University of Hamburg, Institute of Mineralogy and Petrology

Raman and IR spectroscopy in materials science. Symmetry analysis of normal phonon modes

Boriana Mihailova

CrystallographyOnline:
InternationalSchoolon
theUseandApplications
ofheBilbao
Crystallographic
Server

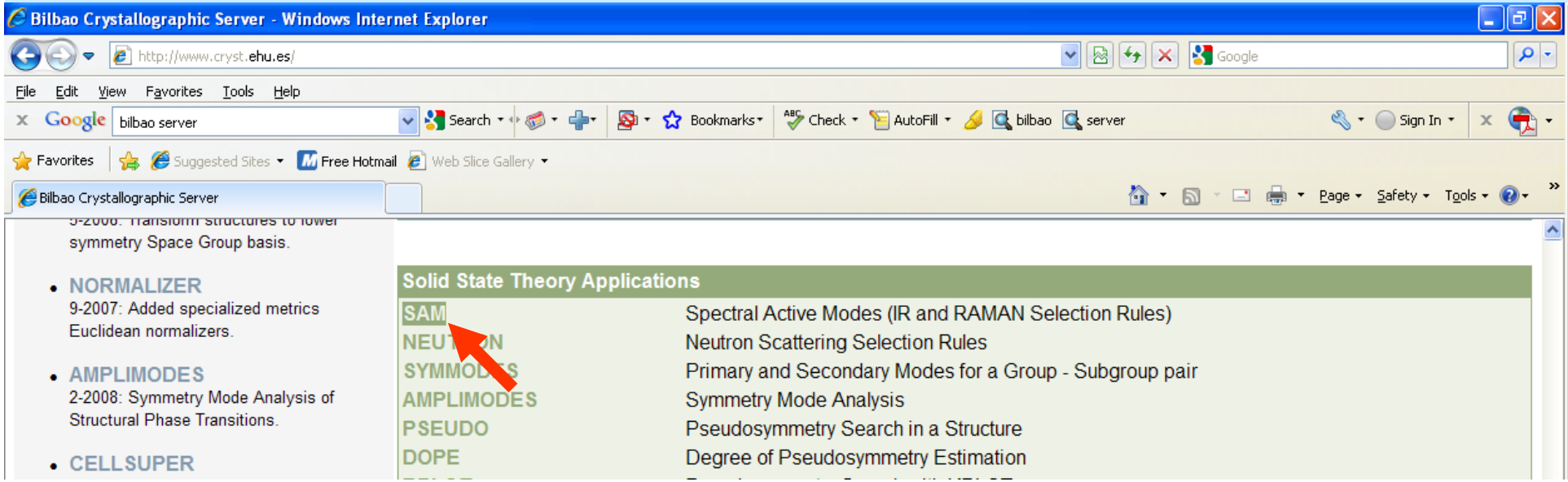
Lekeitio, Spain, 21-27 june 2009

Outline

1. **The dynamics of atoms in crystals. Phonons**

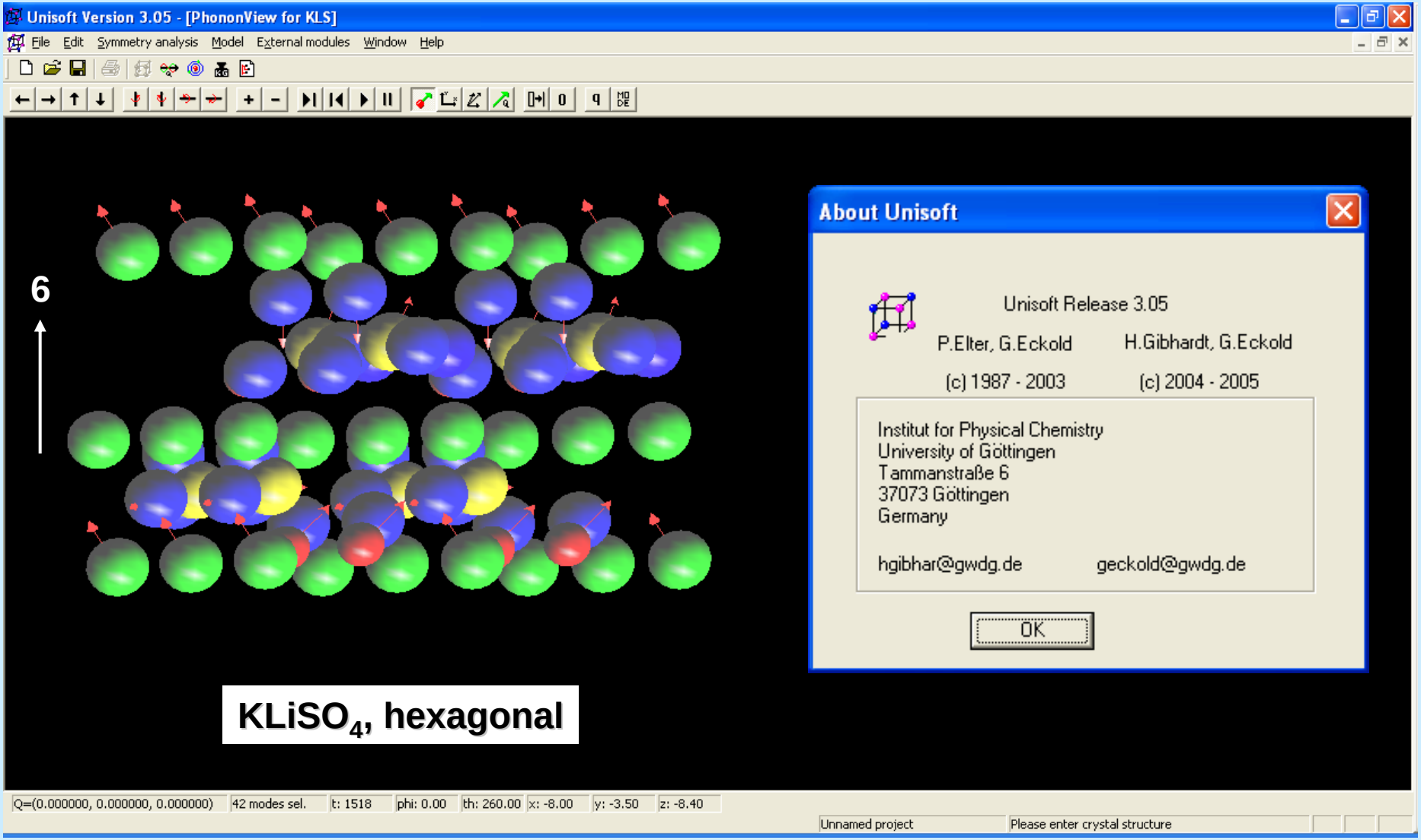
2. **Raman and IR spectroscopy :**
   most commonly used methods to study atomic dynamics

3. **Group theory analysis :**
   phonon modes allowed to be observed in IR and Raman spectra



Atomic dynamics in crystals

Visualization: UNISOFT, Prof. G. Eckold et al., University of Göttingen

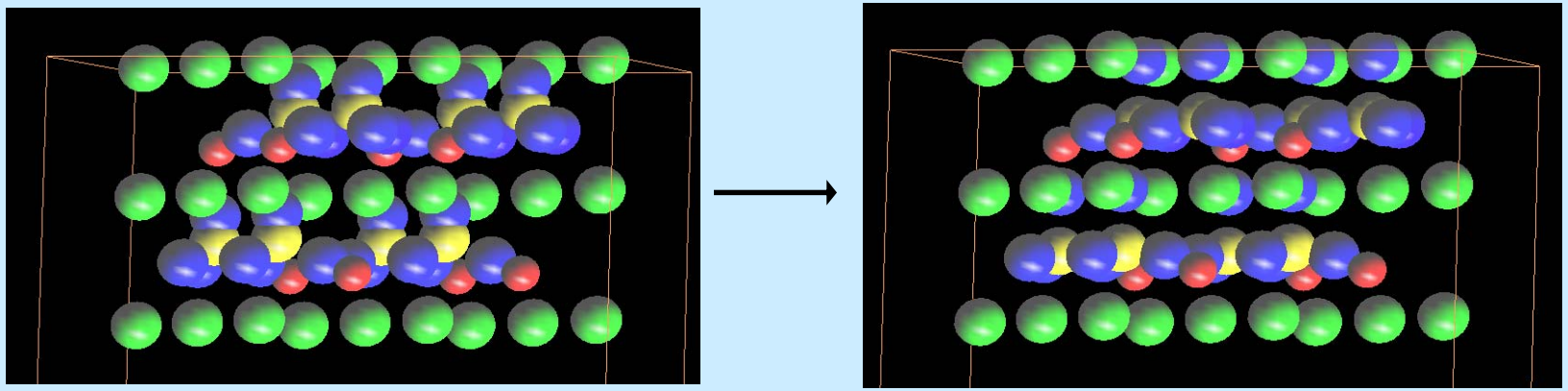


Crystal normal modes (eigenmodes)

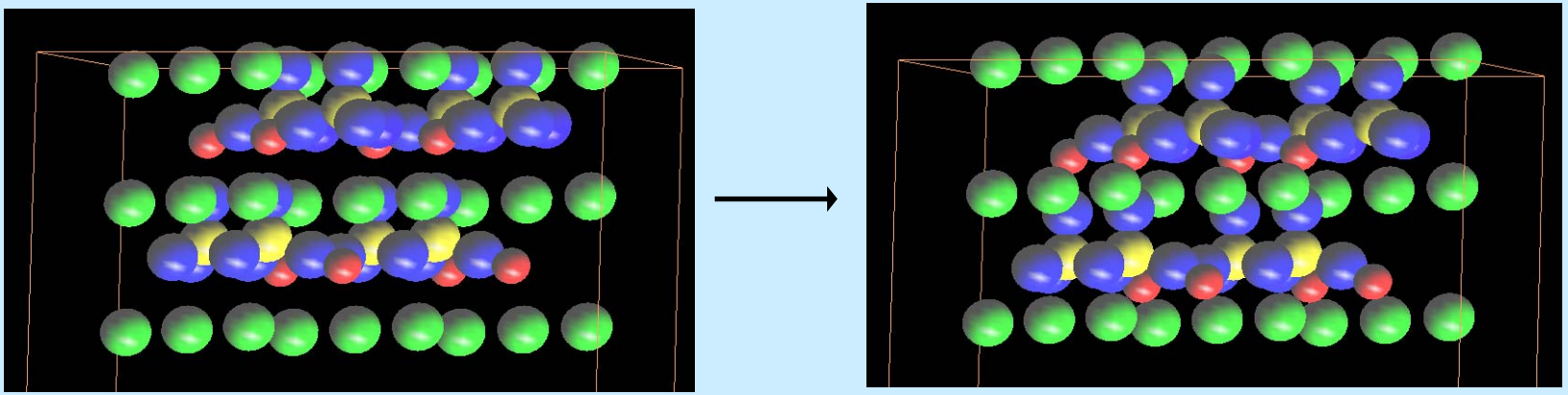
Atomic vibrations in crystals = Superposition of normal modes (eigenmodes)

e.g.,

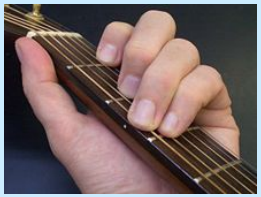
a mode involving mainly S-O_t bond stretching



a mode involving SO_4 translations and Li motions vs K atoms



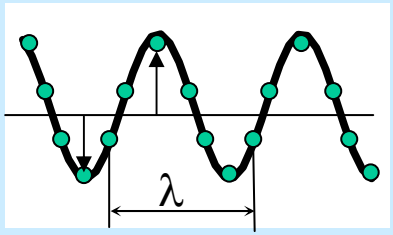
Phonons



Atomic vibrations in a *periodic* solid

⇳

standing elastic waves ≡ normal modes (ω_S, $\{\mathbf{u}_i\}_s$)



crystals : ***N*** atoms in the primitive unit cell vibrating in the ***3D*** space

