CECAM Tutorial: "Dynamical, dielectric and magnetic properties of solids with ABINIT"
Lyon, 12-16 may 2014

Symmetries of phonons

Gian-Marco Rignanese

UCL Université catholique de Louvain

ETSF

European Theoretical Spectroscopy Facility

IMCN

Institute of Condensed Matter and Nanosciences,
B-1348 Louvain-la-Neuve, Belgique

Introduction

- The phonon frequencies and eigenvectors are the solution of the following **generalized eigenvalue problem**:

$$\sum_{\kappa'\alpha'} \tilde{C}_{\kappa\alpha,\kappa'\alpha'}(\mathbf{q}) U_{m\mathbf{q}}(\kappa'\alpha') = M_\kappa \omega^2_{m\mathbf{q}} U_{m\mathbf{q}}(\kappa\alpha)$$

$\kappa'\alpha'$: atom; direction (α'=1,2,3)

$U_{m\mathbf{q}}(\kappa'\alpha')$: phonon displacement pattern

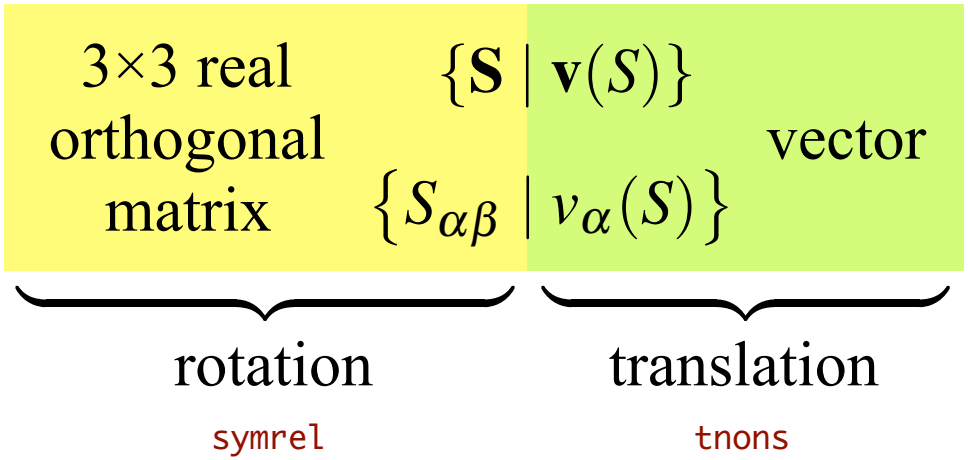
M_κ: masses

$\omega^2_{m\mathbf{q}}$: square of phonon frequencies

- The aim of this lecture is to show how it is possible to determine the symmetries of the phonon modes $U_{m\mathbf{q}}(\kappa\alpha)$ at a wave vector $\mathbf{q}$ using group theory.
- For pedagogic purposes, we focus on practical aspects without giving the formal justifications of the formulas presented here, which may be found in the litterature [1,2].

Symmetries

- In the following, we adopt the **Seitz notation** for the symmetry operations of the crystal:



smaller than any primitive translation vector of the crystal

- Applied to the equilibrium position vector of atom κ relative to the origin of the cell $\boldsymbol{\tau}_\kappa$, this symmetry transforms it as:

$$\{\mathbf{S} \mid \mathbf{v}(S)\}\,\tau_\kappa = \mathbf{S}\tau_\kappa + \mathbf{v}(S) = \tau_{\kappa'} + \mathbf{R}^a$$

$$\{S_{\alpha\beta} \mid v_\alpha(S)\}\,\tau_{\kappa\alpha} = S_{\alpha\beta}\,\tau_{\kappa\alpha} + v_\alpha(S) = \tau_{\kappa'\alpha} + R^a_\alpha$$

where $\mathbf{R}^a$ is a translation vector of the crystal.

