Introduction to group theory

From an experimentalist's perspective…😱

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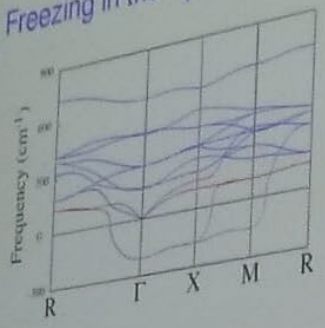
The primitive unit cell of orthorhombic perovskite (Pnma), has four formula units ABO_3 (in total 20 atoms), giving 60 Γ-point vibrational modes. Factor group analysis yields to the following modes:

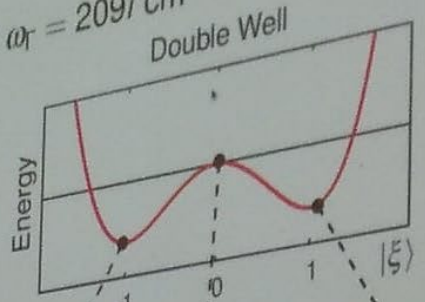
$$\Gamma_{(\mathrm{Pnma})} = 8A_u + 10B_{1u} + 8B_{2u} + 10B_{3u} + 7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g} \quad (3)$$

where $7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}$, a total of 24 modes, are Raman active (Zheng et al. 2004).

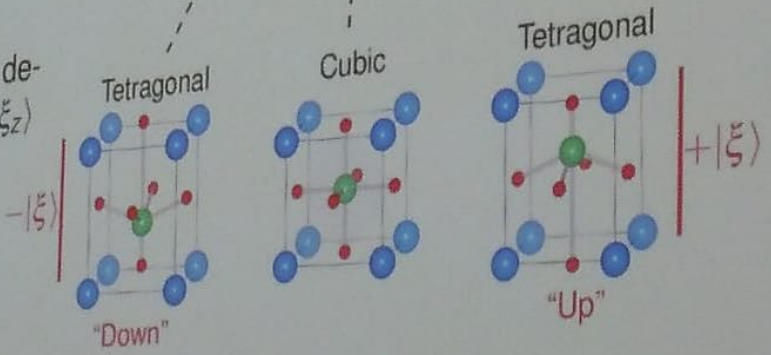
Example 1: Application to $BaTiO_3$

Freezing in the Γ_4^- polar instability: $\omega_\Gamma = 209i\ cm^{-1}$





Instability at Γ triply degenerated: $|\xi_x\rangle$, $|\xi_y\rangle$, $|\xi_z\rangle$



Polar instability: mode effective charge $\overline{Z}^* = 9.2$ (infrared active mode)

Disclaimers

- (almost no) equation
- (way too much) text
- (almost no) mathematical rigour

Molecular and crystal symmetry

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Symmetry operations and notations

Rotations

- Noted *n* or C_n for a rotation by $2\pi/n$
- Always anti-clockwise

Mirror planes

- Noted m_u or σ_u, *u* being a normal to the plane

Inversion center

- Noted -1 or *i*
- For a molecule:
  - Always at the origin, when it exists
  - Unique or non-existant

Molecular and crystal symmetry

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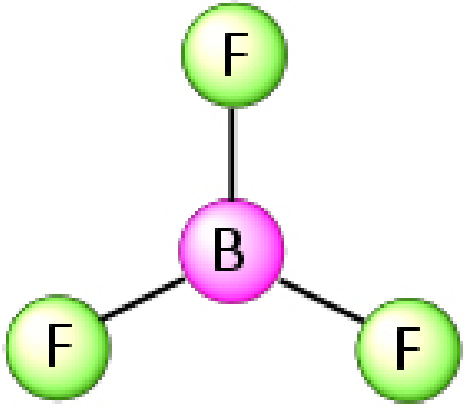
Symmetry operations and notations for molecules

Improper rotations or rotoinversion

- Combination of a rotation + inversion
- Noted $-n$, or S_n for a rotation by $2\pi/n$
- May leave a molecule invariant even if the rotation and inversion alone do not

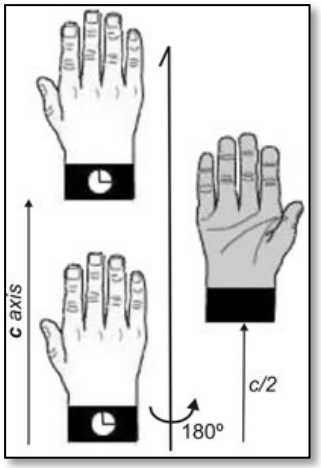


Molecular and crystal symmetry

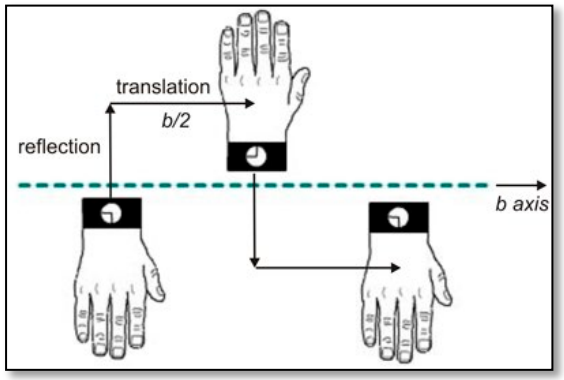
Additional symmetry elements for crystals:

- **Translations by lattice vectors**
- **Skrew axis:** Combination of a rotation and a translation along the rotation axis by a fraction of a lattice vector.
- **Glide planes:** Combination of a mirror symmetry with a translation parallel to the mirror plane by a fraction of a lattice vector

Skrew axis



Glide plane



Molecular and crystal symmetry

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Definition of a group

A group is a set, *G*, together with an operation "o" that combines any two elements *a* and *b* to form another element, denoted *a* o *b* or *ab*, such that the following conditions are satisfied*:*

1. Closure:
The combination of two elements of a group must give an element of a group

2. Identity element:
There exists one element of the group such that *a* o *E* = *E o a* = *a*

3. Associativity:
The combination of two group elements is associative A o (B o C) = (A o B) o C

4. Inverse:
Every element has its inverse element (also element of the group).
A o A^{-1}= A^{-1} o A = *E*

The set of symmetry elements leaving a molecule or a crystal physically invariant forms a group.

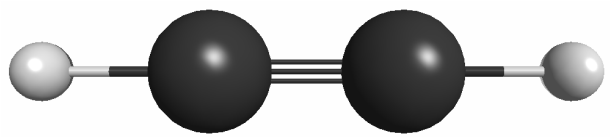
Molecular and crystal symmetry

For crystal symmetry:

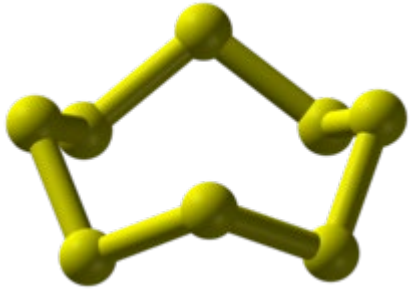
- Rotations are limited to 2,3,4 and 6 by the crystallographic restriction theorem
- 32 crystallographic point groups (+ magnetism → 122)
- 230 crystallographic space groups (+ magnetism → 1651)

For molecular symmetry: no particular restrictions in theory…

- crystallographic point groups
- + point groups for linear molecules
- + point groups for permitted rotation invariance (5-fold, 8-fold etc.)
- + Full rotation symmetry for isolated atoms



acetylene
C_2H_2



sulfur
S_8

Molecular and crystal symmetry

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Notion of « site symmetry »

Definition

Site symmetry of an atom A = set of symmetry operations that leave this particular atomic position unchanged

Properties

The site symmetry is described by point group, and is a subgroup of the group of the crystal or molecule.

Can be found by manual inspection, or in the international tables of crystallography.

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates			
8	*d*	1	(1) x,y,z (5) $\bar{x},\bar{y},\bar{z}$	(2) $\bar{x}+\frac{1}{2},\bar{y},z+\frac{1}{2}$ (6) $x+\frac{1}{2},y,\bar{z}+\frac{1}{2}$	(3) $\bar{x},y$ (7) $x,\bar{y}$	
4	*c*	. *m* .	$x,\frac{1}{4},z$	$\bar{x}+\frac{1}{2},\frac{3}{4},z+\frac{1}{2}$	$\bar{x},\frac{3}{4},\bar{z}$	x
4	*b*	$\bar{1}$	$0,0,\frac{1}{2}$	$\frac{1}{2},0,0$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$
4	*a*	$\bar{1}$	$0,0,0$	$\frac{1}{2},0,\frac{1}{2}$	$0,\frac{1}{2},0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$

Classification and notations

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For point groups

Schoenflies notation:
suitable for point groups, molecules → used in spectroscopy, chemistry...

Hermann-Mauguin notation (International notation):
suitable for point groups and space groups → used in physics, crystallography…

Notations for the 32 crystallographic point groups

	Triclinic		Monoclinic			Orthorhombic			Tetragonal						
Schoenflies	C_1	C_i	C_2	C_s	C_{2h}	D_2	C_{2v}	D_{2h}	C_4	S_4	C_{4h}	D_4	C_{4v}	D_{2d}	D_{4h}
Hermann-Mauguin	1	$\bar{1}$	2	m	$2/m$	222	$mm2$	mmm	4	$\bar{4}$	$4/m$	422	$4mm$	$\bar{4}2m$	$4/mmm$

	Trigonal					Hexagonal							Cubic				
Schoenflies	C_3	C_{3i}	D_3	C_{3v}	D_{3d}	C_6	C_{3h}	C_{6h}	D_6	C_{6v}	D_{3h}	D_{6h}	T	T_h	O	T_d	O_h
Hermann-Mauguin	3	$\bar{3}$	32	$3m$	$\bar{3}m$	6	$\bar{6}$	$6/m$	622	$6mm$	$\bar{6}m2$	$6/mmm$	23	$m\bar{3}$	432	$\bar{4}3m$	$m\bar{3}m$

Classification and notations

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C_n (for *"cyclic"*) has an *n*-fold rotation axis.

C_{nh} (*h for "horizontal"*) is C_n + a mirror plane perpendicular to the axis of rotation.

C_{nv} (v for "*vertical*") is C_n + *n* mirror planes containing the axis of rotation.

S_{2n} (for "*Spiegel*") contains only a 2*n*-fold rotation-reflection axis.

C_{ni} has only a rotoinversion axis. Redundant for $n>1$ but sometimes used.

D_n (for *"dihedral"*, or two-sided) has an *n*-fold rotation axis plus *n* twofold axes perpendicular to that axis.

D_{nh} is D_n + a horizontal mirror plane and, as a consequence, also *n* vertical mirror planes each containing the *n*-fold axis and one of the twofold axes.

D_{nd} (*d* for *"diagonal"*) is D_n + *n* vertical mirror planes which pass between twofold axes (*diagonal planes*).

Adapted from https://en.wikipedia.org/wiki/Schoenflies_notation

Classification and notations

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T (for *"tetrahedral"*) has the rotation axes of a tetrahedron.

T_d (*d* for *"diagonal"*) includes diagonal mirror planes.