⇨ 3N degrees of freedom ⇨ finite number of normal states

⇨ quantization of crystal vibrational energy

N atoms × **3** dimensions ↔ ***3N* phonons**

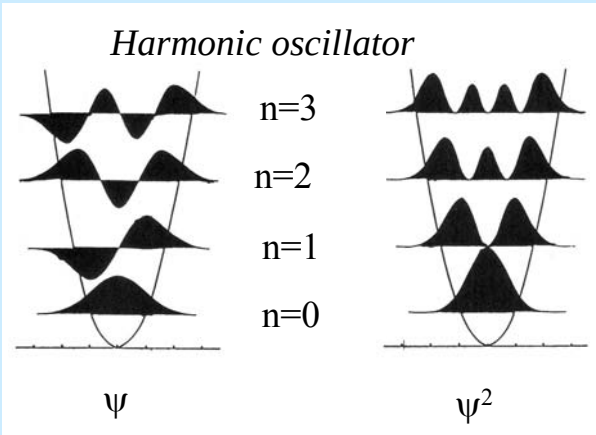
phonon ≡ quantum of crystal vibrational energy

phonons: quasi-particles (elementary excitations in solids)

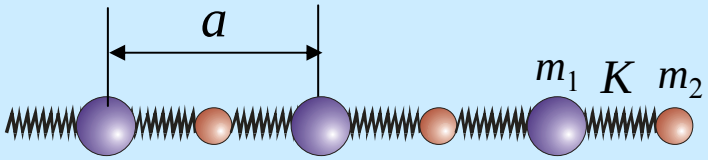
- $E_n = (n+1/2)\hbar\omega$,
- $m_0 = 0$, $\mathbf{p} = \hbar\mathbf{K}$ (quasi-momentum), $\mathbf{K} \equiv \mathbf{q} \in$ RL
- integer spin

  Bose-Einstein statistics: $n(\omega,T)= 1/[\exp(\hbar\omega/k_BT)-1]$

  (equilibrium population of phonons at temperature T)



Phonon frequencies and atom vector displacements



Atomic bonds ↔ elastic springs

Hooke's low : $m\ddot{x} = -Kx \quad \rightarrow \quad \omega = \sqrt{\frac{K}{m}}$

Equation of motion for a **3*D*** crystal with *N* atoms in the primitive unit cell :

$$\omega^2 w_{i\alpha,\mathbf{q}} = \sum_{i'\alpha'} D_{ii',\alpha\alpha'}(\mathbf{q}) w_{i'\alpha',\mathbf{q}}$$

dynamical matrix

$$w_{i\alpha,\mathbf{q}} = \frac{1}{\sqrt{m_i}} u_{i\alpha,\mathbf{q}} \qquad \alpha = 1,2,3 \quad i = 1,\ldots, N$$

atomic vector displacements

$$D_{ss'\alpha\alpha'}(\mathbf{q}) = \frac{1}{\sqrt{m_s m_{s'}}} \Phi_{ss'\alpha\alpha'}(\mathbf{q})$$

second derivatives of the crystal potential

in a matrix form: $\omega^2 \mathbf{w}_\mathbf{q} = \mathbf{D}(\mathbf{q}) \cdot \mathbf{w}_\mathbf{q}$ $\qquad \left(\mathbf{D}(\mathbf{q}) - \omega^2 \boldsymbol{\delta}\right) \cdot \mathbf{w}_\mathbf{q} = 0$

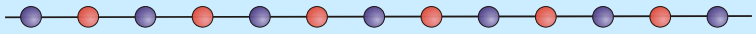
(3*N*×1) (3*N*×3*N*) (3*N*×1)

⇨ phonon ω_S, $\{\mathbf{u}_i\}_s$ ↔ eigenvalues and eigenvectors of $\mathbf{D} = f\,(m_i, K(\{\mathbf{r}_i\}), \{\mathbf{r}_i\})$

⇨ phonon ω_S, $\{\mathbf{u}_i\}_s$ carry essential structural information !

Types of phonons

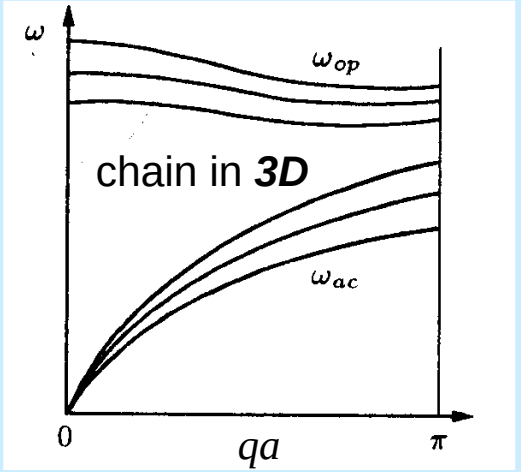
diatomic chain



Acoustic phonon: $\mathbf{u}_1$, $\mathbf{u}_2$, in-phase

Optical phonon: $\mathbf{u}_1$, $\mathbf{u}_2$, out-of-phase

phonon dispersion: $\omega_{ac}(\mathbf{q}) \neq \omega_{op}(\mathbf{q})$, for $q \approx 0$, $\omega_{op} > \omega_{ac}$



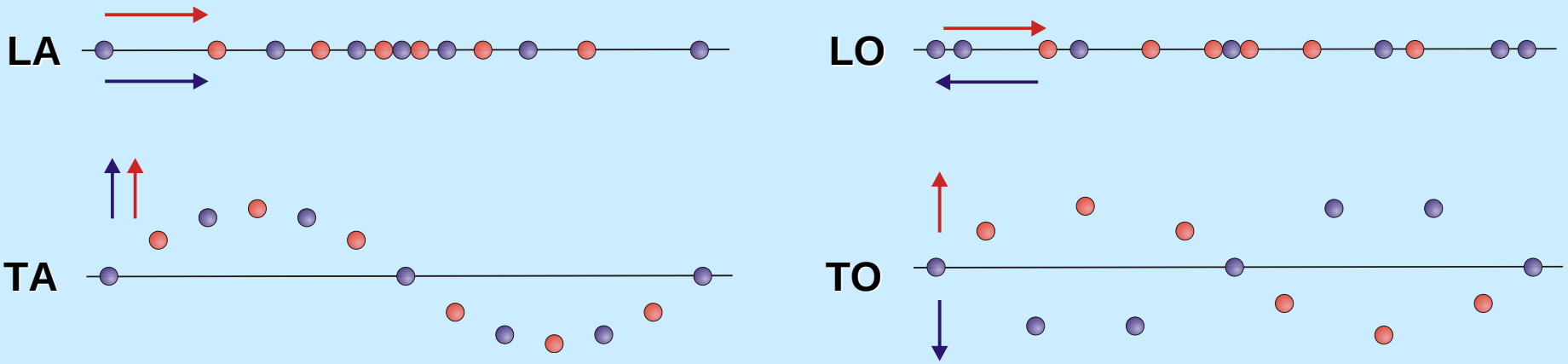
3*D* crystal with ***N*** atoms per cell :

3 acoustic and **3*N* – 3** optical phonons

induced dipole moment
⇨ *interact with light*

1 Longitudinal: wave polarization ($\mathbf{u}$) || wave propagation ($\mathbf{q}$)

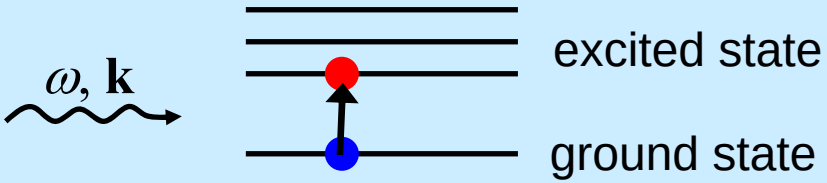
2 Transverse: wave polarization ($\mathbf{u}$) ⊥ wave propagation ($\mathbf{q}$)

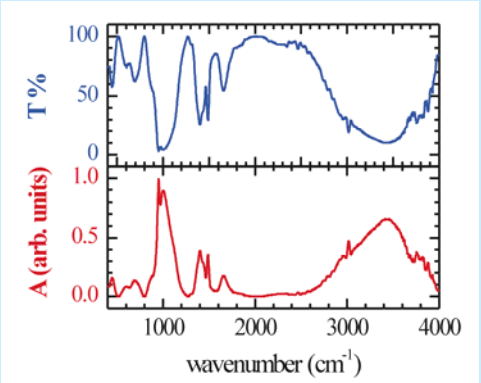


Phonon (Raman and IR) spectroscopy

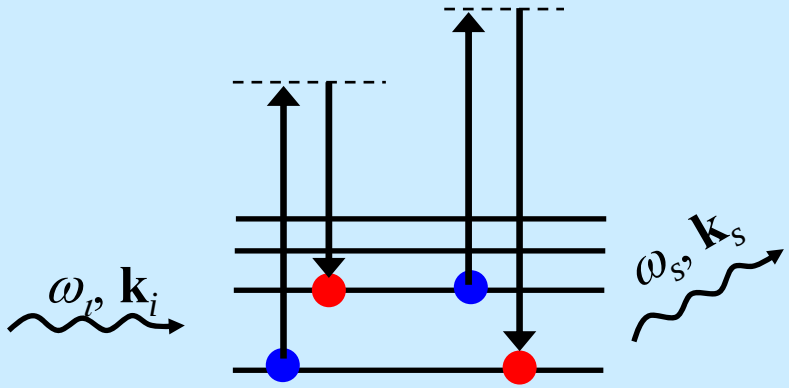
electromagnetic wave as a probe radiation (***photon – opt. phonon interaction***):

Infrared absorption: $\hbar\omega_{photon} = E_{ES}^{(phonon)} - E_{GS}^{(phonon)}$



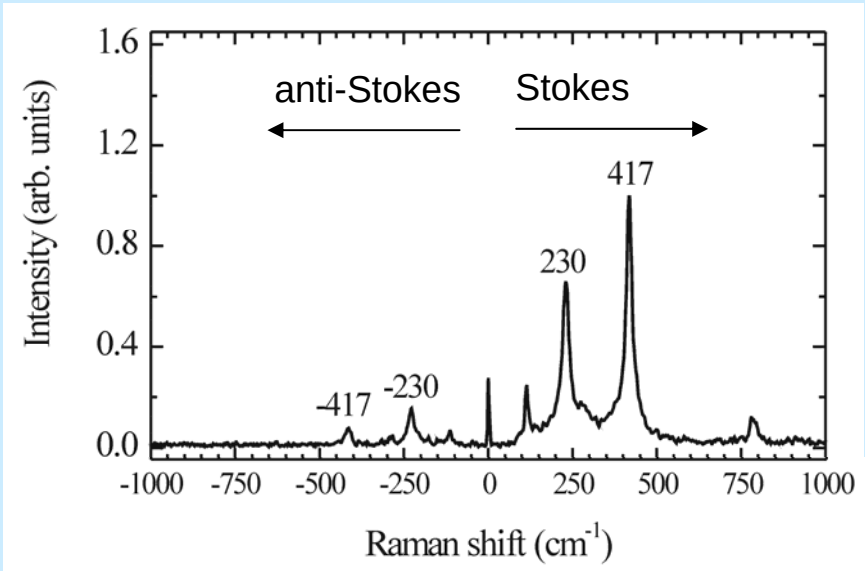


Raman scattering ≡ inelastic light scattering from optical phonons



Stokes $\omega_s = \omega_i - \Omega$ $\mathbf{k}_s = \mathbf{k}_i - \mathbf{K}$

anti-Stokes $\omega_s = \omega_i + \Omega$ $\mathbf{k}_s = \mathbf{k}_i + \mathbf{K}$



Phonon (Raman and IR) spectroscopy

- only optical phonons near the FBZ centre are involved

$\mathbf{k}_i - \mathbf{k}_s = \mathbf{K}$ ⇨ $K_{\max} = \Delta k \approx 2k_i$ (e.g. Raman, 180°-scattering geometry)

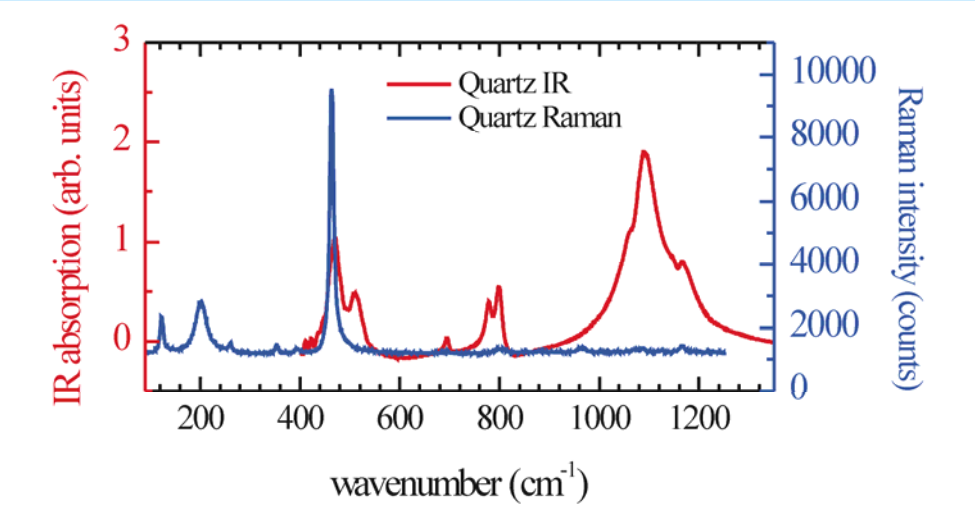
λ_i (IR, vis, UV) ~ $10^3 - 10^5$ Å ⇨ $k_i \sim 10^{-5} - 10^{-3}$ Å $\approx K_{\max}$ ⇨ $K_{\max} << \frac{\pi}{a}$ ($a \sim 10$ Å)

⇨ photon-phonon interaction only for $K \approx 0$

- spectroscopic units: cm^{-1} ⇔ $E = \hbar ck = \hbar c(2\pi/\lambda) = hc(1/\lambda)$

10 [cm^{-1}] ⇔ 1.24 [meV] 10 [cm^{-1}] ⇔ 0.30 [THz] [Å].[cm^{-1}] = 10^8

- IR and Raman spectra are different for the same crystal



different interaction phenomena ⇨ different selection rules !