Example 1: c-ZrO_2

- with WPASSIGN on the Bilbao Crystallographic Server [3]:

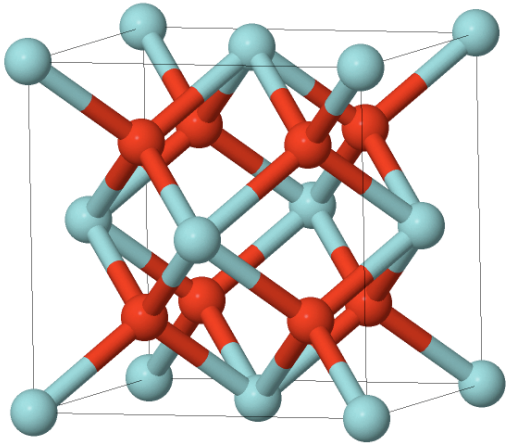
Bilbao Crystallographic Server → Assignment of Wyckoff Positions

Assignment of Wyckoff Positions

Atoms Data:

AT.	WP	SS	Representative	Atomic orbit
Zr1	4a (0,0,0)	m-3m	(0.000000,0.000000,0.000000)	(0.000000,0.000000,0.000000) (0.000000,0.500000,0.500000) (0.500000,0.000000,0.500000) (0.500000,0.500000,0.000000)
O2	8c (1/4,1/4,1/4)	-43m	(0.250000,0.250000,0.250000)	(0.250000,0.250000,0.250000) (0.750000,0.750000,0.250000) (0.750000,0.250000,0.750000) (0.250000,0.750000,0.750000) (0.250000,0.250000,0.750000) (0.750000,0.750000,0.750000) (0.250000,0.750000,0.250000) (0.750000,0.250000,0.250000)

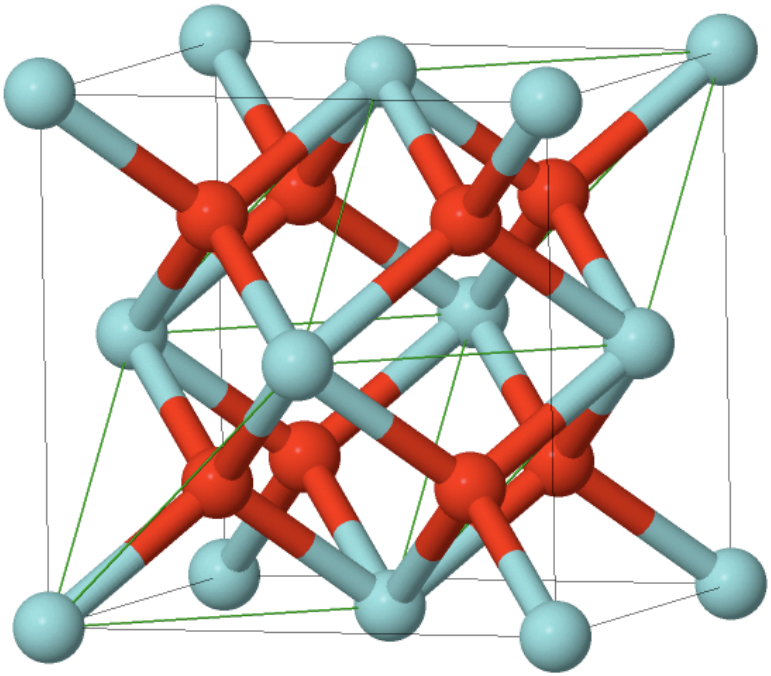
Fm−3m
a=5.010Å
b=5.010Å
c=5.010Å
α=90.0°
β=90.0°
γ=90.0°



Example 1: c-ZrO_2

- with ABINIT:

```
natom         3
rprim    0.0000000000E+00  5.0000000000E-01  5.0000000000E-01
         5.0000000000E-01  0.0000000000E+00  5.0000000000E-01
         5.0000000000E-01  5.0000000000E-01  0.0000000000E+00
typat    1  2  2
 xred    0.0000000000E+00  0.0000000000E+00  0.0000000000E+00
         2.5000000000E-01  2.5000000000E-01  2.5000000000E-01
        -2.5000000000E-01 -2.5000000000E-01 -2.5000000000E-01
```



