David Hicks + Stefano Curtarolo

Symmetry of Crystals

- Group theory
- Point group symmetry
  - ↳ Molecules (non-periodic)
  - ↳ Crystals (periodic)
- Space groups
  - ↳ Operations/symbols
  - ↳ Wyckoff positions
- ITC-A
- Other symmetry groups
- Representation of operators
- AFLOW-SYM

1) Intro to Group Theory

Study of abstract algebraic structures : groups

Suppose a collection of objects g

set : $\{g\} = \{g_1, g_2, g_3 \cdots, g_n\}$

~~Def : group~~

GROUP

A set $\{g\}$ along with an operation relating two elements of a group together ($\otimes$) to form a third element

- Axioms of group

A1) closure : combination of elements results in element already in set

$$\text{e.g., } g_1 + g_2 = g_3 \mid g_3 \in \{g\}$$

A2) identity : exist an element (e) that leave element unchanged

$$\text{e.g., } \exists e \mid e \cdot g = g$$

A3) associativity : order of combining elements is inconsequential (given sequence of operands doesn't change)

$$\text{e.g., } g_1 \cdot (g_2 \cdot g_3) = (g_1 \cdot g_2) \cdot g_3$$

A4) inverse : for each g in $\{g\}$ there exists a corresponding inverse element such that

$$g \cdot g^{-1} = e$$

Represented as : $\{g \mid \cdot\}$ group wrt multiplication operator

Abelian group

All axioms of a group + commutivity

$$\text{e.g., } g_1 \cdot g_2 = g_2 \cdot g_1$$

X2

Examples

① $\mathbb{N}$ = set of natural numbers : $\{0, 1, 2, 3, 4, \ldots\}$

Is $\{\mathbb{N} | +\}$ a group?

A1) closure : yes (addition of any number is in set)

A2) identity : yes (0 is identity/neutral element)

A3) associativity : yes (e.g., $1+(2+3) = (1+2)+3$)

A4) inverse : NO (negative numbers not in set)

② $\mathbb{Z}$ = set of integers : $\{\ldots -3, -2, -1, 0, 1, 2, 3, 4, \ldots\}$

Is $\{\mathbb{Z} | +\}$ a group?

Yes! Inverse is now satisfied

Other algebraic structures

① Rings

Consider two operators : $\{G | +, \cdot\}$

where $\{G|+\}$ is an abelian group, but $\{G|\cdot\}$ is not, but does satisfy A2 and A3 (monoid) + distributive

$\boxed{\text{Ex}}$ $\{\mathbb{Z} | +, \cdot\}$ are a ring

$\{\mathbb{Z} | +\}$ is a group $\Rightarrow$ A1 → A4 satisfied

$\{\mathbb{Z} | \cdot\}$ is not $\Rightarrow$ A1 : yes

A2 : yes (neutral element = 1)

A3 : yes

A4 : NO (need rational #s)

② Fields

$\{G|+\}$ and $\{G|\cdot\}$ form abelian groups $\Rightarrow$ $\{G|+,\cdot\}$ is a field

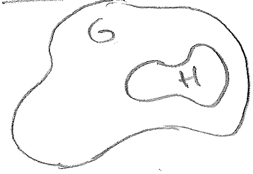
$\boxed{\text{Ex}}$ $\{\mathbb{Q} | +, \cdot\}$: set of rational numbers with + and · form field

X3

Relationships between groups

① subgroups

Ex



A subset H of G that still forms a group

i.e., $H \subset G \mid \{H \mid +\}$ is a group

special case

a) maximal non-isomorphic subgroup

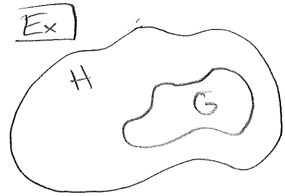
$H \subset G \mid \{H \mid +\}$ is a group

$\nexists J \mid H \subset J \subset G$

Note: H and J must exclude at least one element of G (i.e., proper subgroup)

② supergroups

Ex



A superset H of G that forms a group

i.e., $H \supset G \mid \{H \mid +\}$ is a group

special case

a) minimal non-isomorphic supergroup

$$\left.\begin{array}{l} H \supset G \mid \{H \mid +\} \text{ is a group} \\ \nexists J \mid H \supset J \supset G \end{array}\right\} \text{Again, H and J are proper subgroups}$$