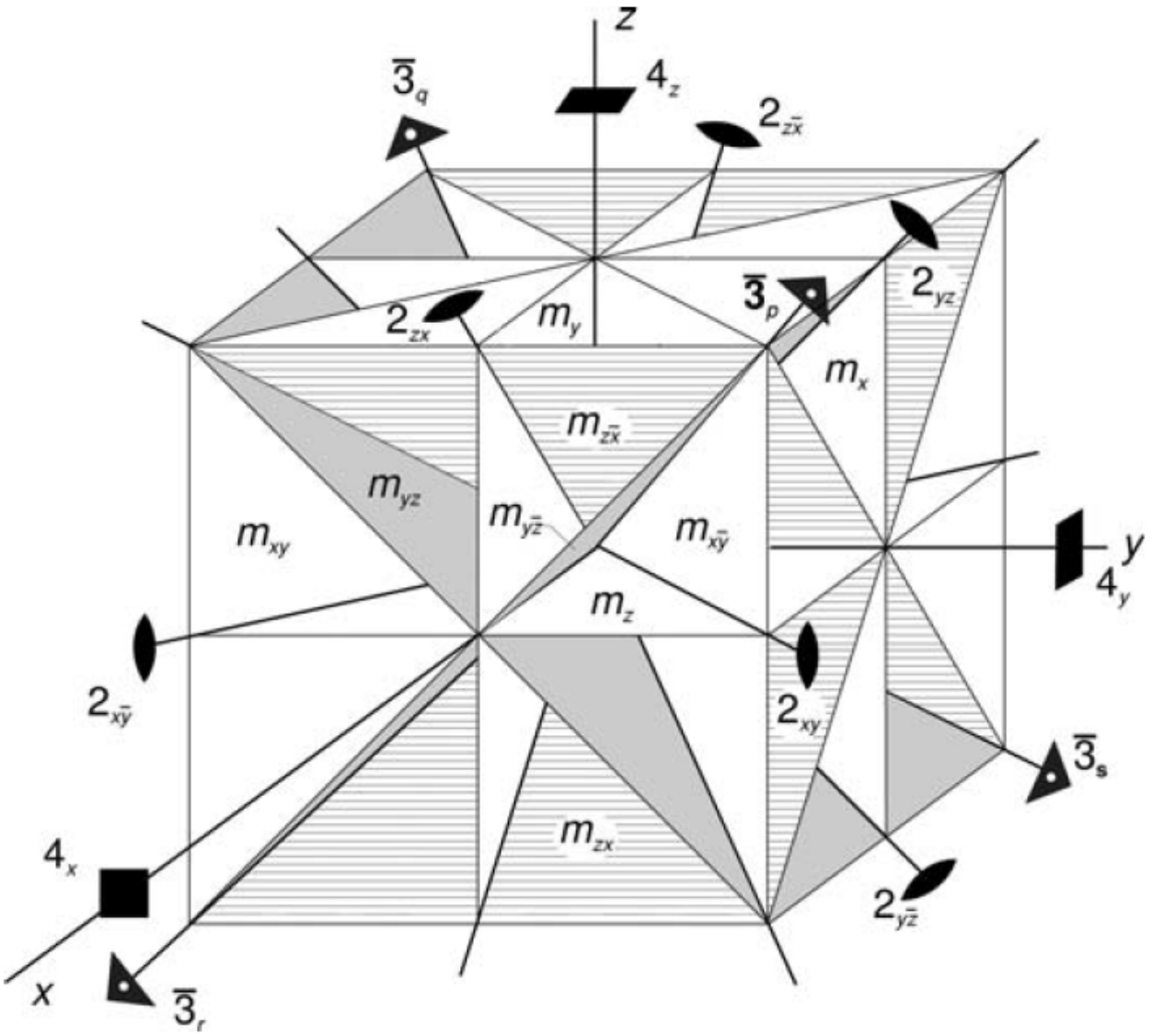
T_h (*h* for *"horizontal"*) includes three horizontal mirror planes. Each plane contains two twofold axes and is perpendicular to the third twofold axis, which results in inversion center **i**.

O (for *"octahedral"*) has the rotation axes of an octahedron or cube (three 4-fold axes, four 3-fold axes, and 6 diagonal 2-fold axes).

O_h (h for *"horizontal"*): includes horizontal mirror planes and, as a consequence, vertical mirror planes. It contains also inversion center and improper rotation operations.

Adapted from https://en.wikipedia.org/wiki/Schoenflies_notation

Classification and notations



Classification and notations

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<table>
<tr><td colspan="3">Crystallographic point groups (32)</td></tr>
<tr><td colspan="2">Piezoelectric (20)</td><td rowspan="2">Non piezoelectric</td></tr>
<tr><td>Polar / pyroelectric (10)</td><td>Non polar</td></tr>
<tr><td>1, 2, m, mm2, 4, 4mm, 3, 3m, 6, 6mm</td><td>222, -4, 422, -42m, 32, -6, 622, -62m, 23, 43m.</td><td>-1, 2/m, mmm, 4/m, 4/mmm, -3m, 6/m, 6/mmm, m-3, 432, -43m, m-3m</td></tr>
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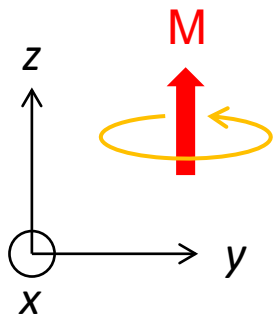
Molecular and crystal symmetry

Additional symmetry elements for magnetism:

- **Time inversion symmetry:** 1’
- **Its combinations** with spatial symmetry operations: e.g. m + 1’ = m’



	1’	-1	m_y	m_y’
P ↑	↑	↓	↑	↑
M ↑	↓	↑	↓	↑

Molecular and crystal symmetry

Additional symmetry elements for magnetism:

- **Time inversion symmetry:** 1’
- **Its combinations** with spatial symmetry operations: e.g. m + 1’ = m’

- 32 + 32 + 58 « Shubnikov » point groups
- 230 + 230 + 1191 magnetic space groups

Cristallographic groups:

- where 1’ does not exist at all
- where 1’ exists as a symmetry operation (and therefore combines with all other operations)
- where 1’ does not exist alone but exists in combination with some spatial symmetry operations

Molecular and crystal symmetry

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Magnetic Point Group Tables

bels are presented in the traditional notation - to see them in UNI notation click here)

Choose a magnetic point group from the next table

1.1.1	1	1.2.2	11'	2.1.3	-1	2.2.4	-11'	2.3.5	-1'	3.1.6	2	3.2.7	21'	3.3.8	2'
4.1.9	m	4.2.10	m1'	4.3.11	m'	5.1.12	2/m	5.2.13	2/m1'	5.3.14	2'/m	5.4.15	2/m'	5.5.16	2'/m'
6.1.17	222	6.2.18	2221'	6.3.19	2'2'2	7.1.20	mm2	7.2.21	mm21'	7.3.22	m'm2'	7.4.23	m'm'2	8.1.24	mmm
8.2.25	mmm1'	8.3.26	m'mm	8.4.27	m'm'm	8.5.28	m'm'm'	9.1.29	4	9.2.30	41'	9.3.31	4'	10.1.32	-4
10.2.33	-41'	10.3.34	-4'	11.1.35	4/m	11.2.36	4/m1'	11.3.37	4'/m	11.4.38	4/m'	11.5.39	4'/m'	12.1.40	422
12.2.41	4221'	12.3.42	4'22'	12.4.43	42'2'	13.1.44	4mm	13.2.45	4mm1'	13.3.46	4'm'm	13.4.47	4m'm'	14.1.48	-42m
14.2.49	-42m1'	14.3.50	-4'2'm	14.4.51	-4'2m'	14.5.52	-42'm'	15.1.53	4/mmm	15.2.54	4/mmm1'	15.3.55	4/m'mm	15.4.56	4'/mm'm
15.5.57	4'/m'm'm	15.6.58	4/mm'm'	15.7.59	4/m'm'm'	16.1.60	3	16.2.61	31'	17.1.62	-3	17.2.63	-31'	17.3.64	-3'
18.1.65	32	18.2.66	321'	18.3.67	32'	19.1.68	3m	19.2.69	3m1'	19.3.70	3m'	20.1.71	-3m	20.2.72	-3m1'
20.3.73	-3'm	20.4.74	-3'm'	20.5.75	-3m'	21.1.76	6	21.2.77	61'	21.3.78	6'	22.1.79	-6	22.2.80	-61'
22.3.81	-6'	23.1.82	6/m	23.2.83	6/m1'	23.3.84	6'/m	23.4.85	6/m'	23.5.86	6'/m'	24.1.87	622	24.2.88	6221'
24.3.89	6'22'	24.4.90	62'2'	25.1.91	6mm	25.2.92	6mm1'	25.3.93	6'mm'	25.4.94	6m'm'	26.1.95	-6m2	26.2.96	-6m21'
26.3.97	-6'm'2	26.4.98	-6'm2'	26.5.99	-6m'2'	27.1.100	6/mmm	27.2.101	6/mmm1'	27.3.102	6/m'mm	27.4.103	6'/mmm'	27.5.104	6'/m'mm'
27.6.105	6/mm'm'	27.7.106	6/m'm'm'	28.1.107	23	28.2.108	231'	29.1.109	m-3	29.2.110	m-31'	29.3.111	m'-3'	30.1.112	432
30.2.113	4321'	30.3.114	4'32'	31.1.115	-43m	31.2.116	-43m1'	31.3.117	-4'3m'	32.1.118	m-3m	32.2.119	m-3m1'	32.3.120	m'-3'm
32.4.121	m-3m'	32.5.122	m'-3'm'												

Molecular and crystal symmetry

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Magnetic Point Group Tables of 2'/m (#5.3.14)

Useful data about magnetic point group 2'/m

Number of elements of the group (order): **4**
This group is **centrosymmetric**
This group is **not polar**
This group is **not compatible with ferromagnetism**

Symmetry operations of the group

N	(x,y,z) form	matrix form	Seitz symbol
1	x,y,z, +1 m_x,m_y,m_z	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	1
2	x,-y,z, +1 $-m_x, m_y, -m_z$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	m_y
3	-x,y,-z, -1 $m_x, -m_y, m_z$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}'$	$2_y'$
4	-x,-y,-z, -1 $-m_x,-m_y,-m_z$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}'$	-1'

Magnetic Point Group Tables of 2'/m' (#5.5.16)

Useful data about magnetic point group 2'/m'

Number of elements of the group (order): **4**
This group is **centrosymmetric**
This group is **not polar**
This group is **compatible with ferromagnetism**

Symmetry operations of the group

N	(x,y,z) form	matrix form	Seitz symbol
1	x,y,z, +1 m_x,m_y,m_z	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	1
2	-x,-y,-z, +1 m_x, m_y, m_z	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	-1
3	-x,y,-z, -1 $m_x, -m_y, m_z$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}'$	$2_y'$
4	x,-y,z, -1 $m_x,-m_y,m_z$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}'$	m_y'

Molecular and crystal symmetry

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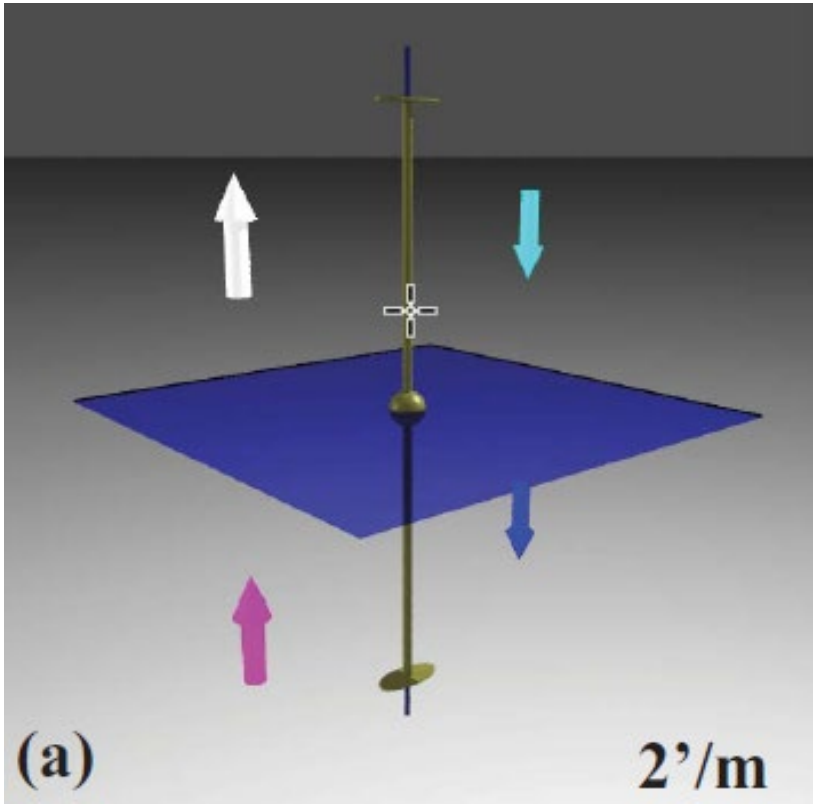
Symmetry operations of the group

N	(x,y,z) form	matrix form	Seitz symbol
1	x,y,z, +1 m_x,m_y,m_z	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	1
2	x,-y,z, +1 $-m_x, m_y, -m_z$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	m_y
3	-x,y,-z, -1 $m_x, -m_y, m_z$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}'$	$2_y'$
4	-x,-y,-z, -1 $-m_x,-m_y,-m_z$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}'$	-1'

But compatible with
*anti*ferromagnetic orders



Group theory and representations

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Definition of a representation

Given a vector space V, a representation R of a group G is a group homorphism from G to $GL_n(V)$, i.e. a mapping

$$G \rightarrow GL_n(V)$$
$$g_i \rightarrow R(g_i)$$

where $R(g_i)$ is a square *n* x *n* matrix, such that

$$R(g_i.g_j) = R(g_i).R(g_j)$$

n is the dimension of the representation.
The *basis* of a representation is the basis of V used to write its matrices.
The *characters* of a representation are the traces of its matrices.