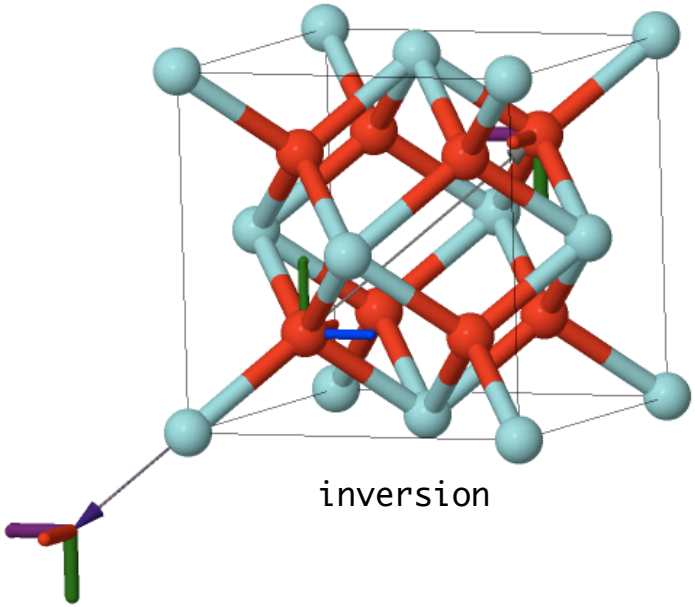
Example 1: c-ZrO_2

- with ABINIT (output file):

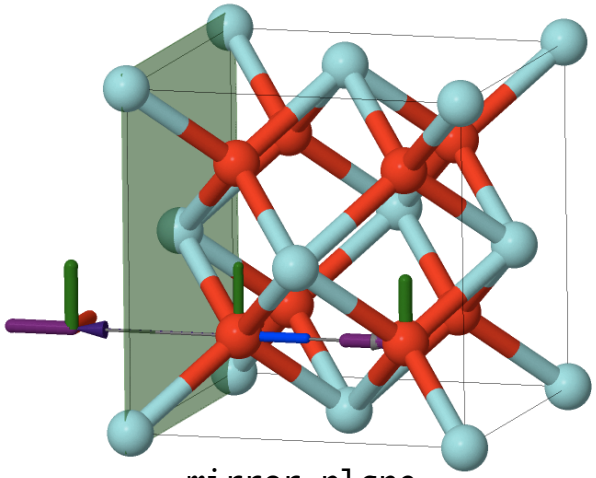
```
Symmetries : space group Fm -3 m (#225); Bravais cF (face-center cubic)
  spgroup       225
   symrel    1  0  0   0  1  0   0  0  1      -1  0  0   0 -1  0   0  0 -1
             0 -1  1   0 -1  0   1 -1  0       0  1 -1   0  1  0  -1  1  0

             ...                               ...

             0  0 -1   1  0 -1   0  1 -1       0  0  1  -1  0  1   0 -1  1
            -1  1  0  -1  0  1  -1  0  0       1 -1  0   1  0 -1   1  0  0
```



inversion



mirror plane

Example 2: Si

- with WPASSIGN on the Bilbao Crystallographic Server [3]:

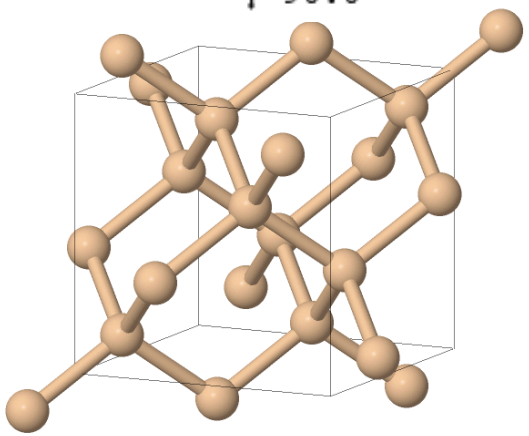
Bilbao Crystallographic Server → Assignment of Wyckoff Positions

Assignment of Wyckoff Positions

Atoms Data:

AT.	WP	SS	Representative	Atomic orbit
Si1	8a (1/8,1/8,1/8)	-43m	(0.125000,0.125000,0.125000)	(0.125000,0.125000,0.125000) (0.625000,0.125000,0.625000) (0.125000,0.625000,0.625000) (0.625000,0.625000,0.125000) (0.875000,0.375000,0.375000) (0.875000,0.875000,0.875000) (0.375000,0.375000,0.875000) (0.375000,0.875000,0.375000)