Raman and IR intensities

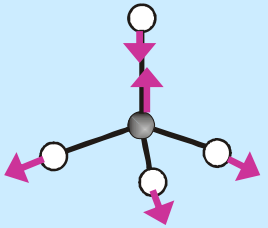
IR activity: induced dipole moment due to the change in the atomic positions

$$\boldsymbol{\mu} = (\mu_x, \mu_y, \mu_z)$$

$$\boldsymbol{\mu}(Q) = \boldsymbol{\mu}_0 + \sum \frac{\partial \boldsymbol{\mu}}{\partial Q_k} Q_k + \ldots$$

Q_k – configurational coordinate

$\neq 0$, IR activity



IR: “asymmetrical”, “one-directional”

Raman activity: induced dipole moment due to deformation of the e^- shell

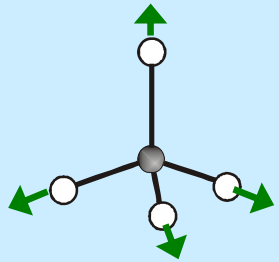
Polarizability tensor: $\boldsymbol{\alpha} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{xy} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{xz} & \alpha_{yz} & \alpha_{zz} \end{pmatrix}$

$$\mathbf{P} = \boldsymbol{\alpha}.\mathbf{E}$$

induced polarization
(dipole moment per unit cell)

$$\boldsymbol{\alpha}(Q) = \boldsymbol{\alpha}_0 + \sum \frac{\partial \boldsymbol{\alpha}}{\partial Q_k} Q_k + \ldots$$

$\neq 0$, Raman activity

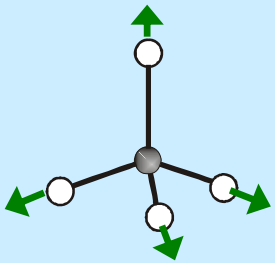


Raman: “symmetrical”, “two-directional”

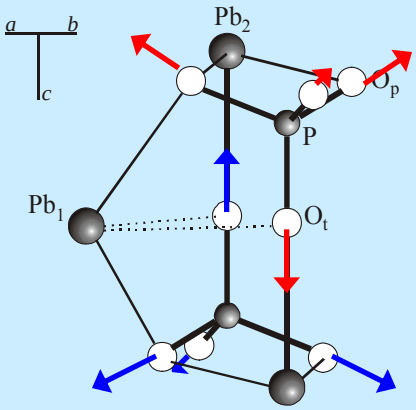
N.B.! simultaneous IR and Raman activity – only in non-centrosymmetric structures

Raman and IR activity in crystals

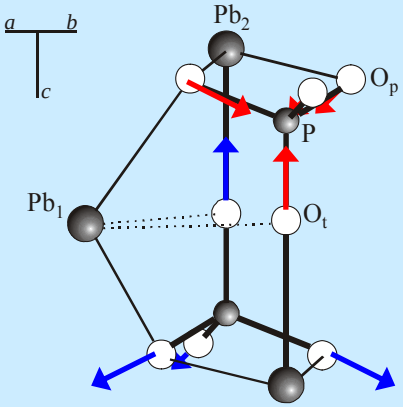
Isolated TO_4 group ⟶ **Crystal: $Pb_3(PO_4)_2$, $R\bar{3}m$**



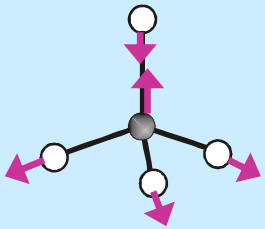
Raman-active



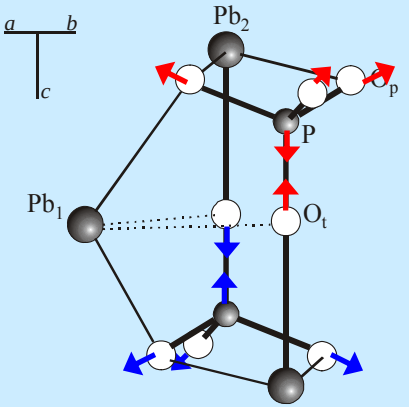
Raman-active



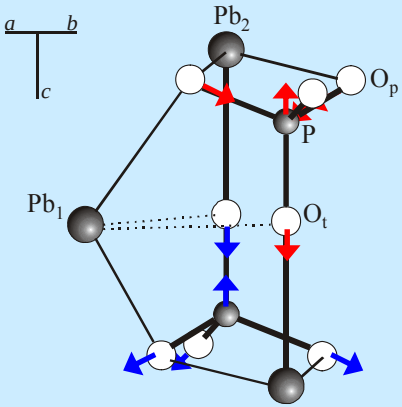
IR-active



IR-active



Raman-active



IR-active

Methods for normal phonon mode determination

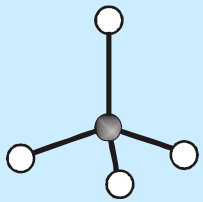
Three techniques of selection rule determination at the Brillouin zone centre:

- Factor group analysis

  the effect of each symmetry operation in the factor group on each type of atom in the unit cell

- Molecular site group analysis

  symmetry analysis of the ionic group (molecule) → site symmetry of the central atom + factor group symmetry



✓ • **Nuclear site group analysis**

site symmetry analysis is carried out on every atom in the unit cell
☺ *set of tables ensuring a great ease in selection rule determination*
preliminary info required: space group and occupied Wyckoff positions

Rousseau, Bauman & Porto, J. Raman Spectrosc. **10**, (1981) 253-290

✓ **Bilbao Server, SAM,** http://www.cryst.ehu.es/rep/sam.html

N.B.! Tabulated information for:

first-order, **linear-response**, **non-resonance** interaction processes

(*one phonon only*) (*one photon only*) ($\hbar\omega_i < E_{ES}^{electron} - E_{GS}^{electron}$)

Symbols and notations

Symmetry element	Schönflies notation	International (Hermann-Mauguin)
Identity	E	1
Rotation axes	C_n	$n = 1, 2, 3, 4, 6$
Mirror planes	σ	m
$\perp$ to n-fold axis	σ_h	m, m_z
$\parallel$ to n-fold axis	σ_v	m_v,
bisecting $\angle(2,2)$	σ_d	m_d, m'
Inversion	I	$\bar{1}$
Rotoinversion axes	S_n	$n = \bar{1},\bar{2},\bar{3},\bar{4},\bar{6}$
Translation	t_n	t_n
Screw axes	C_n^k	n_k
Glide planes	σ^g	a, b, c, n, d

Point groups:

Triclinic		Monoclinic		Trigonal (Rhombohedral)		Tetragonal		Hexagonal		Cubic	
C_1	1	C_2	2	C_3	3	C_4	4	C_6	6	T	23
C_i	$\bar{1}$	C_S	m	C_{3i}	$\bar{3}$	S_4	$\bar{4}$	C_{3h}	$\bar{6}$		
		C_{2h}	$2/m$			C_{4h}	$4/m$	C_{6h}	$6/m$	T_h	$m\bar{3}$
		C_{2v}	$mm2$	C_{3v}	$3m$	C_{4v}	$4mm$	C_{6v}	$6mm$		
				D_{3d}	$\bar{3}m$	D_{2d}	$42m$	D_{3h}	$6m2$	T_d	$\bar{4}3m$
		D_2	222	D_3	32	D_4	422	D_6	622	O	432
		D_{2h}	mmm			D_{4h}	$4/mmm$	D_{6h}	$6/mmm$	O_h	$m\bar{3}m$

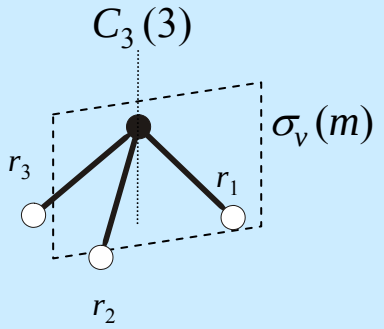
D_n: E, C_n; $nC_2 \perp$ to C_n; T: tetrahedral symmetry; O: octahedral (cubic) symmetry

Symbols and notations

normal phonon modes ↔ irreducible representations

Reminder: Symmetry element: matrix representation **A**

Character: $\mathrm{Tr}(\mathbf{A}) = \sum_i A_{ii}$



Point group C_{3v} (3m)		1	3	m
reducible		3	0	1
irreducible	A_1	1	1	1
	E	2	-1	0
	$A_1 + E$	3	0	1

characters

Mulliken symbols

$$1: \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \rightarrow \left(\begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & 1 & 0 \\ 0 & 0 & 1 \end{array}\right)$$

$$3: \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \rightarrow \left(\begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{array}\right)$$

$$m: \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \rightarrow \left(\begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & 1 & 0 \\ 0 & 0 & -1 \end{array}\right)$$

reducible *irreducible (block-diagonal)*

Mulliken symbols

A, B : **1*D*** representations ↔ non-degenerate (single) mode

only one set of atom vector displacements ($\mathbf{u}_1$, $\mathbf{u}_2$,…,$\mathbf{u}_N$) for a given wavenumber ω

A: symmetric with respect to the principle rotation axis n (C_n)

B: anti-symmetric with respect to the principle rotation axis n (C_n)

E: **2*D*** representation ↔ doubly degenerate mode

two sets of atom vector displacements ($\mathbf{u}_1$, $\mathbf{u}_2$,…,$\mathbf{u}_N$) for a given wavenumber ω

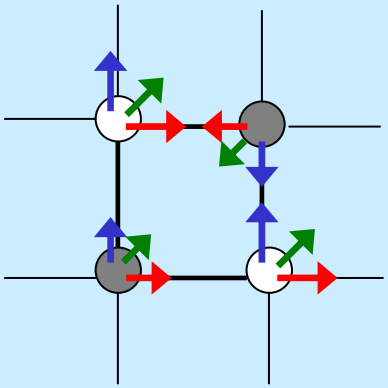
T (F): **3*D*** representation ↔ triply degenerate mode

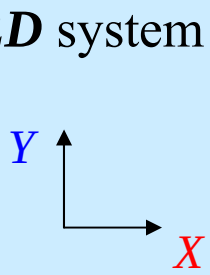
three sets of atom vector displacements ($\mathbf{u}_1$, $\mathbf{u}_2$,…,$\mathbf{u}_N$) for a given wavenumber ω

subscripts g, u (X_g, X_u) : symmetric or anti-symmetric to inversion $\bar{1}$

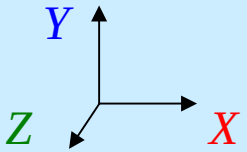
superscripts ’,” (X’, X”) : symmetric or anti-symmetric to a mirror plane m

subscripts 1,2 (X_1, X_2) : symmetric or anti-symmetric to add. m or C_n





E mode



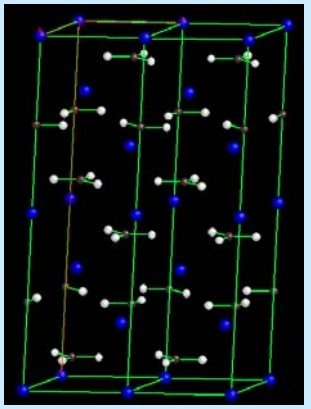
T mode

Bilbao Crystallographic Server, SAM

Working example: $CaCO_3$, **calcite**, $R\bar{3}c$ (167) D_{3d}^6

(0,0,0)+ (2/3,1/3,1/3)+ (1/3,2/3,2/3)+

Ca:	(6b)	0	0	0
C :	(6a)	0	0	0.25
O :	(18e)	0.25682	0	0.25



http://www.cryst.ehu.es/ or google “Bilbao server”

- **AMPLIMODES for FullProf**
  10-2008: Refine your structures with FullProf using symmetry modes.
- **TRANSTRU**
  5-2008: Transform structures to lower symmetry Space Group basis.
- **NORMALIZER**
  9-2007: Added specialized metrics Euclidean normalizers.