Common vector space *V* in condensed matter physics:

- Quantum states of electrons, nuclei…
- Atomic displacements for vibrations and phase transitions
- Tensor describing physical properties (polarization, magnetization, elastic constants etc.)

Group theory and representations

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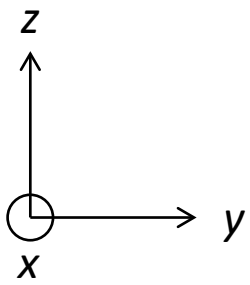

Example for the mm2 point group

1	2_z	m_x	m_y
[…]	[…]	[…]	[…]

Group theory and representations

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Example: the totally symmetric representation

$G \rightarrow GL_1(V)$

$g_i \rightarrow (1)$

1	2_z	m_x	m_y
1	1	1	1

- It always exists.
- All scalar properties *transform like* it (temperature, entropy etc).
- It is not « faithful ».

Group theory and representations

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Reducible vs. irreducible representation

A representation is reducible if the vector space V can be decomposed into (proper) subspaces stable by all symmetry operations, i.e. all matrices can be written as:

	1	2_z	m_x	m_y
R	$\begin{bmatrix} A_1 & & 0 \\ & B_1 & \\ 0 & & C_1 \end{bmatrix}$	$\begin{bmatrix} A_{2z} & & 0 \\ & B_{2z} & \\ 0 & & C_{2z} \end{bmatrix}$	$\begin{bmatrix} A_{mx} & & 0 \\ & B_{mx} & \\ 0 & & C_{mx} \end{bmatrix}$	$\begin{bmatrix} A_{my} & & 0 \\ & B_{my} & \\ 0 & & C_{my} \end{bmatrix}$

If this is not possible, the representation is called irreducible (an « irrep »).

Group theory and representations

The reducible representation can be reduced into a *direct sum* of irreducible representations (« irreps »):

	1	2_z	m_x	m_y
A	A_1	A_{2z}	A_{mx}	A_{my}
B	B_1	B_{2z}	B_{mx}	B_{my}
C	C_1	C_{2z}	C_{mx}	C_{my}

$$R = A \oplus B \oplus C$$
$$\dim(R) = \dim(A) + \dim(B) + \dim(C)$$
$$X(R) = X(A) + X(B) + X(C)$$

Group theory and representations

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The « everything-works-nicely-for-us » theorems

- Maschke's theorem
- Schur's lemma
- Wonderful (or great) orthogonality theorem
- …

- The irreps we need are known, tabulated and independant of a particular choice of basis.
- Every representation can be decomposed into a sum of irreps, and this decomposition is unique.
- All you need is the character tables.

- The irreps of a group gives you a tool to describe how things transform under all the symmetry operations of the group.

Group theory and representations

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Space-group symmetry

Magnetic Symmetry and Applications

Group-Subgroup Relations of Space Groups

Representations and Applications

	Point and Space Groups
REPRES	Space Groups Representations
Representations PG	Irreducible representations of the crystallographic Point Groups
Representations SG	Irreducible representations of the Space Groups
Get_irreps	Irreps and order parameters in a space group-subgroup phase transition
DIRPRO	Direct Products of Space Group Irreducible Representations
CORREL	Correlations relations between the irreducible representations of a group-subgroup pair
POINT	Point Group Tables
SITESYM	Site-symmetry induced representations of Space Groups
COMPATIBILITY RELATIONS	Compatibility relations between the irreducible representations of a space group
MECHANICAL REP.	Decomposition of the mechanical representation into irreps

Group theory and representations

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Character tables

Point group symbol

Symmetry operations
Grouped by classes

List of irreducible representations

C_{2v}(mm2)	#	1	2_z	m_y	m_x	functions
A_1	Γ_1	1	1	1	1	z,x^2,y^2,z^2
A_2	Γ_3	1	1	-1	-1	xy,J_z
B_1	Γ_2	1	-1	1	-1	x,xz,J_y
B_2	Γ_4	1	-1	-1	1	y,yz,J_x

Mulliken symbol

Koster notation

Some basis « functions »:

- x, y, z: span the vectors, i.e. the translations, polarization, etc.
- x^2, y^2 ,z^2 , xy, yz, zx: span spaces of a 2^{nd} rank tensors (dielectric constant, Raman tensor…)
- J_x, J_y, J_z: span the rotations

Group theory and representations

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Character tables

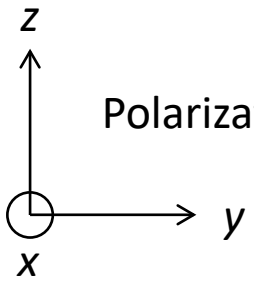
C_{2v}(mm2)	#	1	2_z	m_y	m_x	functions
A_1	Γ_1	1	1	1	1	z,x^2,y^2,z^2
A_2	Γ_3	1	1	-1	-1	xy,J_z
B_1	Γ_2	1	-1	1	-1	x,xz,J_y
B_2	Γ_4	1	-1	-1	1	y,yz,J_x

Check the orthogonality of the irreps and characters…

Group theory and representations

Example: how polarisation transforms

2mm point group



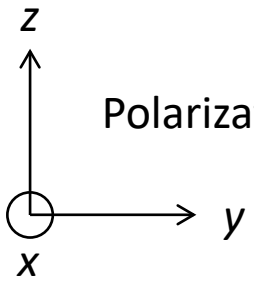
Polarization **P** = (P_x, P_y, P_z)

	1	2_z	m_y	m_x
P	$\begin{pmatrix} 1 & . & . \\ . & 1 & . \\ . & . & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & . & . \\ . & -1 & . \\ . & . & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & . & . \\ . & -1 & . \\ . & . & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & . & . \\ . & 1 & . \\ . & . & 1 \end{pmatrix}$

3-dimensional, reducible representation

Group theory and representations

Example: how polarisation transforms
2mm point group



Polarization **P** = (P_x, P_y, P_z)

	1	2_z	m_y	m_x
P_x	⊙	⊗	⊙	⊗
P_y	→	←	←	→
P_z	↑	↑	↑	↑

	1	2_z	m_y	m_x
P_x	1	-1	1	-1
P_y	1	-1	-1	1
P_z	1	1	1	1

Group theory and representations

Example: how polarisation transforms
2mm point group

	1	2_z	m_y	m_x
P_x	1	-1	1	-1
P_y	1	-1	-1	1
P_z	1	1	1	1

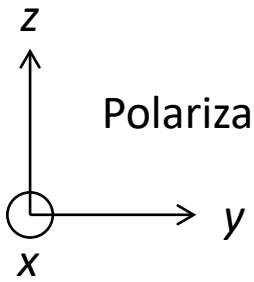
C_{2v}(mm2)	#	1	2_z	m_y	m_x	functions
A_1	Γ_1	1	1	1	1	z,x^2,y^2,z^2
A_2	Γ_3	1	1	-1	-1	xy,J_z
B_1	Γ_2	1	-1	1	-1	x,xz,J_y
B_2	Γ_4	1	-1	-1	1	y,yz,J_x

3-dimensional, reducible representation

Decomposition into $B_1 \oplus B_2 \oplus A_1$

Group theory and representations

Example: how polarisation transform
4mm point group



Polarization **P** = (P_x, P_y, P_z)

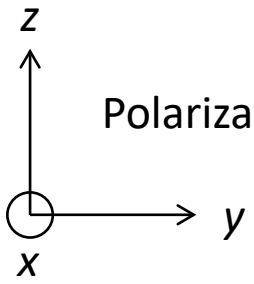
	1	2_z	4_z	m_x	m_{-xy}
P_x	⊙	⊗	→	⊗	→
P_y	→	←	⊗	→	⊙
P_z	↑	↑	↑	↑	↑

	1	2_z	4_z	m_x	m_{-xy}
P	$\begin{pmatrix} 1 & . & . \\ . & 1 & . \\ . & . & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & . & . \\ . & -1 & . \\ . & . & 1 \end{pmatrix}$	$\begin{pmatrix} . & -1 & . \\ 1 & . & . \\ . & . & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & . & . \\ . & 1 & . \\ . & . & 1 \end{pmatrix}$	$\begin{pmatrix} . & 1 & . \\ 1 & . & . \\ . & . & 1 \end{pmatrix}$

3-dimensional, reducible representation

Group theory and representations

Example: how polarisation transform
4mm point group



Polarization **P** = (P_x, P_y, P_z)

Character Table of the group C_{4v}(4mm)*

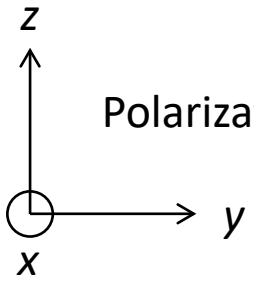
C_{4v}(4mm)	#	1	2	4	m_{100}	$m_{1\text{-}10}$	functions
Mult.	-	1	1	2	2	2	·
A_1	Γ_1	1	1	1	1	1	z, x^2+y^2, z^2
A_2	Γ_2	1	1	1	-1	-1	J_z
B_1	Γ_3	1	1	-1	1	-1	x^2-y^2
B_2	Γ_4	1	1	-1	-1	1	xy
E	Γ_5	2	-2	0	0	0	$(x,y),(xz,yz),(J_x,J_y)$

	1	2_z	4_z	m_x	m_{-xy}
P	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

Decomposition into E $\oplus$ A_1

Group theory and representations

Example: how polarisation transform
4mm point group



Polarization **P** = (P_x, P_y, P_z)

Character Table of the group C_{4v}(4mm)*

C_{4v}(4mm)	#	1	2	4	m_{100}	$m_{1\text{-}10}$	functions
Mult.	-	1	1	2	2	2	·
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A_2	Γ_2	1	1	1	-1	-1	J_z
B_1	Γ_3	1	1	-1	1	-1	x^2-y^2
B_2	Γ_4	1	1	-1	-1	1	xy
E	Γ_5	2	-2	0	0	0	$(x,y),(xz,yz),(J_x,J_y)$

P *transforms like* E $\oplus$ A_1…

This representation *contains* the totally symmetric irrep A_1…

There is at least one component of P that is invariant under all symmetry operations of the group…

4mm allows for the existence of a permanent polarization.

Group theory and representations

Is piezoelectricity (linear coupling between Polarization and Strain) allowed?

$\alpha \times P \times S$?

For the 4mm point group:

- P transforms like $A_1 + E$
- S transforms like $2A_1 + B_1 + B_2 + E$
- The product transforms like A1 + …, i.e. contains A1 => YES!

For 422 point group:

- P transforms like $A_2 + E$ (non polar group)
- S transforms like $2A_1 + B_1 + B_2 + E$
- Also YES!

Write your own Landau potential with all the weird symmetry-allowed coupling you can think of… piezoelectric, magnetoelectric, piezomagnetic…

(You may stop at the 17th order)

Classification and notations

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For representations

Mulliken symbol:
Suitable for molecular vibrations and lattice vibration at the Γ-point -> suitable for Raman and infrared spectroscopy

Koster / BSW notations:
Suitable for the description of symmetries of phonons (or other phenomena) in the whole Brillouin zone -> necessary for theoretical solid state physics, neutron scattering…

$mm2\ (C_{2v})$		$222\ (D_2)$		E	C_{2z}	σ_y	σ_x
				E	C_{2z}	C_{2y}	C_{2x}
A_1	Γ_1	A	Γ_1	1	1	1	1
B_2	Γ_4	B_3	Γ_4	1	−1	−1	1
A_2	Γ_3	B_1	Γ_3	1	1	−1	−1
B_1	Γ_2	B_2	Γ_2	1	−1	1	−1

$$mmm = 222 \otimes \bar{1}\ (D_{2h} = D_2 \otimes C_i)$$

Bradley & Cracknell, *The mathematical theory of symmetry in solids*, Clarendon Press, 1972.

Classification and notations

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Meaning of the Mulliken symbol

A	(one dimensional) symmetric with respect to rotation of the principle axis
B	(one dimensional) anti-symmetric with respect to rotation of the principle axis
E	doubly degenerate or two dimensional
T (or F)	thirdly degenerate or three dimensional
Subscript 1	symmetric with respect to the C_n principal axis, if no perpendicular axis, then it is with respect to σ_v
Subscript 2	anti-symmetric with respect to the C_n principal axis, if no perpendicular axis, then it is with respect to σ_v
Subscript g	symmetric with respect to the inverse
Subscript u	anti-symmetric with respect to the inverse
prime	symmetric with respect to σ_h (reflection in horizontal plane)
double prime	anti-symmetric with respect to σ_h (opposite reflection in horizontal plane)

R. S. Mulliken, J. Chem. Phys 23, 1997 (1955); J. Chem. Phys. 24, 1118 (1956); Adapted from http://chemwiki.ucdavis.edu/.