F d 3 m
a=5.431Å
b=5.431Å
c=5.431Å
α=90.0°
β=90.0°
γ=90.0°



- with ABINIT

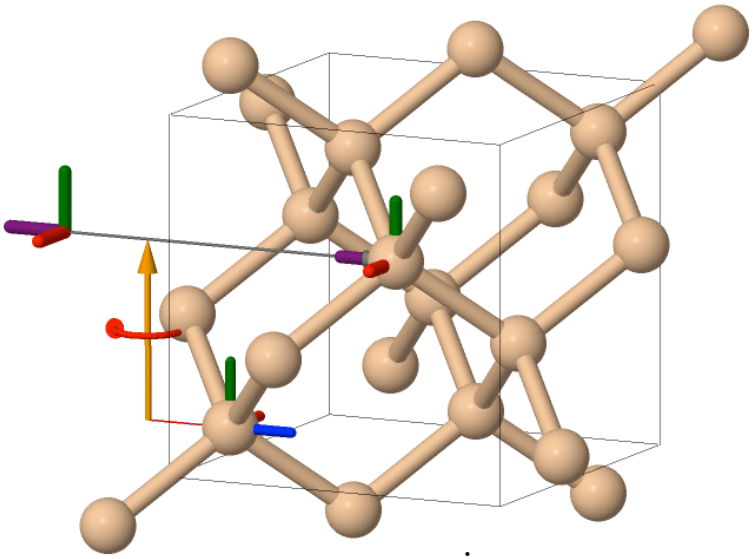
```
natom         2
rprim    0.0000000000E+00  5.0000000000E-01  5.0000000000E-01
         5.0000000000E-01  0.0000000000E+00  5.0000000000E-01
         5.0000000000E-01  5.0000000000E-01  0.0000000000E+00
typat    1  1
 xred    1.2500000000E-01  1.2500000000E-01  1.2500000000E-01
         8.7500000000E-01  8.7500000000E-01  8.7500000000E-01
```

Example 2: Si

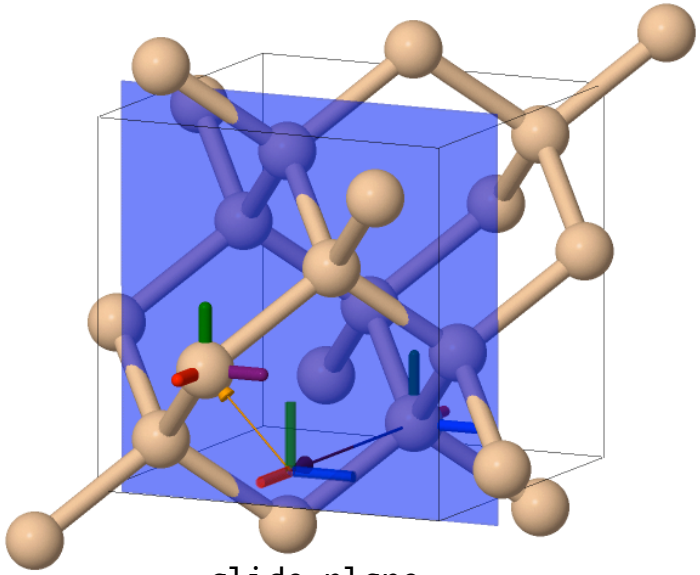
- with ABINIT:

```
Symmetries : space group Fd -3 m (#227); Bravais cF (face-center cubic)
  spgroup      227
   symrel    1  0  0   0  1  0   0  0  1      -1  0  0   0 -1  0   0  0 -1
             0 -1  1   0 -1  0   1 -1  0       0  1 -1   0  1  0  -1  1  0
             ...                               ...

    tnons    0.0000000  0.0000000  0.0000000    0.0000000  0.0000000  0.0000000
             0.0000000  0.5000000  0.0000000    0.0000000  0.5000000  0.0000000
             ...                               ...
```



screw axis



glide plane

Group of the wave vector q

- The first step is to determine $G_{\mathbf{q}}$ the group consisting of the symmetry operations of the crystal $\{\mathbf{S} \mid \mathbf{v}(S)\}$ whose purely rotational part $\{\mathbf{S}\}$ have the property:

$$\mathbf{Sq} = \mathbf{q} + \mathbf{G}$$

where **G** is a translational vector of the reciprocal lattice.

rem 1: **G** vanishes if **q** lies inside the first Brillouin zone.

rem 2: **G** can only be non-zero if **q** is on the border of the zone.

rem 3: if **q**=Γ, the group of the wave vector is simply the point group of the crystal.