Mappings between groups

Define a mapping function $\phi : G_1 \longrightarrow G_2$

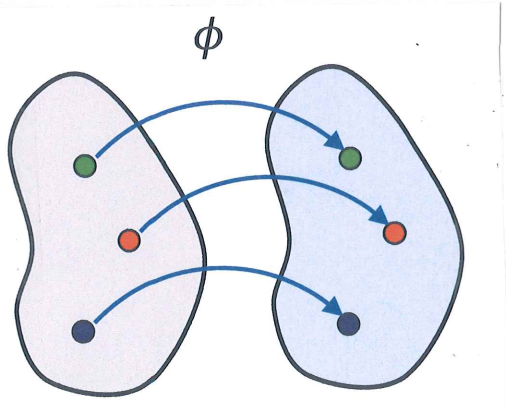
Mapping conditions

i) ϕ is one-to-one and onto (bijective)

ii) $\phi(ab) = \phi(a)\phi(b) \quad \forall\, a,b \in G_1$

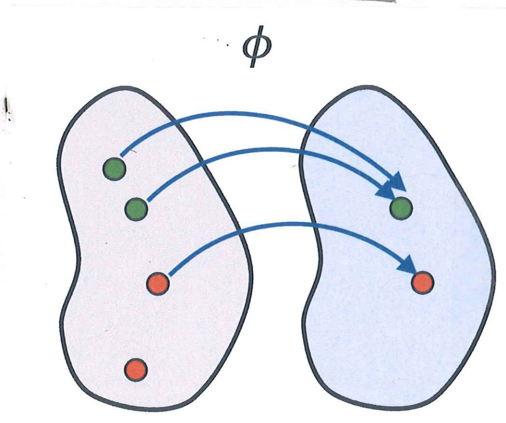
↳ preserves the group operations

① Isomorphisms



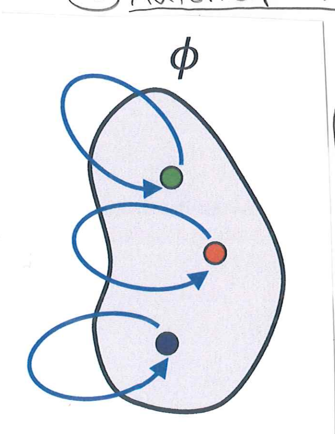
i) + ii)

② Homomorphisms



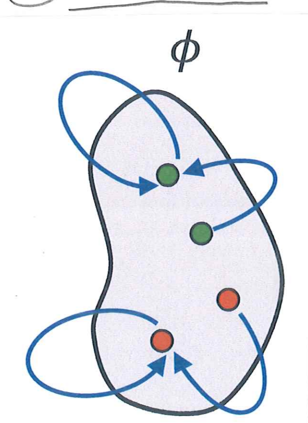
ii) only

③ Automorphisms



i) + ii)
onto itself

④ Endomorchisms



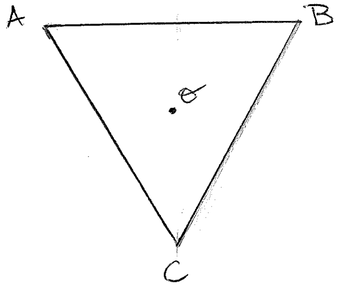
ii) only onto itself

2) Symmetry

The set of transformations that leave an object invariant (unaltered)

A simple example:

Rotations of an equilateral triangle



rotations (about θ)

$\frac{2\pi}{3} \Rightarrow C_3$

$\frac{4\pi}{3} \Rightarrow C_3 \cdot C_3 = C_3^2$

$2\pi \Rightarrow E$ (identity)

The set of rotations $\{R\}$ form a group

A1) closure : Yes

A2) identity : yes (E)

A3) associativity : yes

A4) inverse : yes

$\{E, C_3, C_3^2\} \xrightarrow{\text{inverses}} \{E, C_3^2, C_3\}$

Multiplicative table (1st ←; 2nd ↓)

	E	C_3	C_3^2
E	E	C_3	C_3^2
C_3	C_3	C_3^2	E
C_3^2	C_3^2	E	C_3

Abelian? : yes (~~[illegible]~~)

table is symmetric about diagonal

A) Point group symmetry

Group of symmetry operations that transform an object about a fixed point

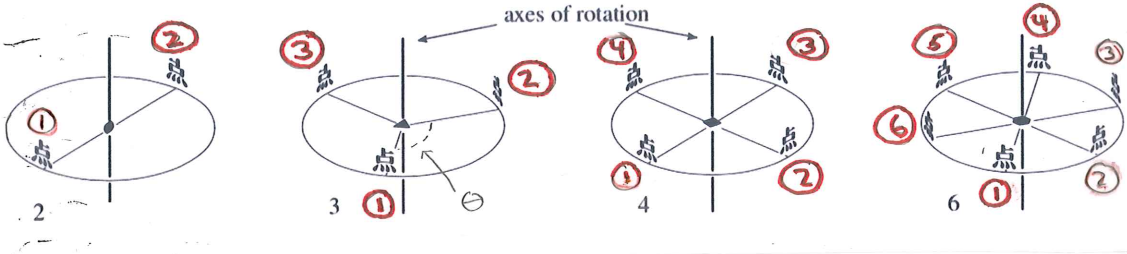
Includes (in 3D):