Classification and notations

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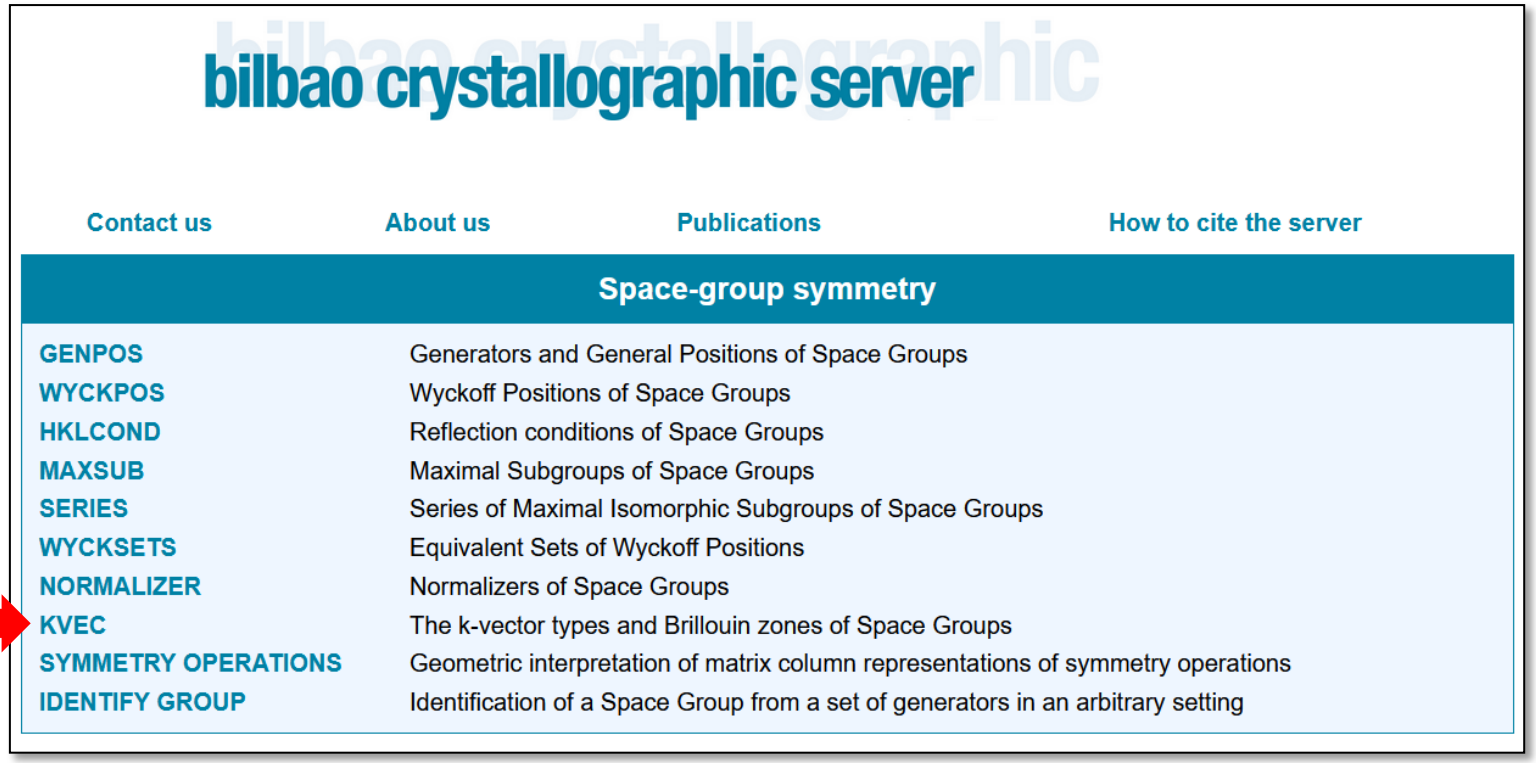
Irreps of space groups

- Labelled by k-vector, with names for special points of the Brillouin zone



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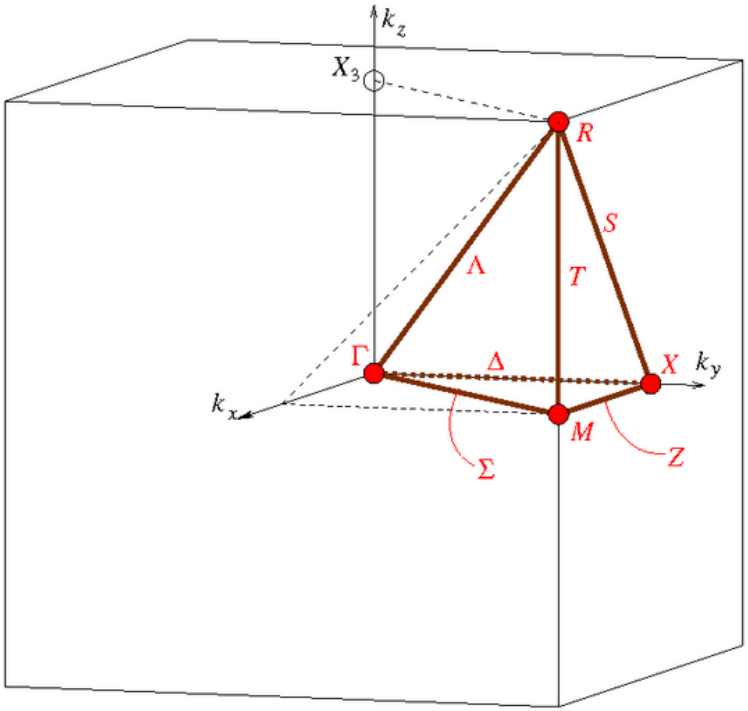
Space-group symmetry

GENPOS	Generators and General Positions of Space Groups
WYCKPOS	Wyckoff Positions of Space Groups
HKLCOND	Reflection conditions of Space Groups
MAXSUB	Maximal Subgroups of Space Groups
SERIES	Series of Maximal Isomorphic Subgroups of Space Groups
WYCKSETS	Equivalent Sets of Wyckoff Positions
NORMALIZER	Normalizers of Space Groups
KVEC	The k-vector types and Brillouin zones of Space Groups
SYMMETRY OPERATIONS	Geometric interpretation of matrix column representations of symmetry operations
IDENTIFY GROUP	Identification of a Space Group from a set of generators in an arbitrary setting

Bradley & Cracknell, *The mathematical theory of symmetry in solids*, Clarendon Press, 1972.

Classification and notations



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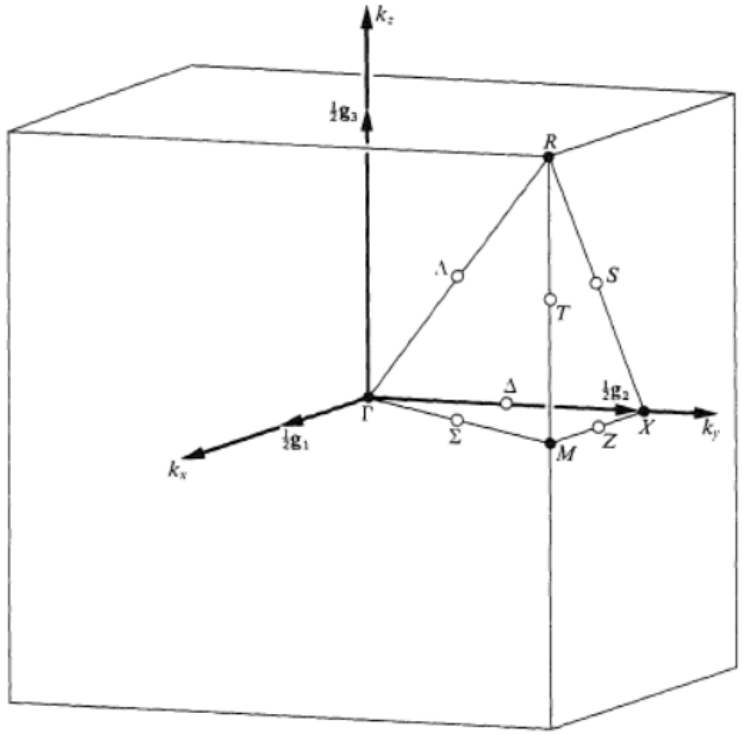

FIG. 3.13. The Brillouin zone for Γ_c. $\Gamma = (000)$; $X = (0\frac{1}{2}0)$; $M = (\frac{1}{2}\frac{1}{2}0)$; $R = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$.

Bradley & Cracknell, *The mathematical theory of symmetry in solids*, Clarendon Press, 1972.

Classification and notations

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The k-vector types of space group $I4_1/a$ (88)

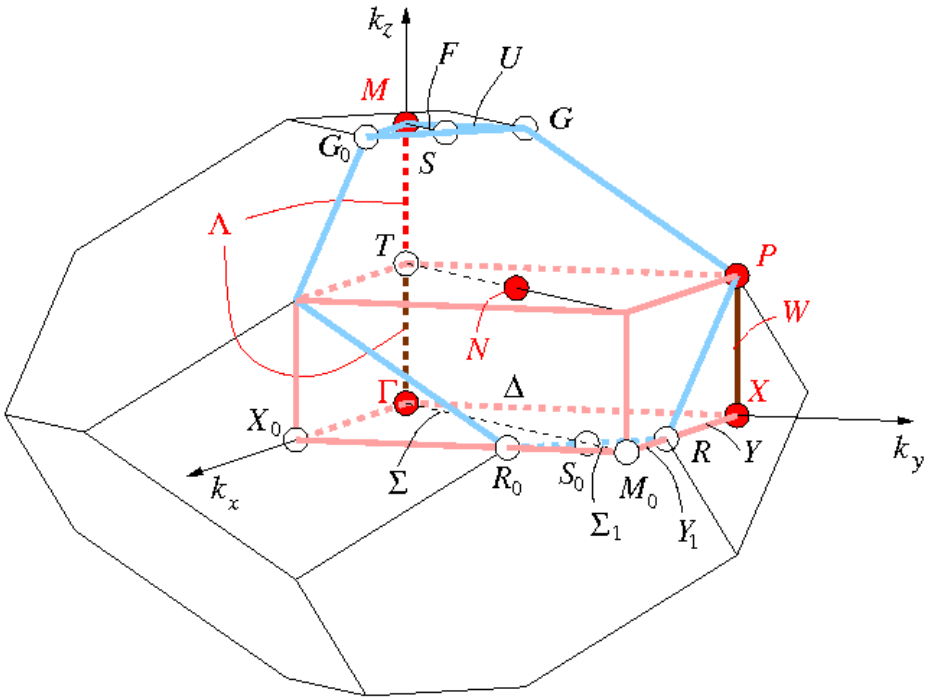
Brillouin zone

(Diagram for arithmetic crystal class 4/mI : c/a>1)

I4/m-C_{4h}^5 (87), $I4_1/a$-C_{4h}^6 (88)

Reciprocal-space group (I4/m)*, No. 87 : c*/a*<1

The table with the k vectors.



Classification and notations

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- Differences in notations (Koster, BSW, Mulliken…).

Table 2.4. Commonly used notations for the irreducible representations of the T_d point group

Koster notation[a]	BSW notation	Molecular notation
Γ_1	Γ_1	A_1
Γ_2	Γ_2	A_2
Γ_3	Γ_{12}	E
Γ_4	Γ_{15}	T_2
Γ_5	Γ_{25}	T_1

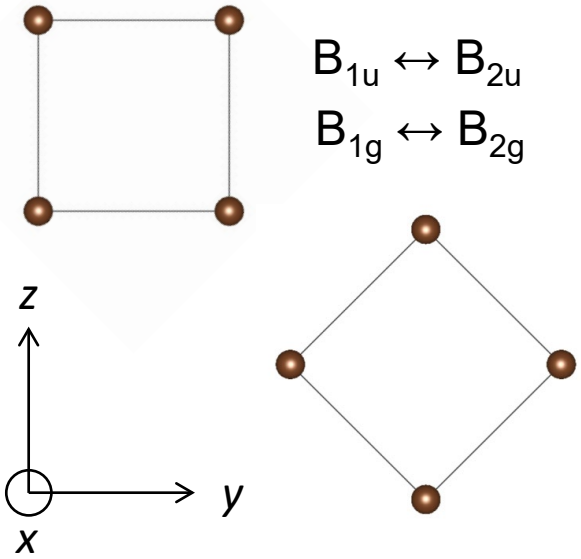
[a] Note that Γ_4 and Γ_5 are sometimes reversed in the literature. We recommend the student to check it whenever he encounters this notation [2.4].