Character table of $G_{\mathbf{q}}$

- The next step is to obtain the character table for the group $G_{\mathbf{q}}$. The various tables for all space groups and special points can be found in books (e.g. [4]).
- Alternatively, the Bilbao Crystallographic Server [3] provides all the tables for the Γ point.

Exemple 1: Si at the L point

representation	basis	$\{E\|0\}$	$2\{C_3\|0\}$	$3\{C_{2'}\|0\}$	$\{i\|0\}$	$2\{iC_3\|0\}$	$3\{iC_{2'}\|0\}$
L_1	$1; xy+yz+xz$	1	1	1	1	1	1
L_2	$yz(y^2-z^2)+xy(x^2-y^2)+xz(z^2-x^2)$	1	1	−1	1	1	−1
L_3	$2x^2-y^2-z^2, y^2-z^2$	2	−1	0	2	−1	0
L_1'	$x(y^2-z^2)+y(z^2-x^2)+z(x^2-y^2)$	1	1	1	−1	−1	−1
L_2'	$x+y+z$	1	1	−1	−1	−1	1
L_3'	$y-z, 2x-y-z$	2	−1	0	−2	1	0

Example 2: c-ZrO_2 and Si at the Γ point

- with POINT on the Bilbao Crystallographic Server [3]:

O_h(m-3m)	#	E	4	2	3	2'	I	-4	m	-3	m'	functions
Mult.	-	1	6	3	8	6	1	6	3	8	6	·
A_{1g}	Γ_1^+	1	1	1	1	1	1	1	1	1	1	$x^2+y^2+z^2$
A_{1u}	Γ_1^-	1	1	1	1	1	-1	-1	-1	-1	-1	·
A_{2g}	Γ_2^+	1	-1	1	1	-1	1	-1	1	1	-1	·
A_{2u}	Γ_2^-	1	-1	1	1	-1	-1	1	-1	-1	1	·
E_g	Γ_3^+	2	0	2	-1	0	2	0	2	-1	0	$(2z^2-x^2-y^2,x^2-y^2)$
E_u	Γ_3^-	2	0	2	-1	0	-2	0	-2	1	0	·
T_{2u}	Γ_5^-	3	-1	-1	0	1	-3	1	1	0	-1	·
T_{2g}	Γ_5^+	3	-1	-1	0	1	3	-1	-1	0	1	(xy,xz,yz)
T_{1u}	Γ_4^-	3	1	-1	0	-1	-3	-1	1	0	1	(x,y,z)
T_{1g}	Γ_4^+	3	1	-1	0	-1	3	1	-1	0	-1	(J_x,J_y,J_z)

Irreducible representation

- The symmetries of phonons are related to the transformation properties of the displacement vectors $U_{m\mathbf{q}}(\kappa\alpha)$.
- In group theoretical terms, this implies to take direct product of the irreducible representations for the vector (x, y, z) with those of the various atomic sites: $\chi_V \otimes \chi_{atomic\ sites}$
- Step 1: find χ_V

Exemple 1: Si at the L point

representation	basis	$\{E\|0\}$	$2\{C_3\|0\}$	$3\{C_{2'}\|0\}$	$\{i\|0\}$	$2\{iC_3\|0\}$	$3\{iC_{2'}\|0\}$
L_1	$1; xy+yz+xz$	1	1	1	1	1	1
L_2	$yz(y^2-z^2)+xy(x^2-y^2)+xz(z^2-x^2)$	1	1	−1	1	1	−1
L_3	$2x^2-y^2-z^2, y^2-z^2$	2	−1	0	2	−1	0
L_1'	$x(y^2-z^2)+y(z^2-x^2)+z(x^2-y^2)$	1	1	1	−1	−1	−1
L_2'	$x+y+z$	1	1	−1	−1	−1	1
L_3'	$y-z, 2x-y-z$	2	−1	0	−2	1	0