Solid State Theory Applications

SAM	Spectral Active Modes (IR and RAMAN Selection Rules)
NEUTRON	Neutron Scattering Selection Rules
SYMMODES	Primary and Secondary Modes for a Group - Subgroup pair
AMPLIMODES	Symmetry Mode Analysis
PSEUDO	Pseudosymmetry Search in a Structure
DOPE	Degree of Pseudosymmetry Estimation
BPLOT	Pseudosymmetry Search with KPLOT
TRANPATH	Transition Paths (Group not subgroup relations)

Bilbao Crystallographic Server → IR and Raman Modes Help

IR and Raman Modes

Symmetry Adapted Modes

Given a space group in ITA notation and selected the Wyckoff positions for the atoms in a structure the program calculates the symmetry adapted modes for gamma point and classifies them in IR

Please, enter the sequential number of group as given in *International Tables for Crystallography*, Vol. A or choose it: 167

Select Wyckoff Positions

or input, then click

Bilbao Crystallographic Server, SAM

Calcite

Choose the Wyckoff Positions of the atoms in your structure for the space group R -3 c (167) [h axes]

Check	WP	Representative
☐	36f	x,y,z
☑	18e	x,0,1/4
☐	18d	1/2,0,0
☐	12c	0,0,z
☑	6b	0,0,0
☑	6a	0,0,1/4

Show

Ca:	(6b)	0	0	0
C :	(6a)	0	0	0.25
O :	(18e)	0.25682	0	0.25

Bilbao Crystallographic Server, SAM

Calcite

IR and Raman Modes for R -3 c (167) [h axes]

Point group

symmetry operations

number of operation of each class

Character Table

D_{3d}(-3m)	1	3	2	-1	-3	m_d	functions
Mult.	1	2	3	1	2	3	·
A_{1g}	1	1	1	1	1	1	x^2+y^2,z^2
A_{1u}	1	1	1	-1	-1	-1	·
A_{2g}	1	1	-1	1	1	-1	J_z
A_{2u}	1	1	-1	-1	-1	1	z
E_u	2	-1	0	-2	1	0	(x,y)
E_g	2	-1	0	2	-1	0	$(x^2-y^2,xy),(J_x,J_y)$ (xz,yz)

selection rules

Raman-active $\alpha_{xx} = \alpha_{yy} \neq \alpha_{zz}$ *non-zero components*

IR-active $\mu_z \neq 0$

μ_x , $\mu_y \neq 0$

+ acoustic

$\alpha_{xx} = -\alpha_{yy} \neq \alpha_{xy}$

$\alpha_{xz} \neq \alpha_{yz}$

rotation (inactive)

normal modes

[List of irreducible representations in matrix form]

characters

Mechanical Representation

WP	A_{1g}	A_{1u}	A_{2g}	A_{2u}	E_u	E_g	Modes
18e	1	1	2	2	3	3	Show
6b	·	1	·	1	2	·	Show
6a	·	·	1	1	1	1	Show

[Show] option to obtain the symmetry adapted mo

Ca: (6b) : $A_{1u} + A_{2u} + 2E_u$ → acoustic: $A_{2u}+E_u$ (***the heaviest atom***)

C : (6a) : $A_{2g} + A_{2u} + E_g + E_u$

O : (18a) : $A_{1g} + A_{1u} + 2A_{2g} + 2A_{2u} + 3E_g + 3E_u$

Total: 10A + 10E = 30 ⇔ $3N = 30$ (N = 6:3 +6:3+18:3 = 10)

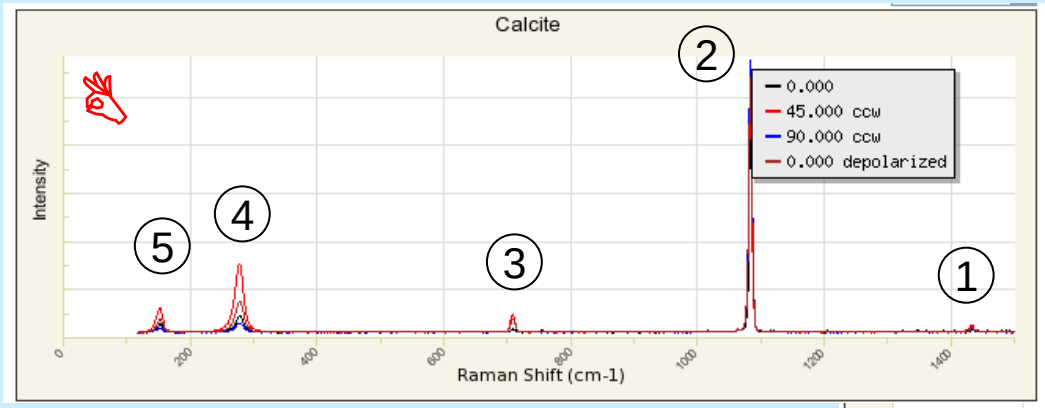
$\Gamma_{opt} = A_{1g}(R) + 2A_{1u}(ina) + 3A_{2g}(ina) + 3A_{2u}(IR) + 4E_g(R) + 5E_u(IR)$

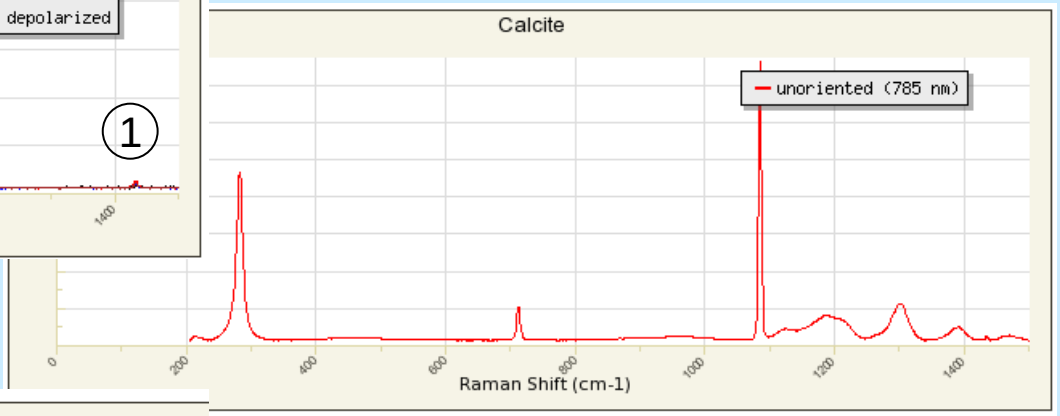
⇨ 5 Raman peaks and 8 IR peaks are expected

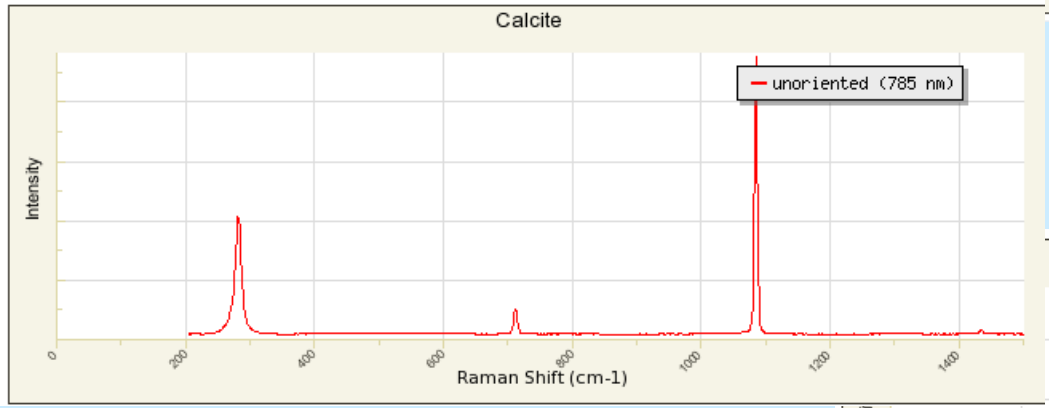
Spectra from

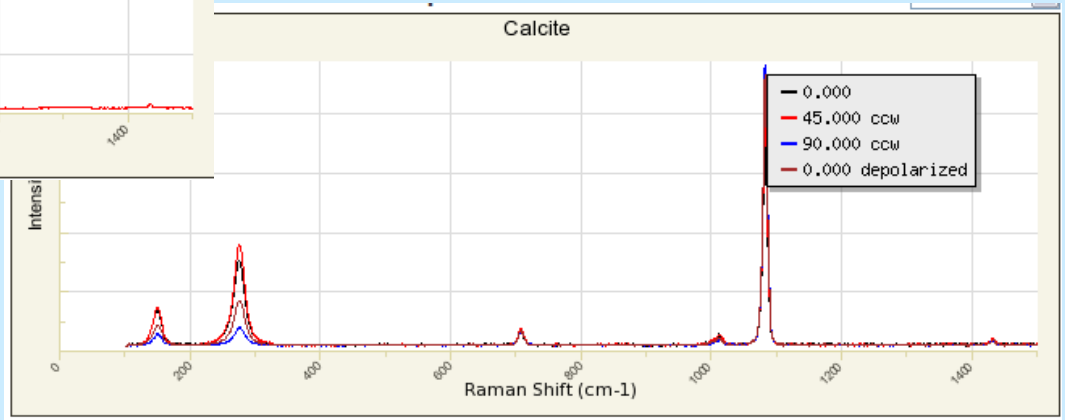
RRUFF Home | UA Mineralogy | Caltech Mineralogy | The IMA Mineral List | Login