$222\ (D_2)$		E E	C_{2z} C_{2z}	σ_y C_{2y}	σ_x C_{2x}
A	Γ_1	1	1	1	1
B_3	Γ_4	1	−1	−1	1
B_1	Γ_3	1	1	−1	−1
B_2	Γ_2	1	−1	1	−1

Yu and Cardona / Bradley and Cracknell.

Classification and notations

- Differences in notations (Koster, BSW, Mulliken…).
- Some arbitrariness
  - in the choice of coordinate system
  - in the choice of a particular setting for a space group



$B_{1u} \leftrightarrow B_{2u}$

$B_{1g} \leftrightarrow B_{2g}$

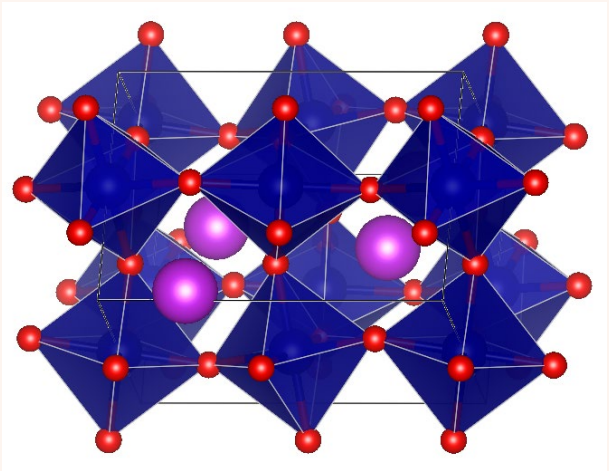
C_{2v}(mm2)	#	1	2_z	m_y	m_x	functions
A_1	Γ_1	1	1	1	1	z,x^2,y^2,z^2
A_2	Γ_3	1	1	-1	-1	xy,J_z
B_1	Γ_2	1	-1	1	-1	x,xz,J_y
B_2	Γ_4	1	-1	-1	1	y,yz,J_x

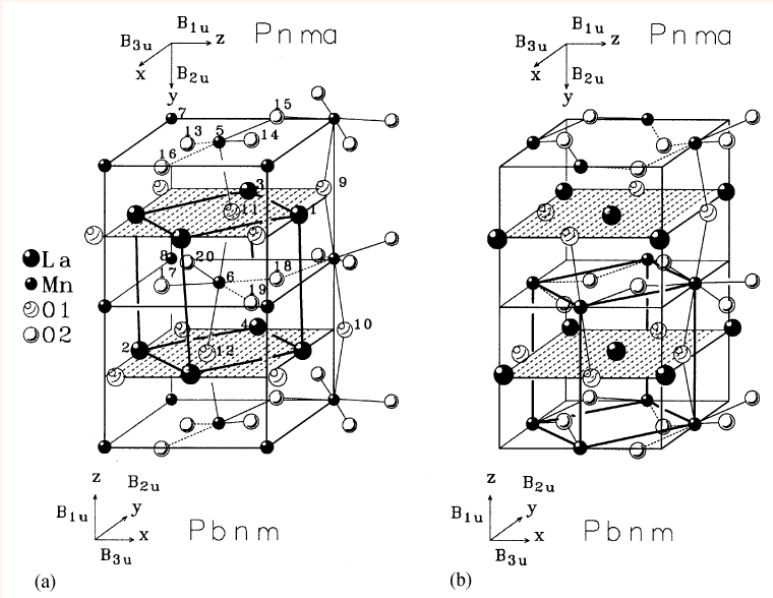
Classification and notations

- Differences in notations (Koster, BSW, Mulliken…).
- Some arbitrariness
  - in the choice of coordinate system
  - in the choice of a particular setting for a space group

Pnma vs. Pbnm(62) in tilted perovskites

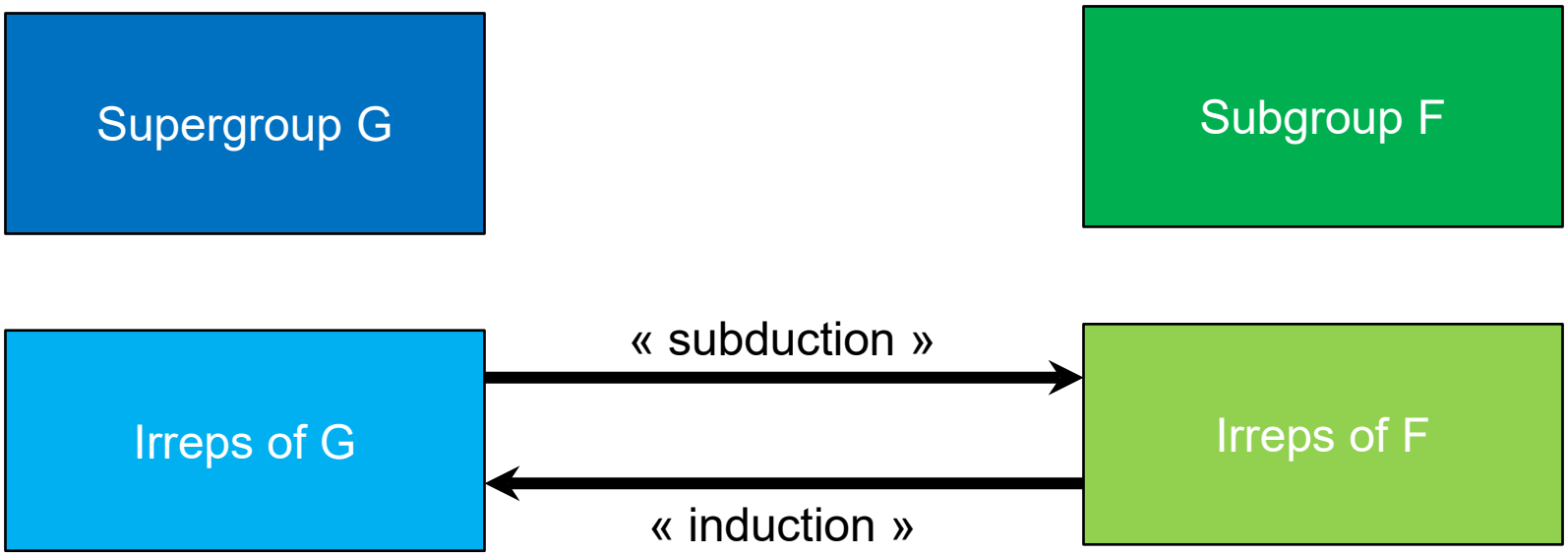
$CaTiO_3$, $GdFeO_3$, $TbMnO_3$





Smirnova, Physica B 262, 247 (1999)

Subduction and crystal field splitting



Subduction and crystal field splitting

Examples of « subduction »

C_{2v}(mm2)	#	1	2_z	m_y	m_x	functions
A_1	Γ_1	1	1	1	1	z,x^2,y^2,z^2
A_2	Γ_3	1	1	-1	-1	xy,J_z
B_1	Γ_2	1	-1	1	-1	x,xz,J_y
B_2	Γ_4	1	-1	-1	1	y,yz,J_x

C_s(m)	#	1	m	functions
A'	Γ_1	1	1	x,y,x^2,y^2,z^2,xy,J_z
A''	Γ_2	1	-1	z,xz,yz,J_x,J_y

Subduction and crystal field splitting

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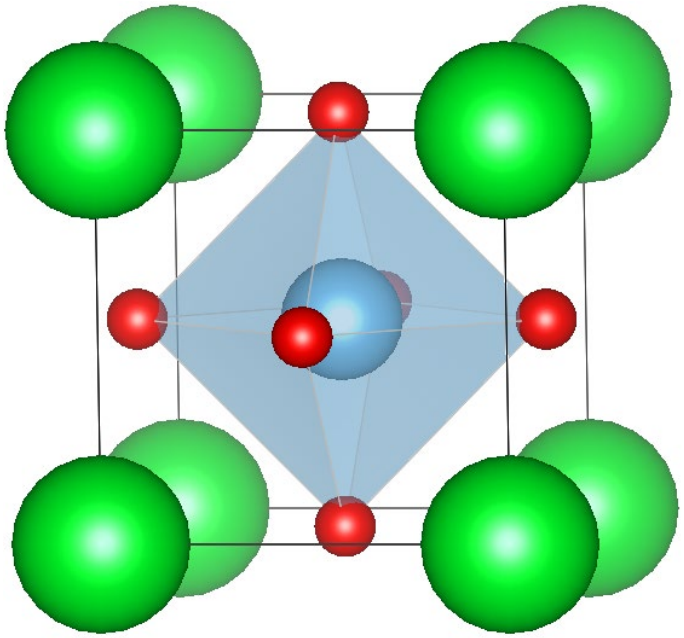
Examples of « subduction »

C_{4v}(4mm)	#	1	2	4	m_x	m_d	functions
Mult.	-	1	1	2	2	2	·
A_1	Γ_1	1	1	1	1	1	z,x^2+y^2,z^2
A_2	Γ_2	1	1	1	-1	-1	J_z
B_1	Γ_3	1	1	-1	1	-1	x^2-y^2
B_2	Γ_4	1	1	-1	-1	1	xy
E	Γ_5	2	-2	0	0	0	$(x,y),(xz,yz),(J_x,J_y)$

C_{2v}(mm2)	#	1	2_z	m_y	m_x	functions
A_1	Γ_1	1	1	1	1	z,x^2,y^2,z^2
A_2	Γ_3	1	1	-1	-1	xy,J_z
B_1	Γ_2	1	-1	1	-1	x,xz,J_y
B_2	Γ_4	1	-1	-1	1	y,yz,J_x

Subduction and crystal field splitting

Example: *d* orbitals (L=2) of a transition metal ion in a cubic environment



Supergroup: SO(3)
Group of the isolated ion

Subgroup: m-3m
Group the ion in the octahedron

All rotations are lost except 4, 2, 3, 2'

Subduction and crystal field splitting

O_h(m-3m)	#	1	4	2	3	2'	-1	-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	Γ^+	1	1	1	1	1	1	1	1	1	1	

Problem:
What is the effect of the symmetry lowering experiences by the ion on the degeneracy of its energy levels?

Method:

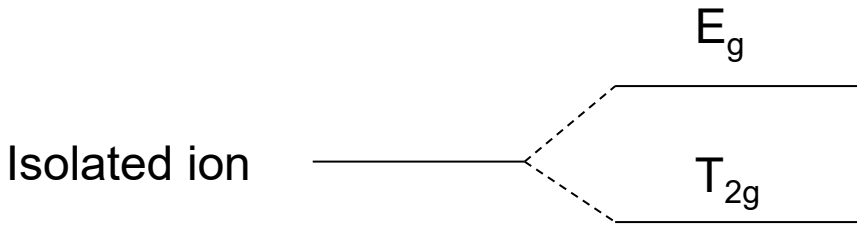
- Calculate the characters of the preserved symmetry operations.
- Reduce the obtained representation

Subduction and crystal field splitting

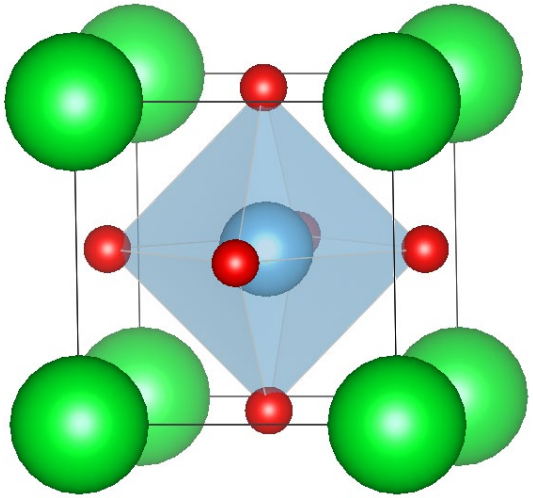
	1	4	2	3	2’	-1	-4	m	-3	m'
Γ	5	-1	1	-1	1	5	-1	1	-1	1