$$\chi_V = L_2' \oplus L_3'$$

Example 2: c-ZrO_2 and Si at the Γ point

O_h(m-3m)	#	E	4	2	3	2'	I	-4	m	-3	m'	functions
Mult.	-	1	6	3	8	6	1	6	3	8	6	·
A_{1g}	Γ_1^+	1	1	1	1	1	1	1	1	1	1	$x^2+y^2+z^2$
A_{1u}	Γ_1^-	1	1	1	1	1	-1	-1	-1	-1	-1	·
A_{2g}	Γ_2^+	1	-1	1	1	-1	1	-1	1	1	-1	·
A_{2u}	Γ_2^-	1	-1	1	1	-1	-1	1	-1	-1	1	·
E_g	Γ_3^+	2	0	2	-1	0	2	0	2	-1	0	$(2z^2-x^2-y^2, x^2-y^2)$
E_u	Γ_3^-	2	0	2	-1	0	-2	0	-2	1	0	·
T_{2u}	Γ_5^-	3	-1	-1	0	1	-3	1	1	0	-1	·
T_{2g}	Γ_5^+	3	-1	-1	0	1	3	-1	-1	0	1	(xy,xz,yz)
T_{1u}	Γ_4^-	3	1	-1	0	-1	-3	-1	1	0	1	(x,y,z)
T_{1g}	Γ_4^+	3	1	-1	0	-1	3	1	-1	0	-1	(J_x,J_y,J_z)

$$\chi_V = T_{1u}$$

Irreducible representation

- Step 2: find $\chi_{atomic\ sites}$
  - ★ Each atomic site is also characterized by one or more symmetry operations that map the atomic site onto itself. The collection of these symmetry operations define the site group (usually labeled using Wyckoff notation). The site group can be one of the 32 crystallographic point groups and must be a subgroup of the space group.
  - ★ For each site, the characters $\chi_{atomic\ sites}$ represent the number of atoms that are invariant under the symmetry operations of the group.

Example: c-ZrO_2

- with ABINIT (log file):

```
symspgr : the symmetry operation no.   1 is the identity
symspgr : the symmetry operation no.   2 is an inversion
symaxes : the symmetry operation no.   3 is a 2-axis
symplanes : the symmetry operation no.   4 is a mirror plane
symaxes : the symmetry operation no.   5 is a 2-axis
symplanes : the symmetry operation no.   6 is a mirror plane
symaxes : the symmetry operation no.   7 is a 2-axis
symplanes : the symmetry operation no.   8 is a mirror plane

...

symplanes : the symmetry operation no.  41 is a mirror plane
symaxes : the symmetry operation no.  42 is a 2-axis
symplanes : the symmetry operation no.  43 is a mirror plane
symaxes : the symmetry operation no.  44 is a 2-axis
symspgr : the symmetry operation no.  45 is a -4 axis
symaxes : the symmetry operation no.  46 is a 4-axis
symspgr : the symmetry operation no.  47 is a -4 axis
symaxes : the symmetry operation no.  48 is a 4-axis
```

Example: c-ZrO_2

- with ABINIT (log file):

```
symatm: atom number    1 is reached starting at atom
  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1
  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1
symatm: atom number    2 is reached starting at atom
  2  3  2  3  2  3  2  3  2  3  2  3  2  3  2  3  2  3  2  3  2  3  2  3
  2  3  2  3  2  3  2  3  2  3  2  3  2  3  2  3  2  3  2  3  2  3  2  3
symatm: atom number    3 is reached starting at atom
  3  2  3  2  3  2  3  2  3  2  3  2  3  2  3  2  3  2  3  2  3  2  3  2
  3  2  3  2  3  2  3  2  3  2  3  2  3  2  3  2  3  2  3  2  3  2  3  2
```

$$\chi_{atom\ site\ 4a} = A_{1g}$$

$$\chi_{atom\ site\ 8c} = A_{1g} \oplus A_{2u}$$

O_h(m-3m)	#	E	4	2	3	2'	I	-4	m	-3	m'	functions
Mult.	-	1	6	3	8	6	1	6	3	8	6	·
A_{1g}	Γ_1^+	1	1	1	1	1	1	1	1	1	1	$x^2+y^2+z^2$
A_{2u}	Γ_2^-	1	-1	1	1	-1	-1	1	-1	-1	1	·