Search **Sample Data** Search **References** **About** RRUFF **Contact** Us

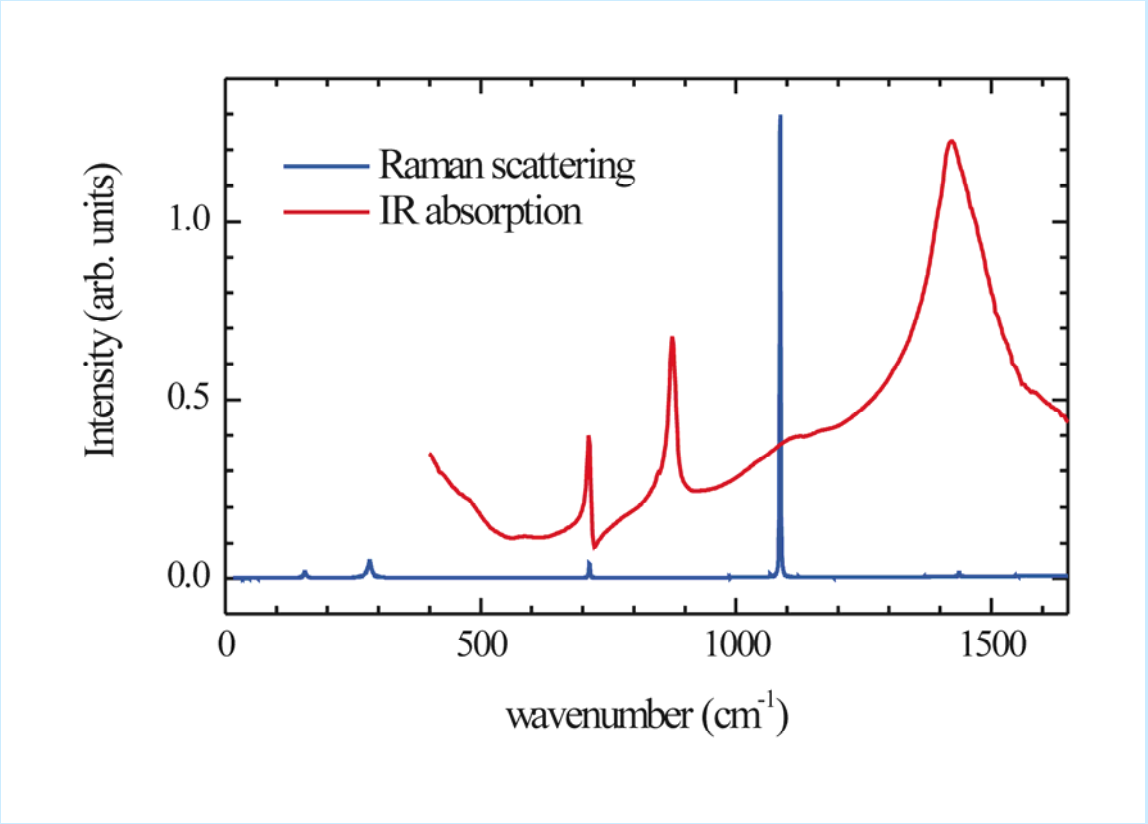








Spectra of Calcite from Hamburg, ☺

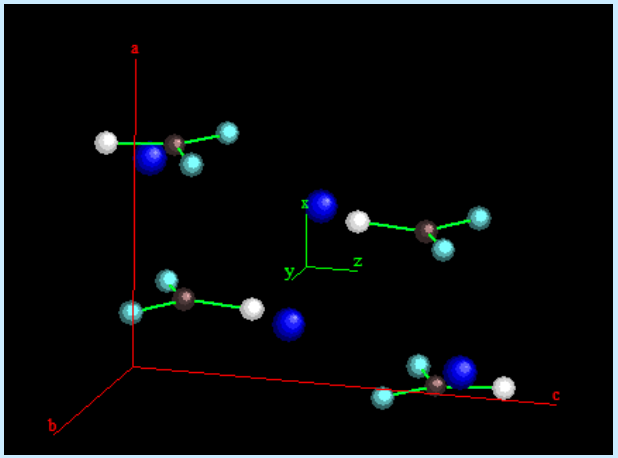


$\Gamma_{Raman\text{-}active} = A_{1g} + 4E_g$

$\Gamma_{IR\text{-}active} = 3A_{2u} + 5E_u$

Bilbao server, SAM

Practical exercise: number of expected Raman and IR peaks of aragonite



$CaCO_3$, aragonite, *Pnma* (62) D_{2h}^{16}

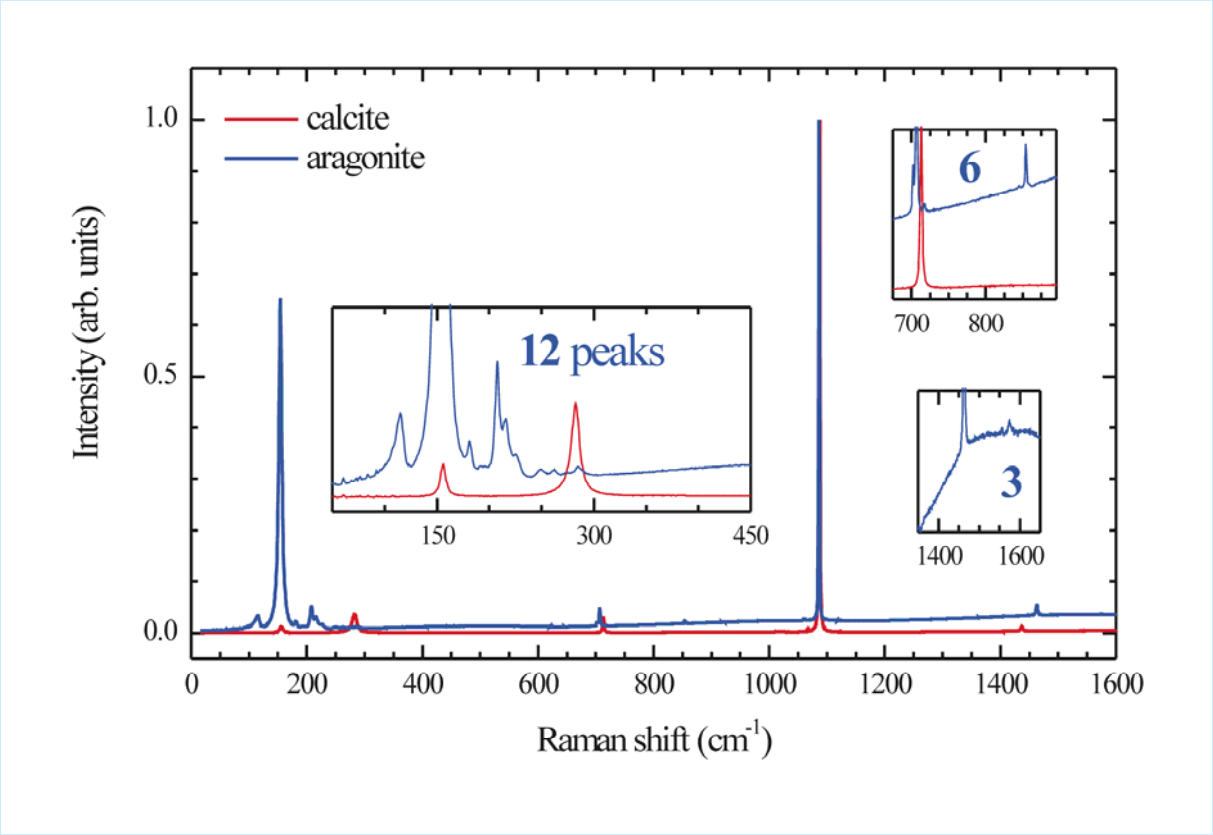
Ca	:	(4c)	0.24046	0.25	0.4150
C	:	(4c)	0.08518	0.25	0.76211
O1	:	(4c)	0.09557	0.25	0.92224
O2	:	(8d)	0.08726	0.47347	0.68065

Solution:

$\Gamma_{opt} = 9A_g(R) + 6A_u(ina) + 6B_{1g}(R) + 8B_{1u}(IR) + 9B_{2g}(R) + 5B_{2u}(IR) + 6B_{3g}(R) + 8B_{3u}(IR)$

⇨ 30 Raman peaks and 21 IR peaks are expected

Spectra of $CaCO_3$



Calcite: $\Gamma_{Raman\text{-}active} = A_{1g} + 4E_g$ ✓

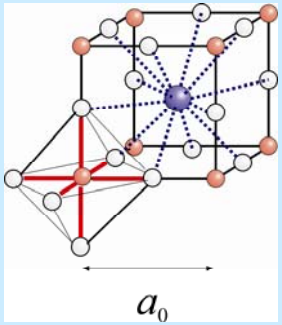
Aragonite: $\Gamma_{Raman\text{-}active} = 9A_g + 6B_{1g} + 9B_{2g} + 6B_{3g}$

22 observed

Bilbao server, SAM

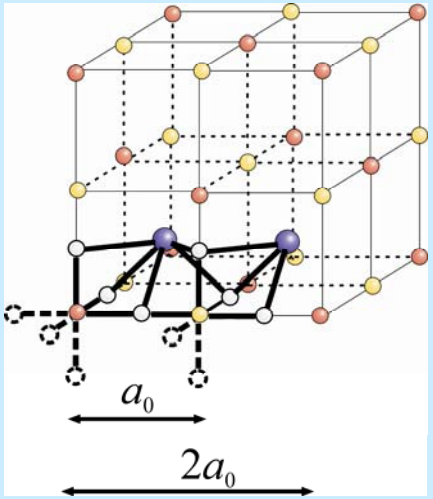
Perovskite-type structure *ABO*$_3$

single perovskite-type



chemical B-site disorder

double perovskite-type



chemical 1:1 B-site order

$A(B',B'')O_3 \quad Pm\bar{3}m \quad (221) \quad O_h^1$

A: (1b): 0.5 0.5 0.5
B'/B'': (1a): 0 0 0
O: (3d): 0.5 0 0

$AB'_{0.5}B''_{0.5}O_3 \quad Fm\bar{3}m \quad (225) \quad O_h^5$

(0,0,0)+ (0,1/2,1/2)+ (1/2,0,1/2)+ (1/2,1/2,0)+

A : (8c) : 0.25 0.25 0.25
B' : (4a) : 0 0 0
B'': (4b) : 0.5 0 0
O : (24e): 0.255 0 0

Bilbao server, SAM

$A(B',B'')O_3$ $Pm\bar{3}m$ (221) O_h^1

A: (1b): T_{1u} → acoustic

B: (1a): T_{1u}

O: (3d): $2T_{1u} + T_{2u}$

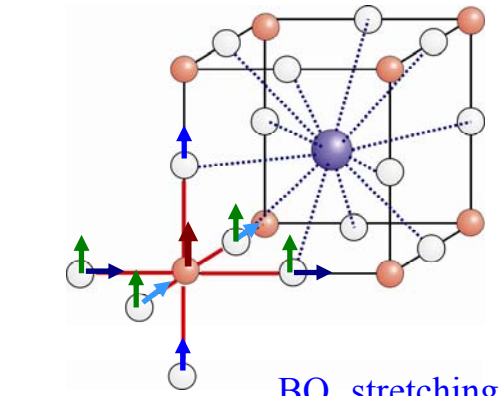
Total: 5T = 15 ⇔ 3*N* (5 atoms)

$\Gamma_{opt} = 3T_{1u}(IR) + T_{2u}(ina)$

Mechanical Representation

WP	A_{1g}	A_{1u}	A_{2g}	A_{2u}	E_u	E_g	T_{2u}	T_{2g}	T_{1u}	T_{1g}	Modes
3d	·	·	·	·	·	·	1	·	2	·	Show
1b	·	·	·	·	·	·	·	·	1	·	Show
1a	·	·	·	·	·	·	·	·	1	·	Show

Note: Click in the [Show] option to obtain the symmetry adapted modes for a given orbit



BO_6 stretching (3 sets)
BO_6 bending (3 sets)
B-c. transl. (3 sets)

Irrep: T_{1u}

M	3d	T_{1u}			T_{1u}		
X_1	(1/2,0,0)	·	1	·	·	·	·
Y_1		·	·	·	·	·	1
Z_1		·	·	·	1	·	·
X_2	(0,1/2,0)	·	·	·	·	1	·
Y_2		·	·	1	·	·	·
Z_2		·	·	·	1	·	·
X_3	(0,0,1/2)	·	·	·	·	1	·
Y_3		·	·	·	·	·	1
Z_3		1	·	·	·	·	·

Irrep: T_{1u}

M	1a	T_{1u}		
X_1	(0,0,0)	·	1	·
Y_1		·	·	1
Z_1		1	·	·

Bilbao server, SAM

$AB'_{0.5}B''_{0.5}O_3 \quad Fm\bar{3}m \quad (225) \quad O_h^5$

Exercise: determine the atom vector displacements for A_{1g}, E_g, T_{2g}, and add. T_{1u}

A : (8c): $T_{1u} + T_{2g}$ ⟶ T_{1u} acoustic
B': (4a): T_{1u}
B'': (4b): T_{1u}
O: (24e): $A_{1g} + E_g + T_{1g} + 2T_{1u} + T_{2g} + T_{2u}$

