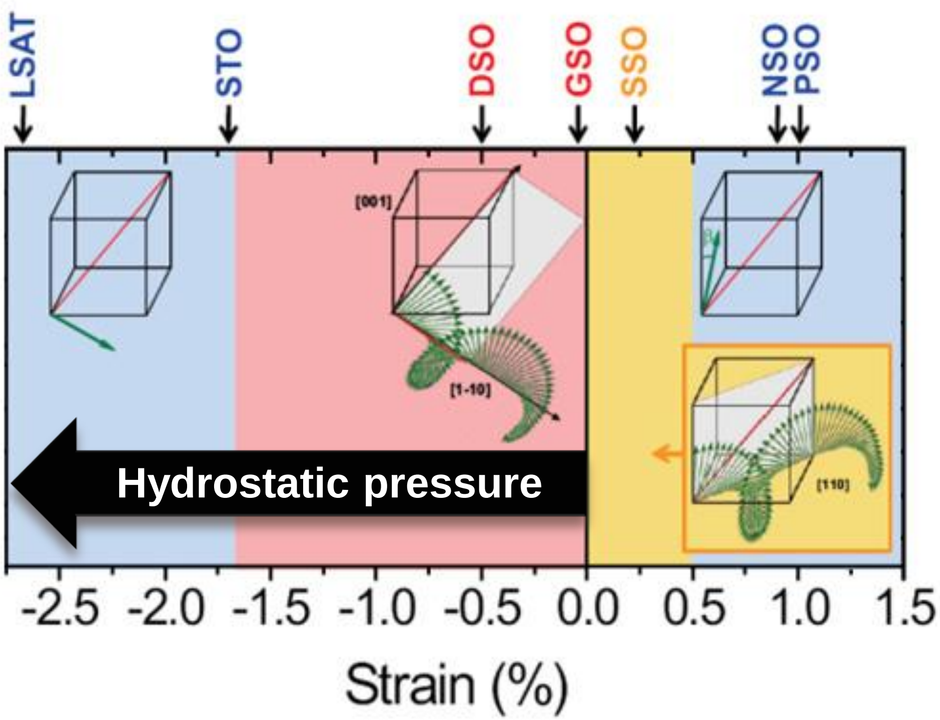
Guennou *et al.* PRB 2011



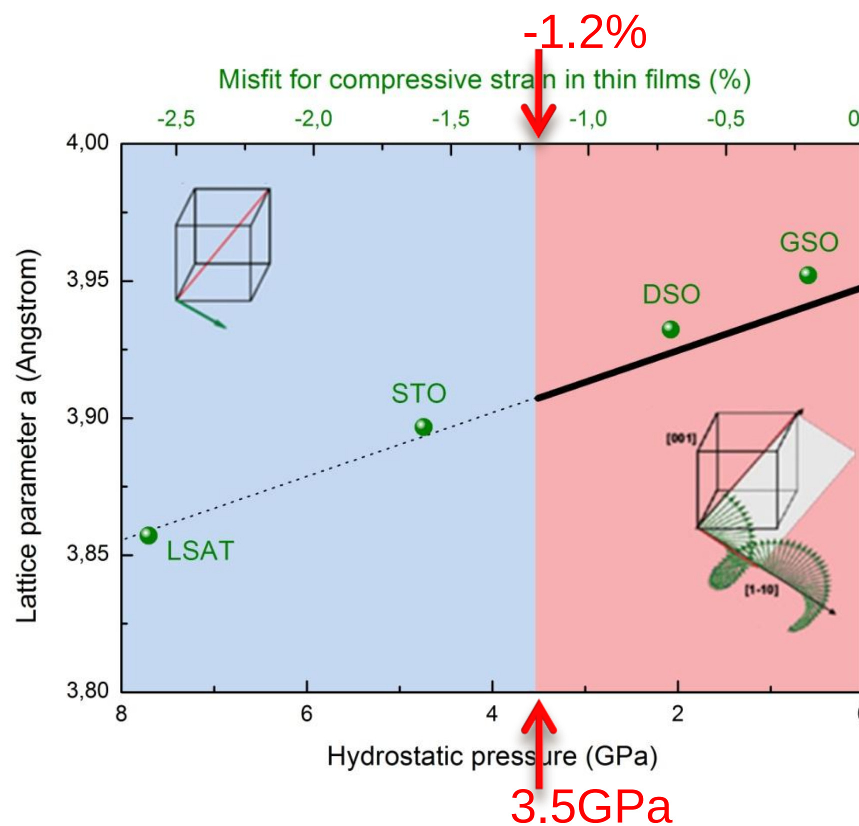
D. Sando et al., Nat. Mater. 12, 641–646,(2013)