Irreducible representation

- Step 3: compute $\chi_V \otimes \chi_{atomic\ sites}$

$$\chi_V \otimes \chi_{atom\ site\ 4a} = T_{1u} \otimes A_{1g} = T_{1u}$$

$$\chi_V \otimes \chi_{atom\ site\ 8c} = T_{1u} \otimes (A_{1g} \oplus A_{2u}) = T_{1u} \oplus T_{2g}$$

$$\Gamma = T_{2g} \oplus T_{1u} \oplus T_{1u}$$

Multiplication Table

O_h(m-3m)	A_{1g}	A_{1u}	A_{2g}	A_{2u}	E_u	E_g	T_{2u}	T_{2g}	T_{1u}	T_{1g}
A_{1g}	A_{1g}	A_{1u}	A_{2g}	A_{2u}	E_u	E_g	T_{2u}	T_{2g}	T_{1u}	T_{1g}
A_{1u}	·	A_{1g}	A_{2u}	A_{2g}	E_g	E_u	T_{2g}	T_{2u}	T_{1g}	T_{1u}
A_{2g}	·	·	A_{1g}	A_{1u}	E_u	E_g	T_{1u}	T_{1g}	T_{2u}	T_{2g}
A_{2u}	·	·	·	A_{1g}	E_g	E_u	T_{1g}	T_{1u}	T_{2g}	T_{2u}
E_u	·	·	·	·	$A_{1g}+A_{2g}+E_g$	$A_{1u}+A_{2u}+E_u$	$T_{2g}+T_{1g}$	$T_{2u}+T_{1u}$	$T_{2g}+T_{1g}$	$T_{2u}+T_{1u}$
E_g	·	·	·	·	·	$A_{1g}+A_{2g}+E_g$	$T_{2u}+T_{1u}$	$T_{2g}+T_{1g}$	$T_{2u}+T_{1u}$	$T_{2g}+T_{1g}$
T_{2u}	·	·	·	·	·	·	$A_{1g}+E_g+T_{2g}+T_{1g}$	$A_{1u}+E_u+T_{2u}+T_{1u}$	$A_{2g}+E_g+T_{2g}+T_{1g}$	$A_{2u}+E_u+T_{2u}+T_{1u}$
T_{2g}	·	·	·	·	·	·	·	$A_{1g}+E_g+T_{2g}+T_{1g}$	$A_{2u}+E_u+T_{2u}+T_{1u}$	$A_{2g}+E_g+T_{2g}+T_{1g}$
T_{1u}	·	·	·	·	·	·	·	·	$A_{1g}+E_g+T_{2g}+T_{1g}$	$A_{1u}+E_u+T_{2u}+T_{1u}$
T_{1g}	·	·	·	·	·	·	·	·	·	$A_{1g}+E_g+T_{2g}+T_{1g}$

[**Note:** the table is symmetric]

Irreducible representation

- Step 3: compute $\chi_V \otimes \chi_{atomic\ sites}$

$$\chi_V \otimes \chi_{atom\ site\ 4a} = T_{1u} \otimes A_{1g} = T_{1u}$$

$$\chi_V \otimes \chi_{atom\ site\ 8c} = T_{1u} \otimes (A_{1g} \oplus A_{2u}) = T_{1u} \oplus T_{2g}$$

$$\Gamma = T_{2g} \oplus T_{1u} \oplus T_{1u}$$

Mechanical Representation

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

Irreducible representation

- Step 3: compute $\chi_V \otimes \chi_{atomic\ sites}$

$$\chi_V \otimes \chi_{atom\ site\ 4a} = T_{1u} \otimes A_{1g} = T_{1u}$$

$$\chi_V \otimes \chi_{atom\ site\ 8c} = T_{1u} \otimes (A_{1g} \oplus A_{2u}) = T_{1u} \oplus T_{2g}$$

$$\Gamma = T_{2g} \oplus T_{1u} \oplus T_{1u}$$

IR Active Modes

WP	A_{1g}	A_{1u}	A_{2g}	A_{2u}	E_u	E_g	T_{2u}	T_{2g}	T_{1u}	T_{1g}
8c	·	·	·	·	·	·	·	·	1	·
4a	·	·	·	·	·	·	·	·	1	·

Raman Active Modes

WP	A_{1g}	A_{1u}	A_{2g}	A_{2u}	E_u	E_g	T_{2u}	T_{2g}	T_{1u}	T_{1g}
8c	·	·	·	·	·	·	·	1	·	·
4a	·	·	·	·	·	·	·	·	·	·