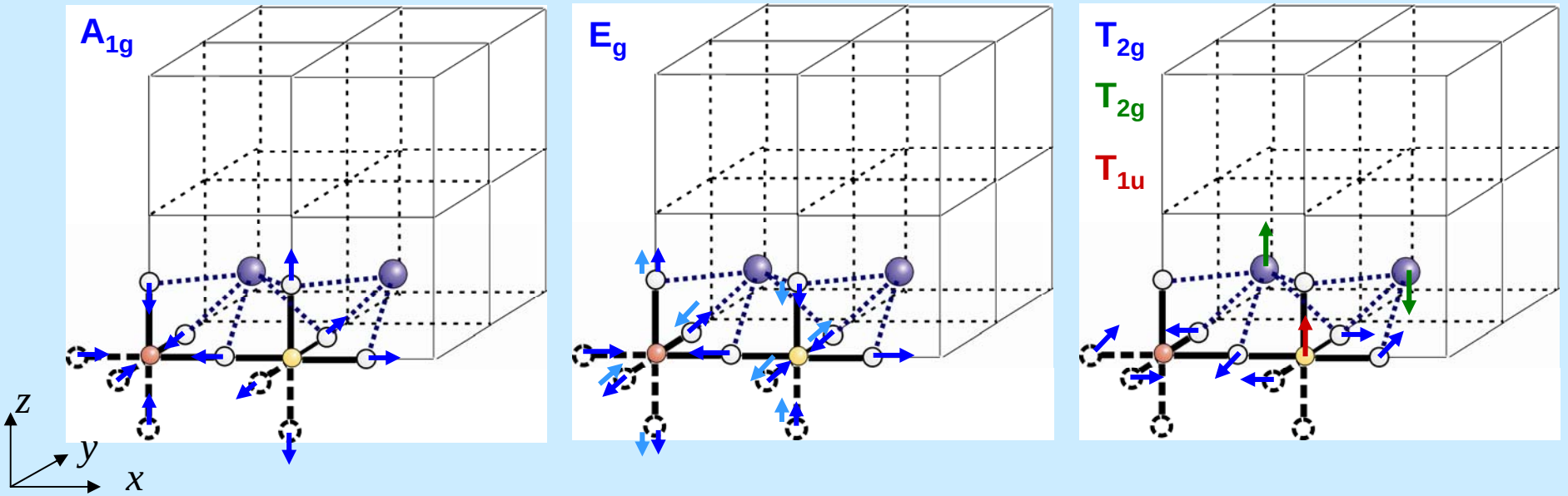
Mechanical Representation

WP	A_{1g}	A_{1u}	A_{2g}	A_{2u}	E_u	E_g	T_{2u}	T_{2g}	T_{1u}	T_{1g}	Modes
24e	1	·	·	·	·	1	1	1	2	1	Show
8c	·	·	·	·	·	·	·	1	1	·	Show
4b	·	·	·	·	·	·	·	·	1	·	Show
4a	·	·	·	·	·	·	·	·	1	·	Show

Note: Click in the [Show] option to obtain the symmetry adapted modes for a given orbit

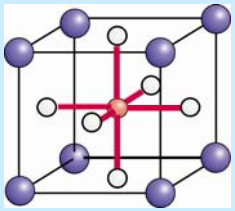
Total: 1A+1E+ 9T = 30 ⇔ 3*N* (*N*=8:4+4:4+4:4+24:4)

$\Gamma_{opt} = A_{1g} + E_g + T_{1g}(ina) + 3T_{1u}(IR) + T_{2u}(ina)$



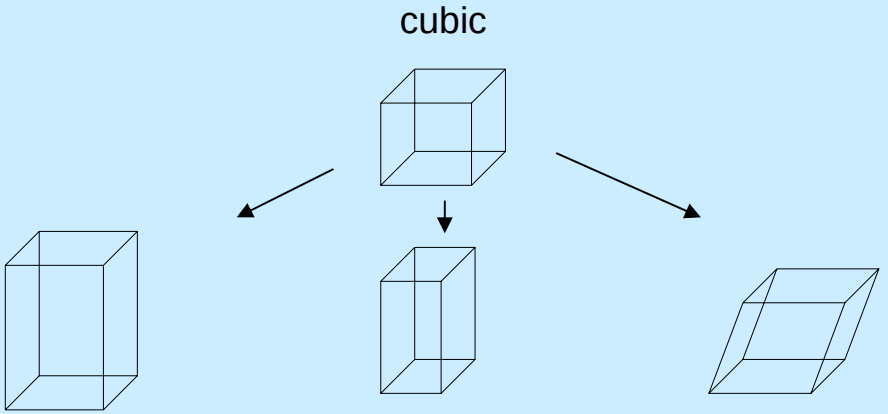
Bilbao server, SAM

Perovskite-type structure ABO_3 : ferroelectric phases



$BaTiO_3$ $Pm\bar{3}m$ (221) O_h^1

Ba: (1a): 0.0 0.0 0.0
Ti: (1b): 0.5 0.5 0.595
O: (3c): 0.5 0 0.5



$P4mm$ (99) C_{4v}^1

Ba: (1a): 0.0 0.0 0.0
Ti: (1b): 0.5 0.5 0.595
O1: (1b): 0.5 0.5 -0.025
O2: (2c): 0.5 0.0 0.489

$Amm2$ (38) C_{2v}^{14}

(0,0,0)+ (0,1/2,1/2)+

Ba: (2a): 0.0 0.0 0.0
Ti: (2b): 0.5 0.5 0.515
O1: (2b): 0.5 0.5 0.009
O2: (4c): 0.5 0.264 0.248

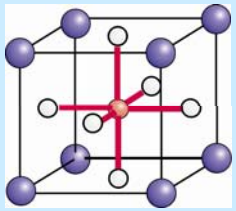
$R3m$ (160) C_{3v}^5

Ba: (1a): 0.0 0.0 0.0
Ti: (1a): 0.4853 0.4853 0.4853
O: (1b): 0.5088 0.5088 0.0185

Bilbao server, SAM

Perovskite-type structure ABO_3 : ferroelectric phases

$BaTiO_3$



	$Pm\bar{3}m$	$P4mm$	$Amm2$	$R3m$
Ba:	T_{1u}	$A_1 + E$	$A_1 + B_1 + B_2$	$A_1 + E$
Ti:	T_{1u}	$A_1 + E$	$A_1 + B_1 + B_2$	$A_1 + E$
O:	T_{1u}	$A_1 + E$	$A_1 + B_1 + B_2$	$A_1 + E$
	T_{1u}	$B_1 + E$	$A_1 + A_2 + B_2$	$A_1 + E$
	T_{2u}			$A_2 + E$

T_{2u}	·
T_{1u}	(x,y,z)

A_1	z,x^2+y^2,z^2
B_1	x^2-y^2
E	$(x,y),(xz,yz),(J_x,J_y)$

A_1	z,x^2,y^2,z^2
A_2	xy,J_z
B_1	x,xz,J_y
B_2	y,yz,J_x

A_1	z,x^2+y^2,z^2
A_2	J_z
E	$(x,y),(xz,yz),(x^2-y^2,xy),(J_x,J_y)$

Polar modes:
simultaneously
Raman and IR active

mode polarization
along μ (~ **u**)

LO: **q** || μ

TO: **q** ⊥ μ

Raman Tensors

A_1,z			B_1			B_2			E,x			E,y		
a	·	·	c	·	·	·	d	·	·	·	e	·	·	·
·	a	·	·	-c	·	d	·	·	·	·	·	·	·	e
·	·	b	·	·	·	·	·	·	e	·	·	e	·	·

α_{xx}^{z}, α_{yy}^{z}, α_{zz}^{z}

Raman Tensors

A_1,z			A_2			B_1,x			B_2,y		
a	·	·	·	d	·	·	·	e	·	·	·
·	b	·	d	·	·	·	·	·	·	·	f
·	·	c	·	·	·	e	·	·	·	f	·

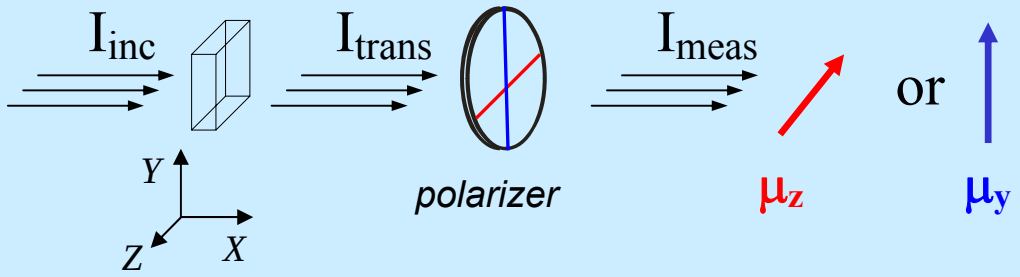
Raman Tensors

A_1,z			E,x			E,y		
a	·	·	c	·	d	·	-c	·
·	a	·	·	-c	·	-c	·	d
·	·	b	d	·	·	·	d	·

Experimental geometry

Infrared transmission (*only* TO *are detectible*)

$I_{IR} \propto \mu_\alpha^2$



Raman scattering

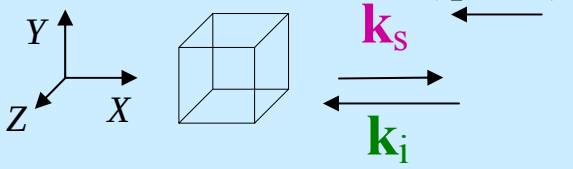
$I_{Raman} \propto \alpha_{\alpha\beta}^2$

Porto's notation: A(BC)D

A, D - directions of the propagation of incident ($\mathbf{k}_i$) and scattered ($\mathbf{k}_s$) light,

B, C – directions of the polarization incident ($\mathbf{E}_i$) and scattered ($\mathbf{E}_s$) light

back-scattering geometry



$\bar{X}(YY)X$ $\quad$ $\bar{X}(ZZ)X$ $\quad$ $\bar{X}(YZ)X$

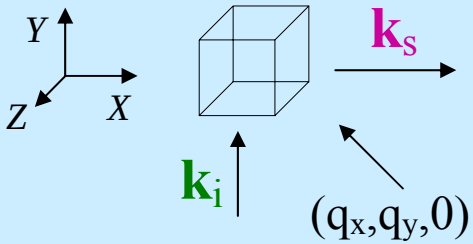
$\mathbf{E}_i \; \mathbf{E}_s$ $\quad$ $\mathbf{E}_i \; \mathbf{E}_s$ $\quad$ $\mathbf{E}_i \; \mathbf{E}_s$

α_{yy} $\quad$ α_{zz} $\quad$ α_{yz}

α_{yy}^n $\quad$ α_{zz}^n $\quad$ α_{yz}^n $\rightarrow$ $n = x$ ⇨ LO; $n = y, z$ ⇨ TO

($\mathbf{k}_i = \mathbf{k}_s + \mathbf{q}$, $\mathbf{E}$ is always $\perp$ to $\mathbf{k}$)

right-angle geometry



$Y(XY)X$ $\quad$ $Y(XZ)X$ $\quad$ $Y(ZY)X$ $\quad$ $Y(ZZ)X$

α_{xy} $\quad$ α_{xz} $\quad$ α_{zy} $\quad$ α_{zz}

α_{xy}^n $\quad$ α_{xz}^n $\quad$ α_{zy}^n $\quad$ α_{zz}^n $\rightarrow$ $n = x,y$ ⇨ LO+TO; $n = z$ ⇨ TO

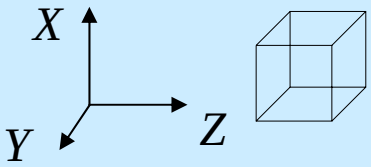
Experimental geometry

cubic system

e.g., T_d ($\bar{4}3m$)

Raman Tensors

A_1			E			E			T_2,x			T_2,y			T_2,z		
a	·	·	b	·	·	$-3^{1/2}$b	·	·	·	·	·	·	·	d	·	d	·
·	a	·	·	b	·	·	$3^{1/2}$b	·	·	·	d	·	·	·	d	·	·
·	·	a	·	·	-2b	·	·	·	·	d	·	d	·	·	·	·	·



$\mathbf{k}_s$

$\mathbf{k}_i$

$\mathbf{E}_i \; \mathbf{E}_s$

$\bar{Z}(YY)Z$ $\quad \alpha_{yy}$ $\quad$ A_1, E

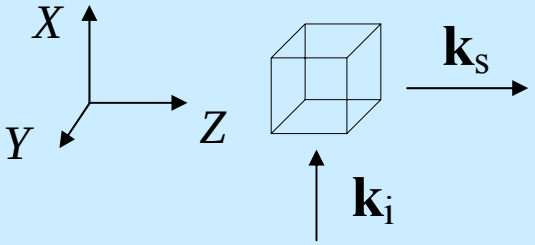
$\mathbf{k}_i = \mathbf{k}_s + \mathbf{q}$

$\mathbf{q} = (0,0,q_z)$

$\mathbf{E}_i \; \mathbf{E}_s$

$\bar{Z}(YX)Z$ $\quad \alpha^{z}_{xy}$ $\quad \mathbf{q} \parallel \boldsymbol{\mu}$ $\quad$ T_2(LO)