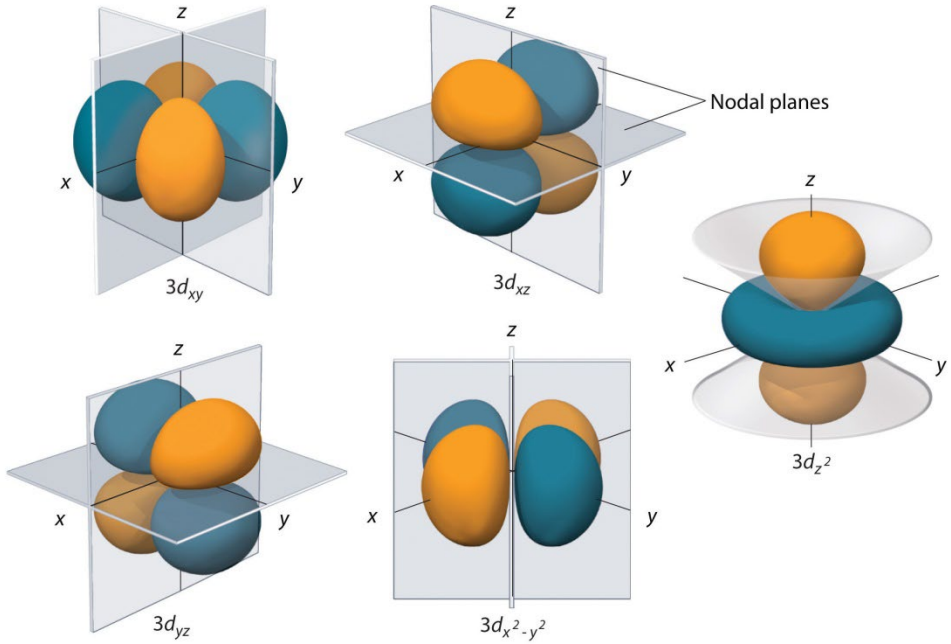
O_h(m-3m)	#	1	4	2	3	2'	-1	-4	m	-3	m'	functions
Mult.	-	1	6	3	8	6	1	6	3	8	6	·
A_{1g}	Γ_1^+	1	1	1	1	1	1	1	1	1	1	$x^2+y^2+z^2$
A_{1u}	Γ_1^-	1	1	1	1	1	-1	-1	-1	-1	-1	·
A_{2g}	Γ_2^+	1	-1	1	1	-1	1	-1	1	1	-1	·
A_{2u}	Γ_2^-	1	-1	1	1	-1	-1	1	-1	-1	1	·
E_g	Γ_3^+	2	0	2	-1	0	2	0	2	-1	0	$(2z^2-x^2-y^2, x^2-y^2)$
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)

Subduction and crystal field splitting



Which level is higher/lower depends on the special configuration.

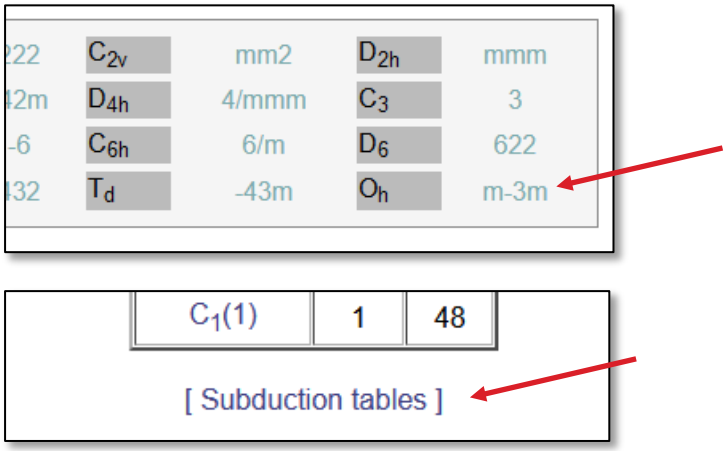




Subduction and crystal field splitting

Further symmetry lowering?

Ex: $LaNiO_3$, $BiFeO_3$…



Correlation relation for group-subgroup pairs

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

Subduction and crystal field splitting

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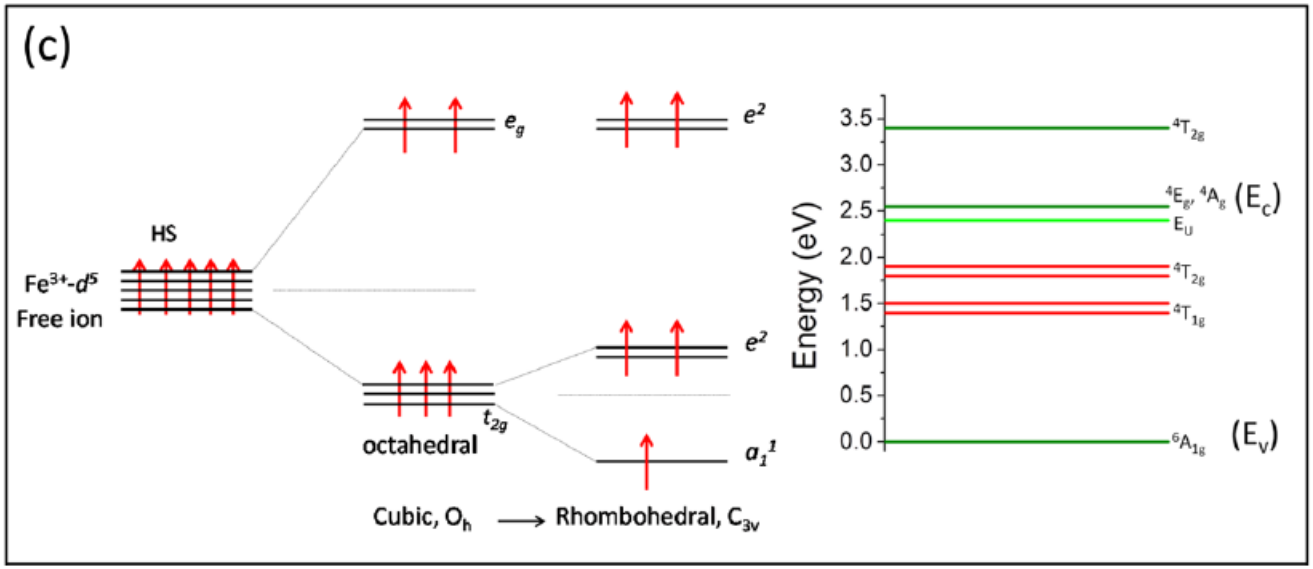
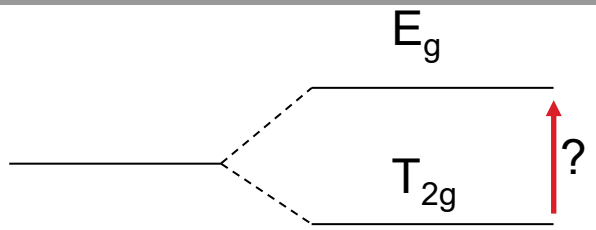
Splitting of energy levels for Fe in $BiFeO_3$



Bai et al., J. Solid. State Chem. (2016)

Transition between states



If:

- the final state transforms like the irrep $\Gamma^{(f)}$
- the initial state transforms like the irrep $\Gamma^{(i)}$
- the perturbation transforms like the irrep $\Gamma^{(H')}$

then the matrix element

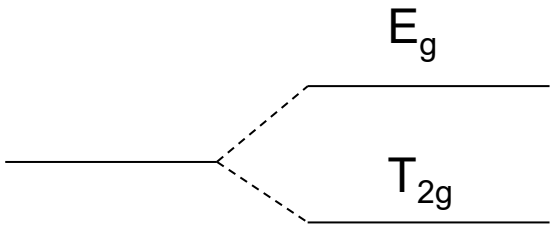
$$\langle \varphi_{final} | H' | \varphi_{initial} \rangle$$

transforms like the direct product

$$\Gamma^{(f)} \times \Gamma^{(H')} \times \Gamma^{(i)}$$

For the transition probability to be non-zero, the direct product must contain the fully symmetric representation, i.e. contain a term that will not vanish upon all symmetry operations of the system.

Transition between states



What are the states accessible from T_{2g} by an electric dipole transition?

$$T_{1u} \times T_{2g} = A_{2u} + E_u + T_{1u} + T_{2u}$$

Symmetry of the Perturbation (electric field)

Symmetry of the initial state

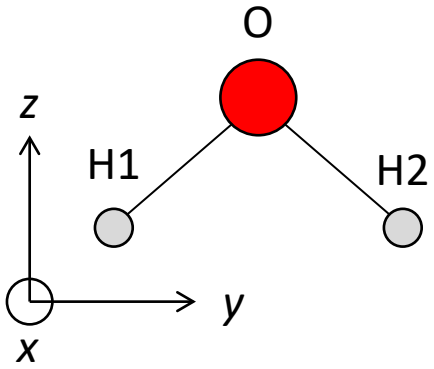
Transitions from T_{2g} states can only be to/from states with A_{2u}, E_u, T_{1u} or T_{2u} symmetry. Optical transitions between E_g and T_{2g} are forbidden (in principle…)

The mechanical representation

The mechanical representation = the representation generated by atomic displacements.

How do atomic displacements transform under the symmetry operations of the group?

How to decompose the displacements onto a symmetry-adapted basis?



H_2O molecule:

Point group C_{2v} = mm2 = {E, 2_z, m_x, m_y}

N = 3 atoms

Γ is a 9-dimensional representation.

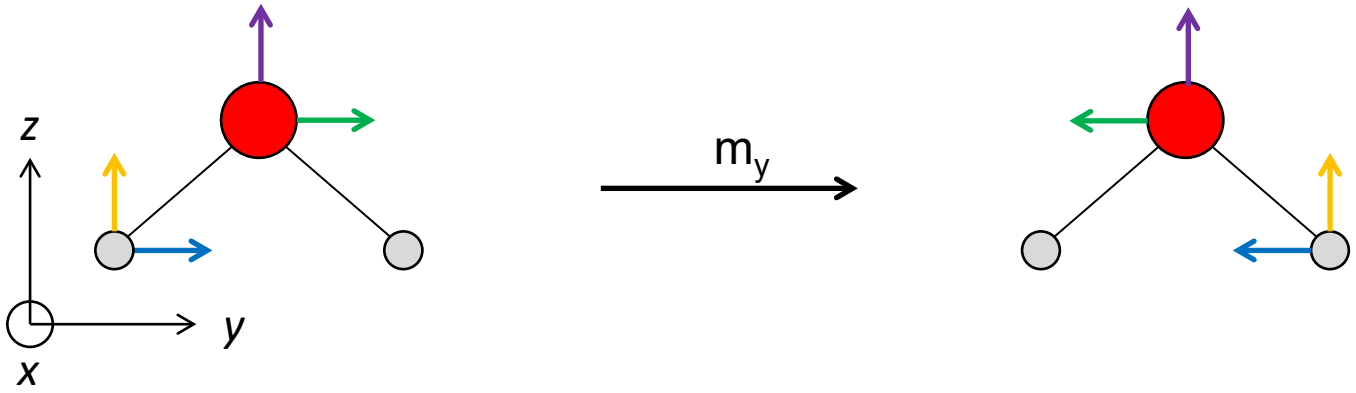
=> *the mechanical representation*

Canonical basis vectors for atomic displacements:

$e_1 = u_x(O)$	$e_4 = u_x(H1)$	$e_7 = u_x(H2)$
$e_2 = u_y(O)$	$e_5 = u_y(H1)$	$e_8 = u_y(H2)$
$e_3 = u_z(O)$	$e_6 = u_z(H1)$	$e_9 = u_z(H2)$

The mechanical representation

Example:



$$\Gamma(m_y) = \begin{pmatrix} 1 & & & & & \\ & -1 & & & & \\ & & 1 & & & \\ & & & 1 & & \\ & & & & -1 & \\ & & & & & 1 \end{pmatrix}$$

The mechanical representation

Reduction of the representation Γ

« Decompose the vector space in subspaces that are stable by all symmetry operations. »

Reduce the *3N*-dimensional reducible representation of the point group into a direct sum of irreducible representations.

Different approaches:

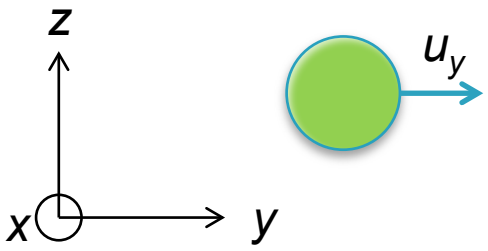
- Calculation of the characters, orthogonality theorem etc.
- The *correlation method*, well-adapted to the vibration problem.

W. G. Fateley *et al.*, Infrared and Raman Selection Rules for Lattice Vibrations: The Correlation Method, Applied Spectroscopy 25, 155 (1971)

The mechanical representation

Basic idea of the correlation method

Consider a molecule with point group G and one of its atoms with site symmetry F.