Irreducible representation

- Step 4: assign each phonon mode m individually

  ★ find its characters $\chi_{m\mathbf{q}}(\{\mathbf{S} \mid \mathbf{v}(S)\})$ with respect to the various symmetry operations of $G_{\mathbf{q}}$:

$$\chi_{m\mathbf{q}}(\{\mathbf{S} \mid \mathbf{v}(S)\}) = \sum_{\kappa\kappa'} \sum_{\alpha\beta} U_{m\mathbf{q}}(\kappa\alpha) S_{\alpha\beta} e^{i\mathbf{q}\cdot[\tau_\kappa - \mathbf{S}\tau_\kappa]} \times \delta(\kappa, F_0(\kappa'; R)) U_{m\mathbf{q}}(\kappa'\beta)$$

  where $F_0(\kappa';\mathrm{S})$ is the label of the atom to which the atom κ' is brought by the symmetry operation $\{\mathbf{S} \mid \mathbf{v}(S)\}$;
  the δ expresses that we only need to take into account those atoms κ' that map on to atom κ by the symmetry operation

  ★ compare the character to the table

Example: c-ZrO_2

- with ANADDB (output file):

```
Analysis of degeneracies and characters (maximum tolerance=0.000001 a.u.)
Symmetry characters of vibration mode #   1
      degenerate with vibration modes #   2 to    3
 3.0 -3.0 -1.0  1.0 -1.0  1.0 -1.0  1.0  1.0 -1.0 -1.0  1.0  1.0 -1.0 -1.0  1.0
 0.0  0.0  0.0  0.0  0.0  0.0  0.0  0.0  1.0 -1.0 -1.0  1.0 -1.0  1.0  1.0 -1.0
 0.0  0.0  0.0  0.0  0.0  0.0  0.0  0.0  1.0 -1.0  1.0 -1.0 -1.0  1.0 -1.0  1.0
Symmetry characters of vibration mode #   4
      degenerate with vibration modes #   5 to    6
 3.0 -3.0 -1.0  1.0 -1.0  1.0 -1.0  1.0  1.0 -1.0 -1.0  1.0  1.0 -1.0 -1.0  1.0
 0.0  0.0  0.0  0.0  0.0  0.0  0.0  0.0  1.0 -1.0 -1.0  1.0 -1.0  1.0  1.0 -1.0
 0.0  0.0  0.0  0.0  0.0  0.0  0.0  0.0  1.0 -1.0  1.0 -1.0 -1.0  1.0 -1.0  1.0
Symmetry characters of vibration mode #   7
      degenerate with vibration modes #   8 to    9
 3.0  3.0 -1.0 -1.0 -1.0 -1.0 -1.0 -1.0  1.0  1.0 -1.0 -1.0  1.0  1.0 -1.0 -1.0
 0.0  0.0  0.0  0.0  0.0  0.0  0.0  0.0  1.0  1.0 -1.0 -1.0 -1.0 -1.0  1.0  1.0
 0.0  0.0  0.0  0.0  0.0  0.0  0.0  0.0  1.0  1.0  1.0  1.0 -1.0 -1.0 -1.0 -1.0
```

- assignments:

modes	E	4	2	3	2'	I	-4	m	-3	m	
1-3	3	1	-1	0	-1	-3	-1	1	0	1	→ F1u
4-6	3	1	-1	0	-1	-3	-1	1	0	1	→ F1u
7-9	3	-1	-1	0	1	3	-1	-1	0	1	→ F2g

Bibliography

1. A.A. Maradudin and S.H. Vosko,
   Symmetry properties of the normal vibrations of a crystal,Rev. Mod. Phys. **40**, 1-37 (1968).
2. M.S. Dresselhaus, G. Dresselhaus, and A. Jorio,
   Group Theory: Application to the Physics of Condensed Matter (Springer-Verlag, Berlin, 2008).
3. Bilbao Crystallographic Server:
   http://www.cryst.ehu.es
4. S.C. Miller and W.S. Love,
   Tables of Irreducible Representations of Space Groups and Co-Representations of Magnetic Space Groups (Pruett Press, Boulder, CO, 1967).