$\boldsymbol{\mu} = (0,0,\mu_z)$



$\mathbf{E}_i \; \mathbf{E}_s$

$X(ZY)Z$ $\quad \alpha^{x}_{yz}$ $\quad \mathbf{q}_x \parallel \boldsymbol{\mu}$ $\quad$ T_2(LO+TO)

$\boldsymbol{\mu} = (\mu_x,0,0)$ $\quad \mathbf{q}_z \perp \boldsymbol{\mu}$

$\mathbf{q} = (q_x,0,q_z)$

$\mathbf{E}_i \; \mathbf{E}_s$

$X(ZX)Z$ $\quad \alpha^{y}_{xz}$ $\quad \mathbf{q} \perp \boldsymbol{\mu}$ $\quad$ T_2(TO)

$\boldsymbol{\mu} = (0,\mu_y,0)$

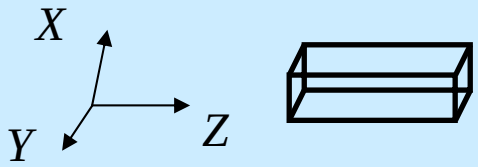
Experimental geometry

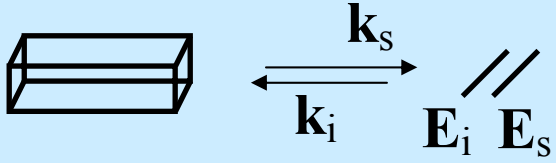
non-cubic system

e.g., trigonal, C_{3v} ($3m$)

A_1,z			E,x			E,y		
a	·	·	c	·	d	·	-c	·
·	a	·	·	-c	·	-c	·	d
·	·	b	d	·	·	·	d	·

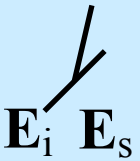
(hexagonal setting)



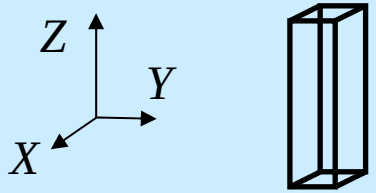


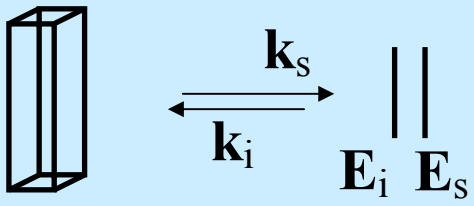
$\bar{Z}(YY)Z$ α^{z}_{yy} $\mathbf{\mu}=(0,0,\mu_z)$, $\mathbf{q}=(0,0,q_z)$ → A_1(LO)

α^{x}_{yy} → $\mathbf{\mu}=(\mu_x,0,0)$ → E(TO)

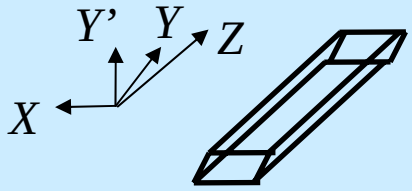


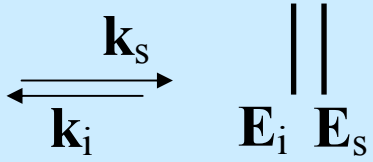
$\bar{Z}(YX)Z$ α^{y}_{xy} $\mathbf{\mu}=(0,\mu_y,0)$, $\mathbf{q}=(0,0,q_z)$ E(TO)





$\bar{Y}(ZZ)Y$ α^{z}_{zz} $\mathbf{\mu}=(0,0,\mu_z)$, $\mathbf{q}=(0,q_y,0)$ A_1(TO)





$X(Y'Y')\bar{X}$ α^{x}_{yy} $\mathbf{\mu}=(\mu_x,0,0)$, $\mathbf{q}=(q_x,0,0)$ E(LO)

contribution from → α^{z}_{yy} → $\mathbf{\mu}=(0,0,\mu_z)$ → A_1(TO)

LO-TO splitting

More peaks than predicted by GTA may be observed *(info is tabulated)*

Cubic systems: LO-TO splitting of T modes: T(LO) + T(TO)

Non-cubic systems: {A(LO) ,A(TO)}; {B(LO),B(TO)}; {E(LO),E(TO)}

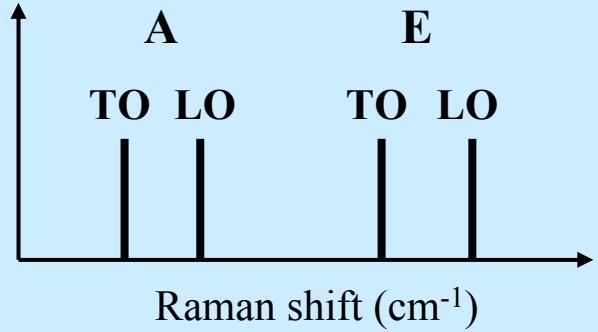
general rule: $\omega(LO) > \omega(TO)$ (*the potential for* LO: U+E; *for* TO: U)

Cubic crystals: LO-TO splitting ⇔ covalency of atomic bonding

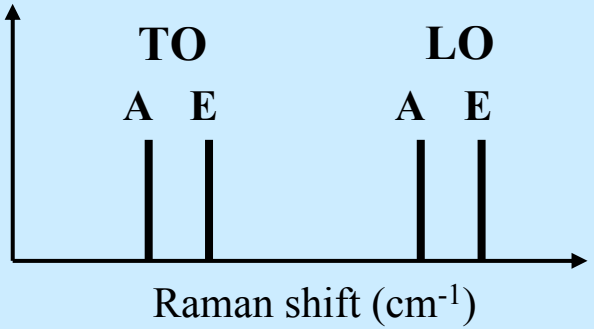
$\Delta\omega_{\text{LO-TO}}$: larger in ionic crystals, smaller in covalent crystals

Uniaxial crystals:

if **short-range** forces dominate:



if **long-range** forces dominate :



under certain propagation and polarization conditions →

quasi-LO and **quasi-TO** phonons of **mixed** A-E character

LO-TO splitting

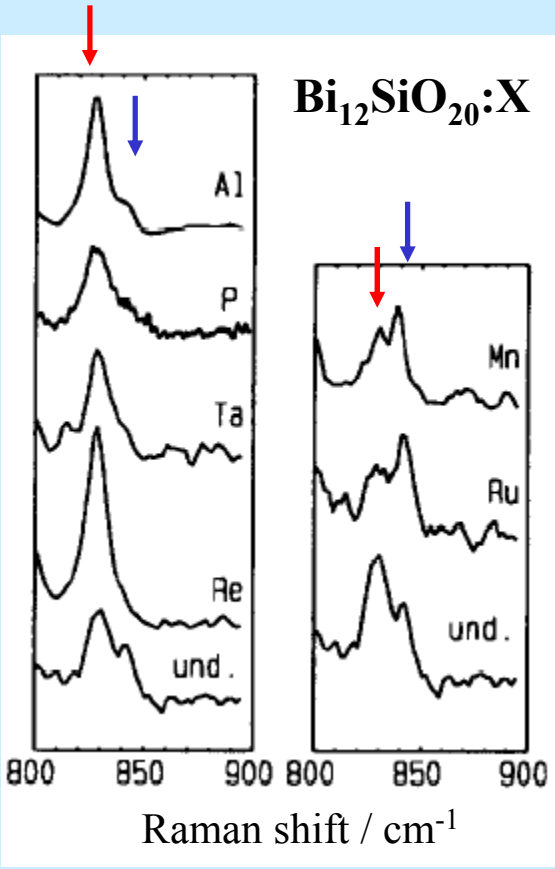
LO-TO splitting: sensitive to local polarization fields induced by point defects

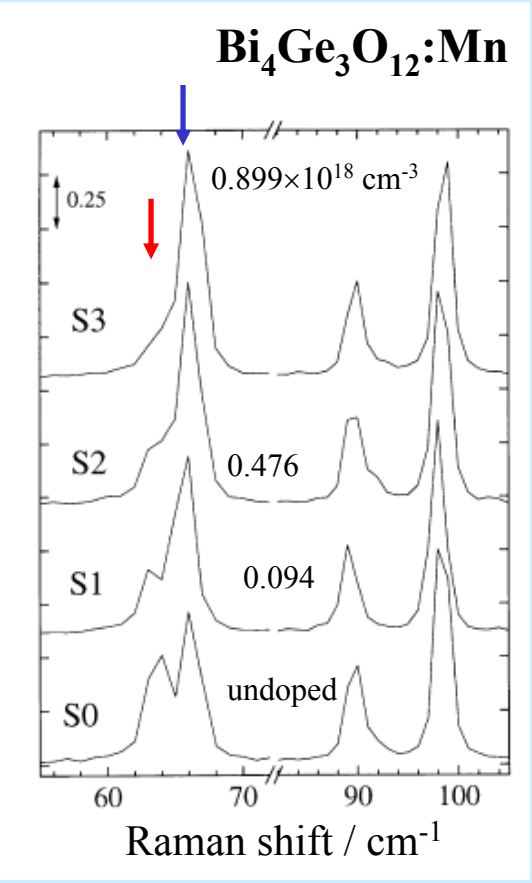
$I23$ (T_0^3)

Bi(24*f*), Si(2*a*),
O1(27*f*),
O2(8*c*), O3(8*c*)

WP	A	E^1	E^2	T
24f	3	3	3	9
8c	1	1	1	3
2a	-	-	-	1

T,x			T,y			T,z		
-	-	-	-	-	d	-	d	-
-	-	d	-	-	-	d	-	-
-	d	-	d	-	-	-	-	-





$I\bar{4}32$ (T_d^6)

Bi(16*c*),
Ge(12*a*),
O(48*e*)

WP	A_1	A_2	E	T_1	T_2
48e	3	3	6	9	9
16c	1	1	2	3	3
12a	-	1	1	2	3

T_2,x			T_2,y			T_2,z		
-	-	-	-	-	d	-	d	-
-	-	d	-	-	-	d	-	-
-	d	-	d	-	-	-	-	-

a change in I_{LO}/I_{TO} depending on type and concentration of dopant

One-mode / two-mode behaviour in solid solutions

different types of atoms in the same crystallogr. position, e.g. $(B'_{1-x}B''_{x})O_y$

two-mode behaviour:

- two peaks corresponding to "pure" *B'*-O and *B"*-O phonon modes
- intensity ratio I(*B'*-O)/I(*B"*-O) depends on *x*

  ✓ covalent character of chemical bonding : short correlation length
  ✓ relatively large difference in *f*(*B'*/*B"*-O) and/or *m*(*B'*/*B"*)

one-mode behaviour:

- one peak corresponding to the mixed *B'*-O/*B"*-O phonon mode
- ~ lineal dependence of the peak position ω on dopant concentration *x*

  ✓ ionic character of chemical bonding : long correlation length
  ✓ similarity in r_i(*B'*/*B"*), *f*(*B'*/*B"*-O) and *m*(*B'*/*B"*)