Comparison with thin films





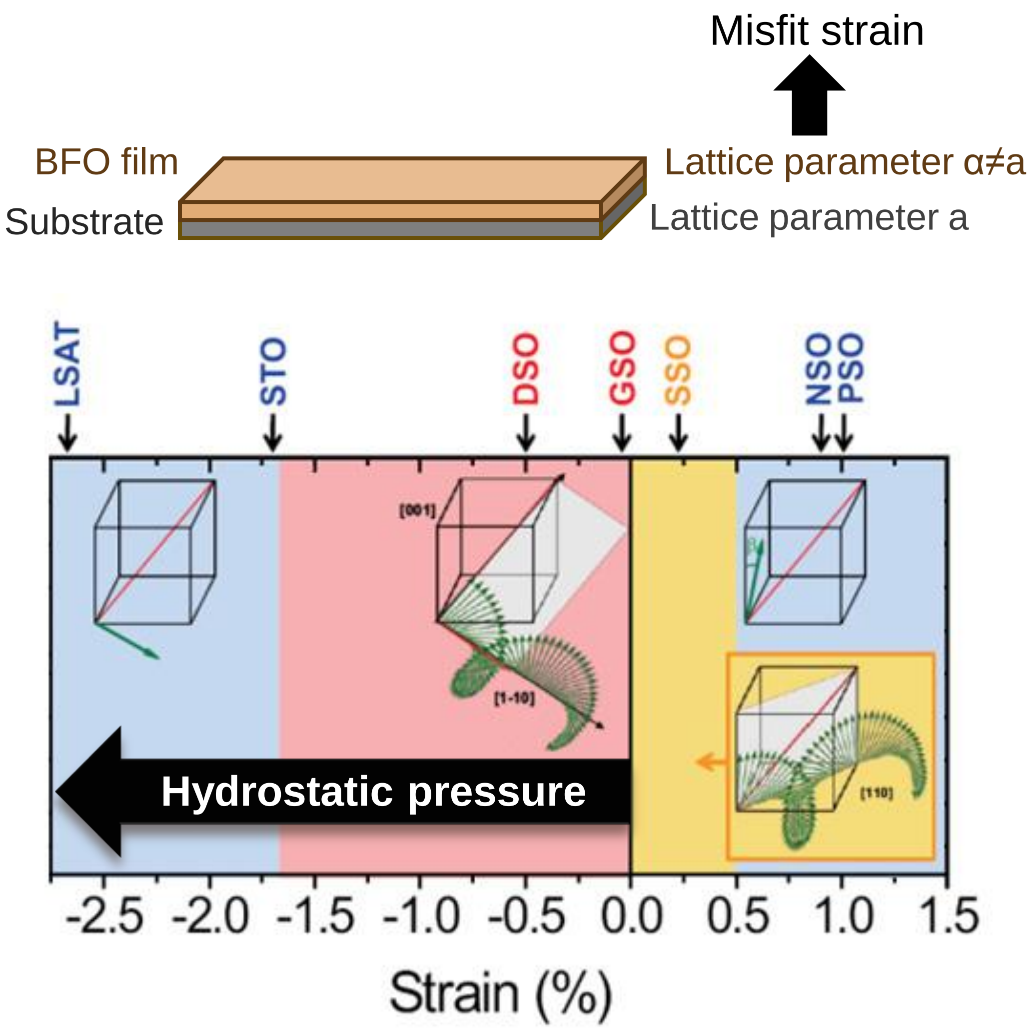
Guennou *et al.* PRB 2011



✓ No structural transition in thin films below -5% of misfit.

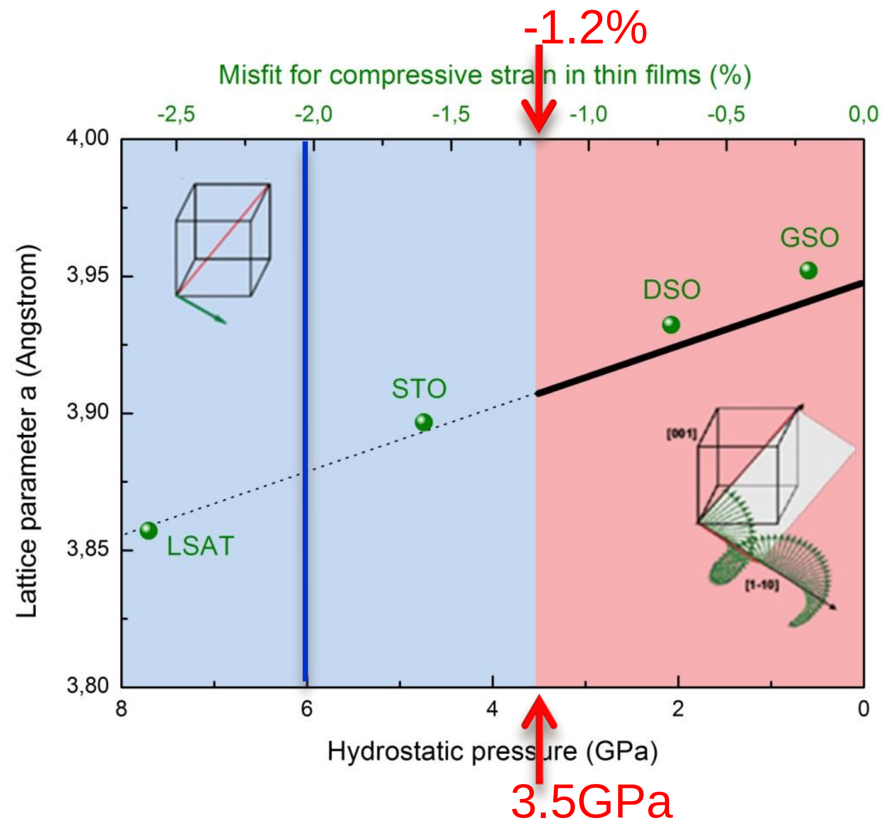
D. Sando et al., Nat. Mater. 12, 641–646,(2013)

Comparison with thin films



D. Sando et al., Nat. Mater. 12, 641–646,(2013)

Guennou *et al.* PRB 2011



✓ No structural transition in thin films below -5% of misfit.

✓ Without the 1st structural transition, theoretical calculations expect the vanishing of the cycloid at about 6GPa.

Conclusion

✓ Under pressure, **new phonon modes** are observed **at low energy** and **four structural phase** transitions occur **from Rhombohedral (R_{3c}) to Orthorhombic (P_{nma})** .

✓ At the first structural transition, **the magnetic cycloid vanishes and an AF order with certainly canted spin takes place**.

✓ **The hydrostatic pressure allows a tuning of the spin state** whereas for thin films, we have only access to discrete misfit strain accordingly to the substrate. Magnetoelectric mechanism: ongoing analysis