The oscillation of the atom around its equilibrium position is represented by a vector; it transforms according to irreps of F associated to translations.

The idea of the correlation method: determine how of this symmetry property is transfered to the symmetry of the whole molecule.

W. G. Fateley *et al.*, Infrared and Raman Selection Rules for Lattice Vibrations: The Correlation Method, Applied Spectroscopy 25, 155 (1971)

The mechanical representation

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General recipe

Ingredients:

- Structure of the molecule (for a crystal: space group and atomic – Wyckoff positions)
- Character tables of point groups
- Correlation tables

Recipe:

1. Identify the point group of the molecule
2. Determine the number of degrees of freedom
3. Determine the site symmetries for each atom in the structure
4. Find the representations of the site symmetry point group associated to translations
5. Find the induced representations for the molecule
6. Sum over all (symmetry independent) atoms
7. Take off rigid translation and rotations

The correlation method

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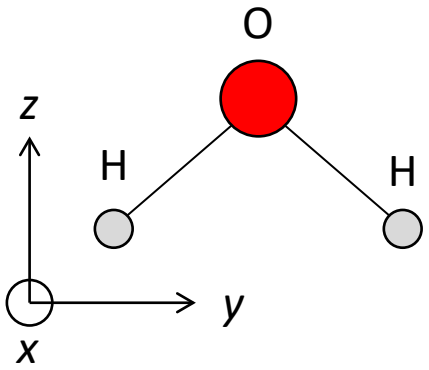
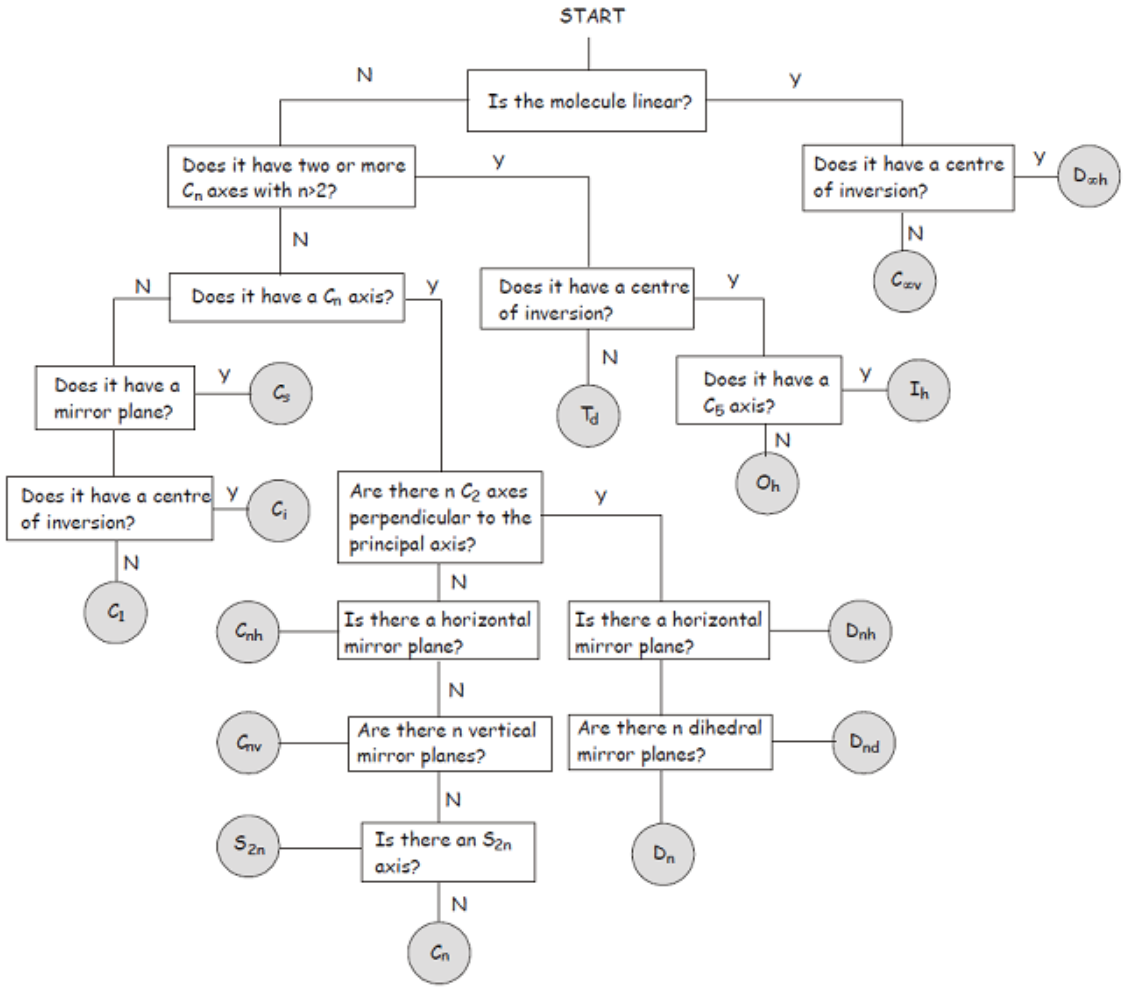
1. Find the point group of the molecule



$C_{2v} = mm2 = m_x m_y 2_z$



The correlation method

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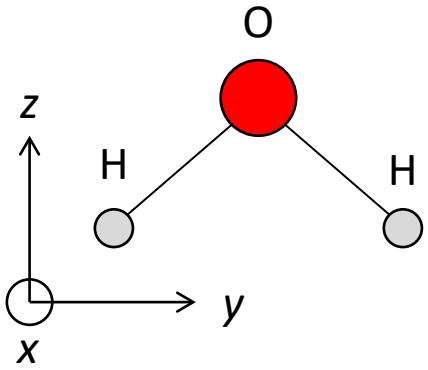
2. Find the number of degrees of freedom



3 atoms → 3 x 3 = 9 degrees of freedom
- 3 rigid translations
- 3 rigid rotations

→ 3 vibration modes

3. Find the site symmetries for all symmetry independent atoms

2 symmetry independent atoms:

O atom: {E, 2, σ_x, σ_y} → site symmetry = C_{2v} = *mm2* = $m_x m_y 2_z$

H atom: {E, ~~2~~, σ_x, ~~σ_y~~} → site symmetry = C_s = m = m_x

The correlation method

4. Find the representations of the site symmetry point groups associated to translations.

H atoms:
Site symmetry C_s

C_s(m)	#	1	m	functions
A'	Γ_1	1	1	x,y,x^2,y^2,z^2,xy,J_z
A''	Γ_2	1	-1	z,xz,yz,J_x,J_y

$$R(T_x) + R(T_y) + R(T_z) = 2A' + A''$$

Translations in the mirror plane

Translation perpendicular to the mirror plane

O atom:
Site symmetry C_{2v}

C_{2v}(mm2)	#	1	2_z	m_y	m_x	functions
A_1	Γ_1	1	1	1	1	z,x^2,y^2,z^2
A_2	Γ_3	1	1	-1	-1	xy,J_z
B_1	Γ_2	1	-1	1	-1	x,xz,J_y
B_2	Γ_4	1	-1	-1	1	y,yz,J_x

$$R(T_x) + R(T_y) + R(T_z) = B_1 + B_2 + A_1$$

Translations
1) In the mirror planes
2) perpendicular to the rotation axis

Translation along the rotation axis

The correlation method

5. Find the induced representations of the point group of the molecule

		= m_y	= m_x	
mm2	2	.m.	m..	1
A_1	A	A'	A'	A
A_2	A	A''	A''	A
B_1	B	A'	A''	A
B_2	B	A''	A'	A

Correlation tables for C_{2v}

O atom: $B_1 + B_2 + A_1$

Sit symmetry = symmetry of the molecule

No change!

→ $B_1 + B_2 + A_1$

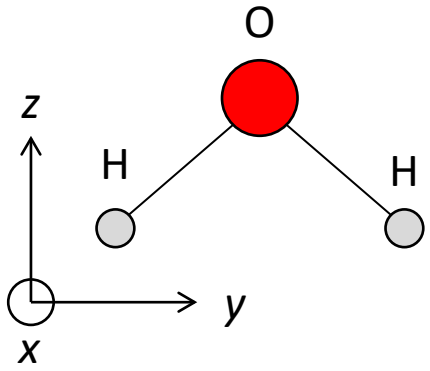
H atoms: 2A' + A''

Correlation between C_{2v} and C_s:

A' → $A_1 + B_2$

A'' → $A_2 + B_1$

→ $2A_1 + A_2 + B_1 + 2B_2$



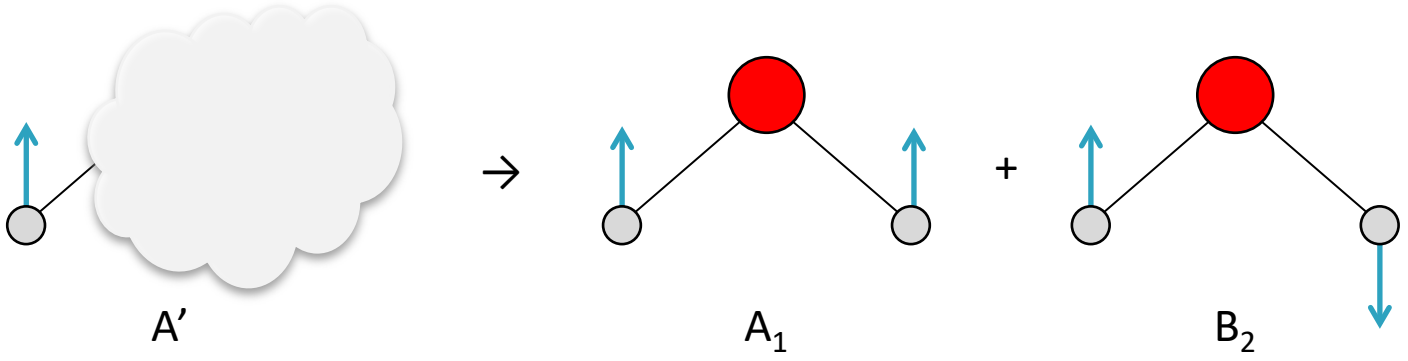
The correlation method

Illustration of A'→ A_1 + B_2

C_s(m)	#	1	m	functions
A'	Γ_1	1	1	x,y,x^2,y^2,z^2,xy,J_z
A''	Γ_2	1	-1	z,xz,yz,J_x,J_y

C_{2v}(mm2)	#	1	2_z	m_y	m_x	functions
A_1	Γ_1	1	1	1	1	z,x^2,y^2,z^2
A_2	Γ_3	1	1	-1	-1	xy,J_z
B_1	Γ_2	1	-1	1	-1	x,xz,J_y
B_2	Γ_4	1	-1	-1	1	y,yz,J_x

Displacements of H atoms along z:



The correlation method

6. Sum over all atoms

$\Gamma_{total} = 3A_1 + A_2 + 2B_1 + 3B_2$

NB: 3 + 1 + 2 + 3 = 9 degrees of freedom

7. Take off rotations and translations

$\Gamma_{total} = 3A_1 + A_2 + 2B_1 + 3B_2$

C_{2v}(mm2)	#	1	2_z	m_y	m_x	functions
A_1	Γ_1	1	1	1	1	z,x^2,y^2,z^2
A_2	Γ_3	1	1	-1	-1	xy,J_z
B_1	Γ_2	1	-1	1	-1	x,xz,J_y
B_2	Γ_4	1	-1	-1	1	y,yz,J_x

Translations (x, y, z):

$\Gamma_{translations} = B_1 + B_2 + A_1$

Rotations (J_x, J_y, J_z):

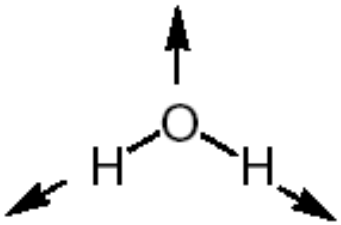
$\Gamma_{rotations} = B_2 + B_1 + A_2$

$\Gamma_{vibrations} = 2A_1 + B_2$

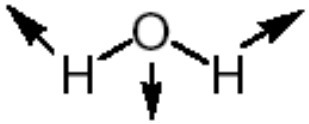
The correlation method

Summary of the procedure and results:

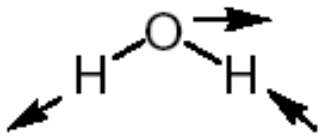
	Site symmetry	Representations of the site-symmetry group for translations	Induced representations of C_{2v}
H	C_s	Along x → A''	$A_2 + B_1$
		Along y → A'	$A_1 + B_2$
		Along z → A'	$A_1 + B_2$
O	C_{2v}	Along x → B_1	B_1
		Along y → B_2	B_2
		Along z → A_1	A_1
		- Rigid translations	$A_1 + B_1 + B_2$
		- Rigid rotations	$A_2 + B_1 + B_2$
		= Vibrations	**$2A_1 + B_2$**



Symmetric stretch
110.8 THz

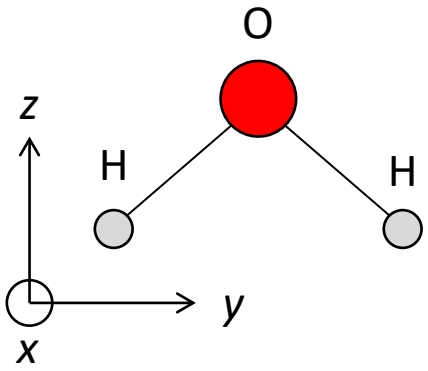


Bending
48.3 THz

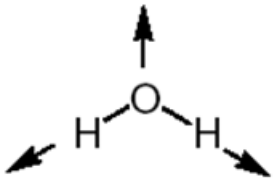
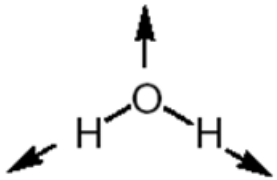
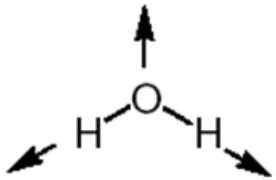
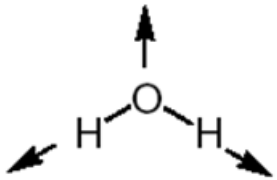
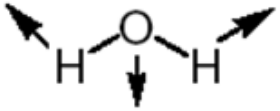
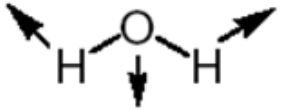
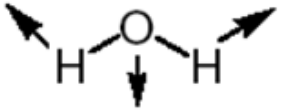
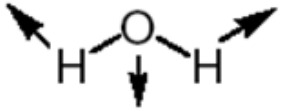
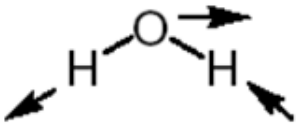
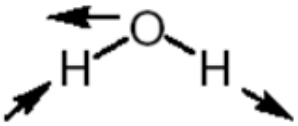
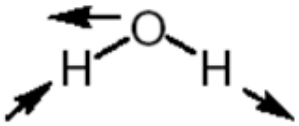
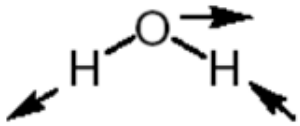


Asymmetric stretching
113.8 THz

The correlation method



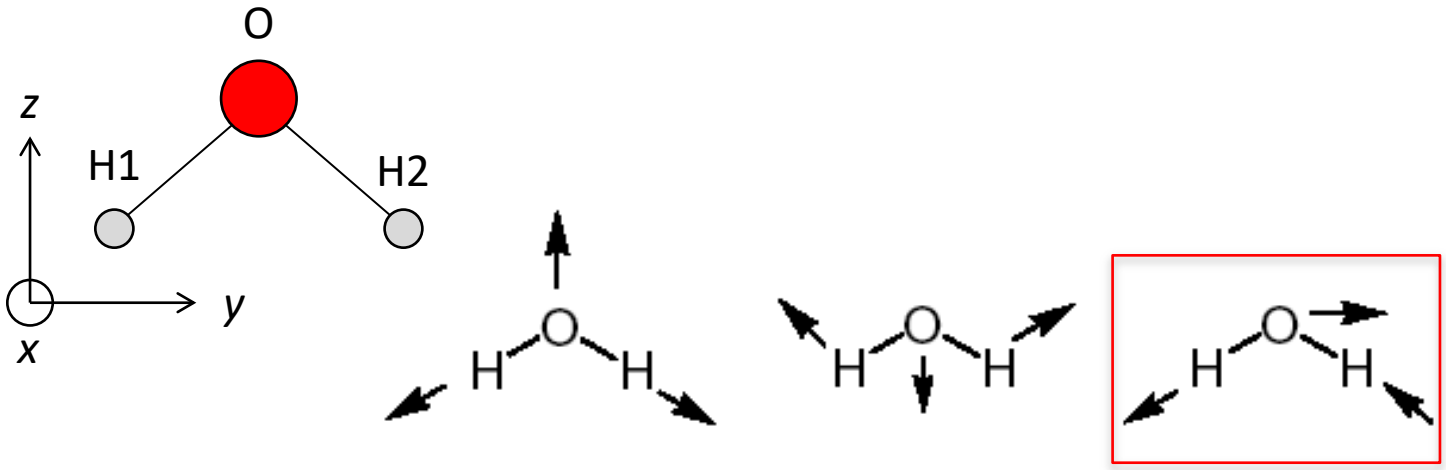
C_{2v}(mm2)	#	1	2_z	m_y	m_x	functions
A_1	Γ_1	1	1	1	1	z,x^2,y^2,z^2
A_2	Γ_3	1	1	-1	-1	xy,J_z
B_1	Γ_2	1	-1	1	-1	x,xz,J_y
B_2	Γ_4	1	-1	-1	1	y,yz,J_x

	1	2_z	m_y	m_x
Symmetric stretching A_1				
Bending A_1				
Asymmetric stretching B_2				

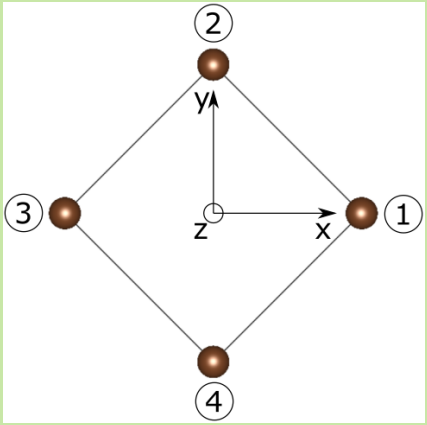
The mechanical representation

	Displacement	Induced representation
H	Along x	$A_2 + B_1$
	Along y	$A_1 + B_2$
	Along z	$A_1 + B_2$
O	Along x	B_1
	Along y → B_2	B_2
	Along z → A_1	A_1
	= Mechanical rep	**$3A_1 + A_2 + 2B_1 + 3B_2$**
	- Rigid translations	$A_1 + B_1 + B_2$
	- Rigid rotations	$A_2 + B_1 + B_2$
	= Vibrations	**$2A_1 + B_2$**

C_{2v}(mm2)	#	1	2_z	m_y	m_x	functions
A_1	Γ_1	1	1	1	1	z,x^2,y^2,z^2
A_2	Γ_3	1	1	-1	-1	xy,J_z
B_1	Γ_2	1	-1	1	-1	x,xz,J_y
B_2	Γ_4	1	-1	-1	1	y,yz,J_x



The mechanical representation



Modeoku

Where are the arrows?...

Find the eigenvectors for the 5 modes.

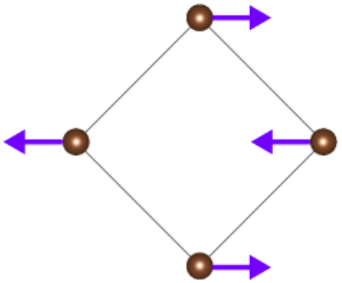
Atom	Site symmetry	Displacements	Induced representations
M1	$m_z 2_x m_y$	Along *x* Along *y* Along *z*	$A_{1g} + B_{1g} + E_u$ $A_{2g} + B_{2g} + E_u$ $A_{2u} + B_{2u} + E_g$
		- Rigid translations - Rigid rotations	$A_{2u} + E_u$ $A_{2g} + E_g$
		= Vibrations	$A_{1g} + B_{1g} + B_{2g} + B_{2u} + E_u$

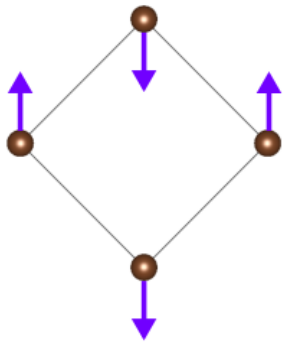
D_{4h}(4/mmm)	#	1	2	4	2_{100}	$2_{1\text{-}10}$	-1	m_z	-4	m_{100}	$m_{1\text{-}10}$	functions
Mult.	-	1	1	2	2	2	1	1	2	2	2	·
A_{1g}	Γ_1^+	1	1	1	1	1	1	1	1	1	1	x^2+y^2,z^2
A_{2g}	Γ_2^+	1	1	1	-1	-1	1	1	1	-1	-1	J_z
B_{1g}	Γ_3^+	1	1	-1	1	-1	1	1	-1	1	-1	x^2-y^2
B_{2g}	Γ_4^+	1	1	-1	-1	1	1	1	-1	-1	1	xy
E_g	Γ_5^+	2	-2	0	0	0	2	-2	0	0	0	$(xz,yz),(J_x,J_y)$
A_{1u}	Γ_1^-	1	1	1	1	1	-1	-1	-1	-1	-1	·
A_{2u}	Γ_2^-	1	1	1	-1	-1	-1	-1	-1	1	1	z
B_{1u}	Γ_3^-	1	1	-1	1	-1	-1	-1	1	-1	1	·
B_{2u}	Γ_4^-	1	1	-1	-1	1	-1	-1	1	1	-1	·
E_u	Γ_5^-	2	-2	0	0	0	-2	2	0	0	0	(x,y)

https://upload.wikimedia.org/wikipedia/commons/e/e1/Black_Man_Relaxing_on_the_Beach_Cartoon_Vector.svg

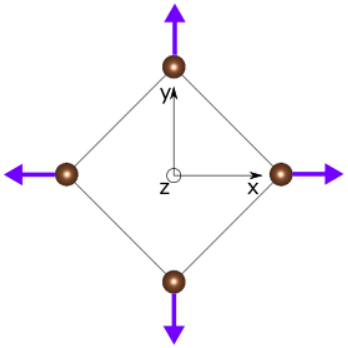
The mechanical representation

Modeoku - solutions

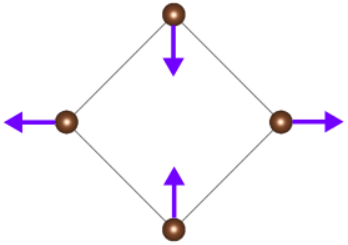




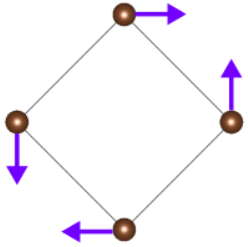
E_u mode



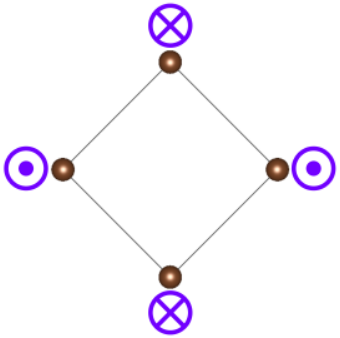
A_{1g} mode



B_{1g} mode



B_{2g} mode



B_{2u} mode

https://upload.wikimedia.org/wikipedia/commons/e/e1/Black_Man_Relaxing_on_the_Beach_Cartoon_Vector.svg

For playing around

- Bilbao crystallographic server http://www.cryst.ehu.es/
  - All data needed for application of the methods, but few explanations on how to use them wisely.
- « Species » for symmetry breaking http://palata.fzu.cz/species/
  - Useful to retrieve the consequence of symmetry breaking on domain structures, physical properties etc.
- ISOTROPY Software suite https://stokes.byu.edu/iso/isotropy.php
  - For studies of phase transitions using Landau theory.

For further reading

- M. S. Dresselhaus, *Applications of Group Theory to the Physics of Solids*
  - (Lecture notes) Starts from scratch, very solid and comprehensive.
- Yu and Cardona, *Fundamentals of semiconductors*, Springer, 2001.
  - Contains a « pedestrian guide to group theory » that can be very useful for a pragmatic use of group theory applied to vibrations and electronic excitations.
- H. Poulet and J.-P. Matthieu, *Spectres de vibration et symétrie de cristaux*, Gordon and Breach, 1970.
  - Quite comprehensive on lattice vibrations, with useful examples.
- C.J. Bradley and A.P. Cracknell, *Mathematical theory of symmetry in solids,* Oxford University Press*, 1972*.
  - The Bible, and about as easy to read.