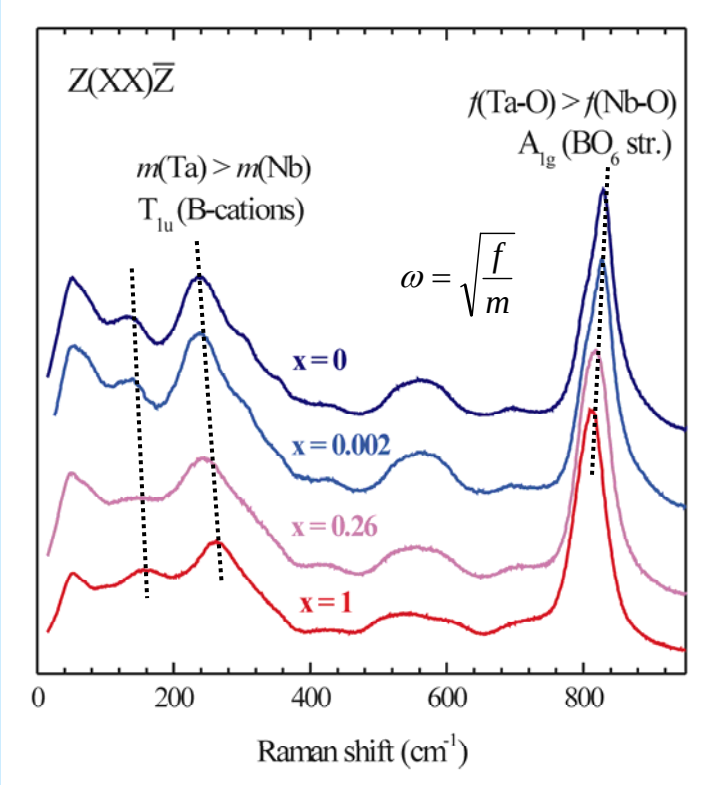
intermediate classes of materials:

two-mode over $x \in (0, x_m)$ and one-mode over $x \in (x_m, 1)$

One-mode / two-mode behaviour in solid solutions

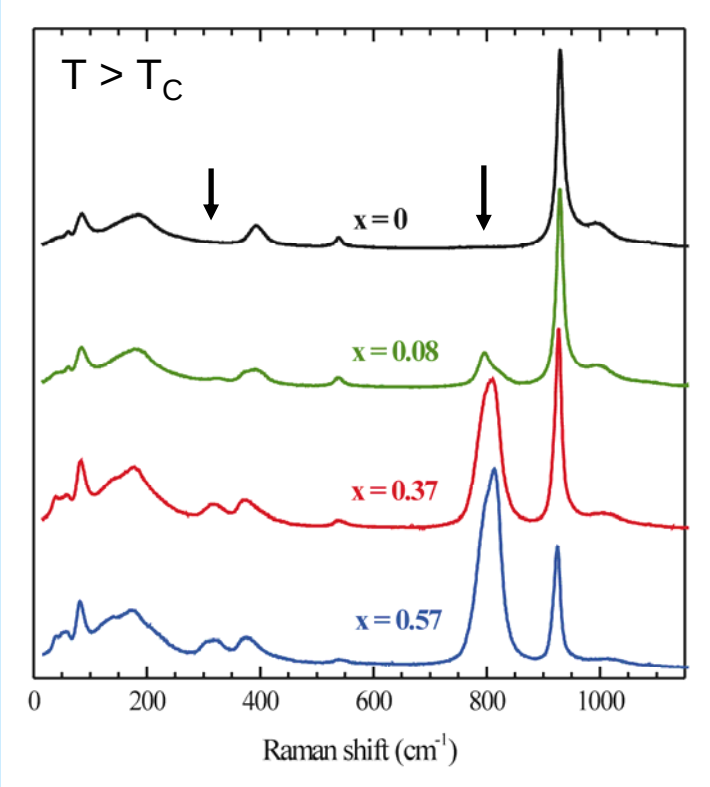
one-mode behaviour

$PbSc_{0.5}(Ta_{1-x}Nb_x)_{0.5}O_3$



two-mode behaviour

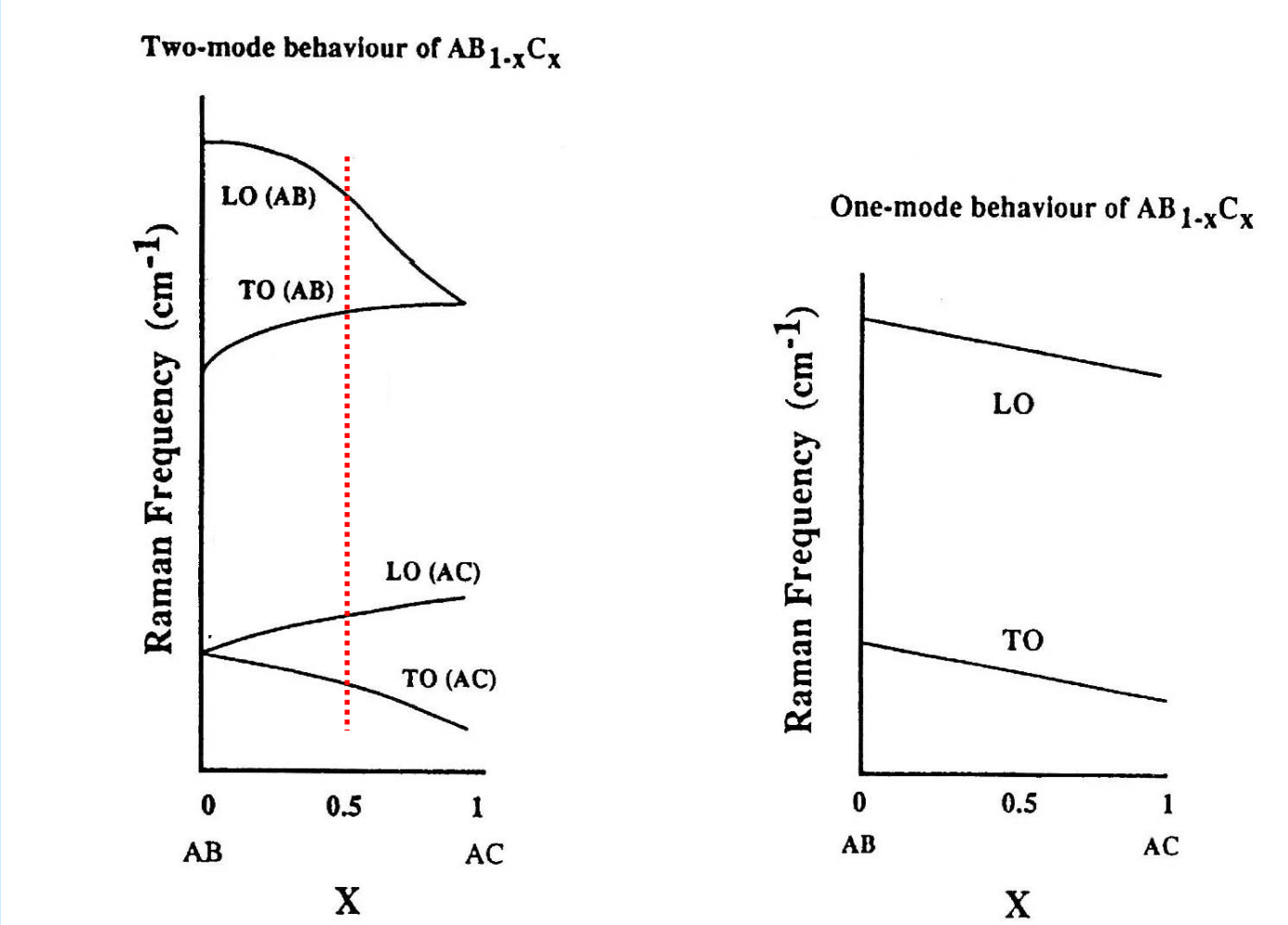
$Pb_3[(P_{1-x}As_x)O_4]_2$



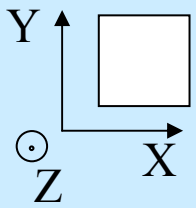
Non-centrosymmetric crystals with compositional disorder

LO-TO splitting + one-mode/**two-mode** behaviour:

we may observe **four** peaks instead of **one** !



Transformation of polarizability tensors

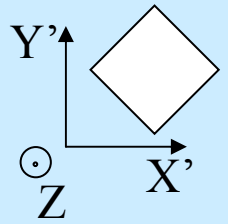


$$\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix}$$

$$\text{rot}_Z(\varphi=45°)$$

$$\alpha' = U^T \alpha U$$

$$\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix}$$

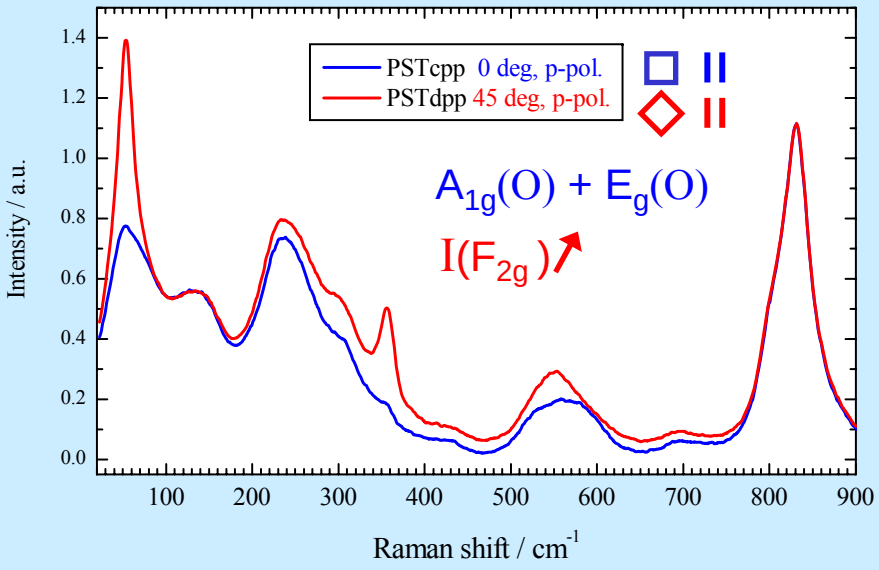


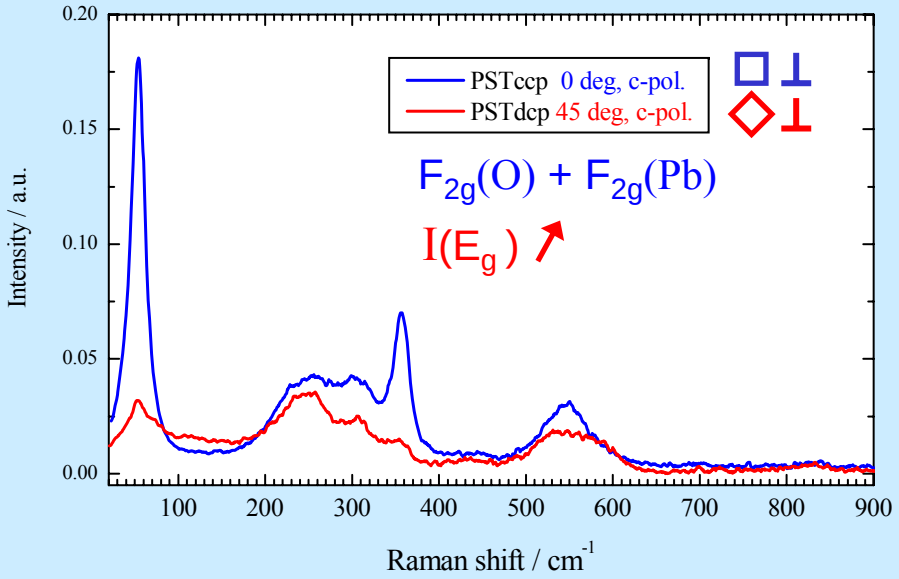
$$\begin{pmatrix} b & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & -2b \end{pmatrix} \quad \begin{pmatrix} \sqrt{3}b & 0 & 0 \\ 0 & -\sqrt{3}b & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\begin{pmatrix} b & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & -2b \end{pmatrix} \quad \begin{pmatrix} 0 & -\sqrt{3}b & 0 \\ -\sqrt{3}b & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & d \\ 0 & d & 0 \end{pmatrix} \quad \begin{pmatrix} 0 & 0 & d \\ 0 & 0 & 0 \\ d & 0 & 0 \end{pmatrix}$$

$$\begin{pmatrix} 0 & 0 & \frac{d}{\sqrt{2}} \\ 0 & 0 & \frac{d}{\sqrt{2}} \\ \frac{d}{\sqrt{2}} & \frac{d}{\sqrt{2}} & 0 \end{pmatrix} \quad \begin{pmatrix} 0 & 0 & \frac{d}{\sqrt{2}} \\ 0 & 0 & -\frac{d}{\sqrt{2}} \\ \frac{d}{\sqrt{2}} & -\frac{d}{\sqrt{2}} & 0 \end{pmatrix} \quad \begin{pmatrix} d & 0 & 0 \\ 0 & -d & 0 \\ 0 & 0 & 0 \end{pmatrix}$$





Conclusions

Group theory: predicts the number of expected IR and Raman peaks

one needs to know: crystal space symmetry + occupied Wyckoff positions

Deviations from the predictions of the group-theory analysis:

- ☺ LO-TO splitting if no centre of inversion (info included in the tables)
- ☺ one-mode – two-mode behaviour in solid solutions
- ☺☺☺ local structural distortions (length scale ~ 2-3 nm, time scale ~ 10^{-12} s)
- ☹ Experimental difficulties (low-intensity peaks, hardly resolved peaks)

What should we do before performing a Raman or IR experiment?