① rotations ② inversion ③ improper rotations

↓

rotation + inversion (or reflection)

① rotations



Defn: circular motion about an axis, i.e., a rotation of $\frac{2\pi}{n}$ about an axis. n: order of rotation (integer)

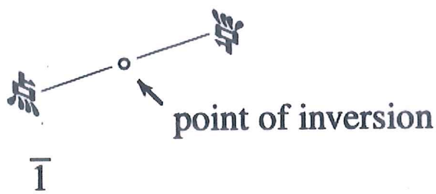
Schoenflies

C_n

Hermann-Mauguin

n ($n = 2, 3, 4, 5, 6, \ldots$)

② inversion



Defn: invert all points through a central point, e.g.,

center: (0,0,0) transforms $(x, y, z) \rightarrow (-x, -y, -z)$

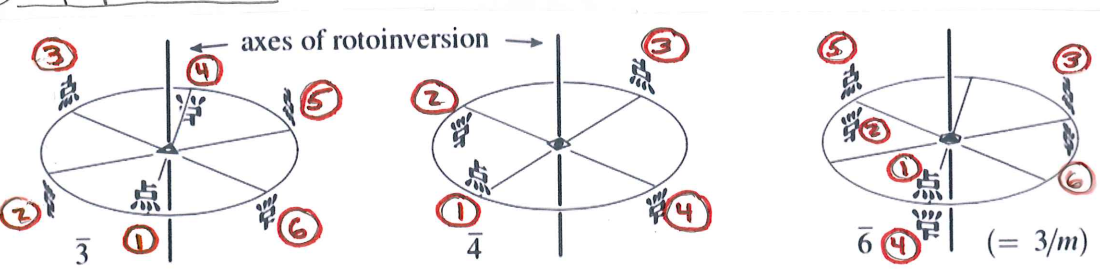
Schoenflies

C_i

Hermann-Mauguin

$\bar{1}$ (one bar)

③ improper rotations



Defn: a rotation of $\frac{2\pi}{n}$ about an axis followed by either:

a) inversion through a point (roto-inversion)

$\boxed{\text{OR}}$

b) reflection in plane ⊥ to axis (roto-reflection)

Schoenflies

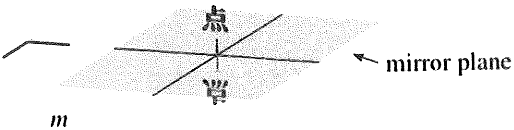
S_n (roto-reflection)

Hermann-Mauguin

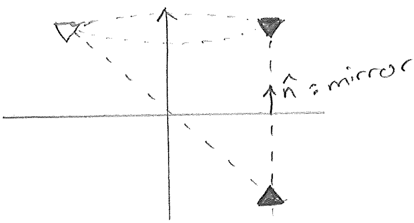
$\bar{n}$ (roto-inversion)

a special case : mirrors

$\boxed{\bar{2} \equiv m}$

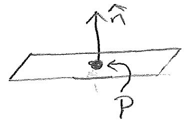


$\hat{n}$: mirror plane direction



Remember

plane defined via normal and point P



Number of point groups

1D

groups = 2

1) identity (C_1)
2) reflection (D_1)

2D

groups = ∞

2 families

1) rotations (C_n)
2) dihedral (D_n)

3D

groups = ∞

7 families (axial)

C_n, S_{2n}, C_{nh}, C_{nv}, D_n, D_{nd}, D_{nh}

7 families (polyhedral)

T, T_d, T_h, O, O_h, I, I_h

Point groups in 3D → Molecular point groups!

Water (H_2O) : C_{2v}

Ethane (C_2H_6, staggered) : D_{3d}

Useful resources

- Point group visualization : Pg. 43 of "Symmetry Relationships between crystal structures"
- Visualize point group symmetries of common molecules
  www.symotter.org/tutorial

B) Crystallographic point group symmetry

Periodic systems $\Rightarrow$ impose translational invariance

Infinitely periodic lattice representing crystal

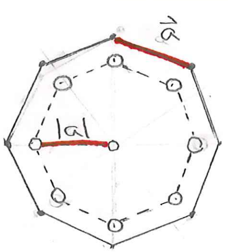
How does symmetry of point group change btwn non-periodic and periodic systems?

3D	non-periodic		periodic
	# groups = ∞	$\longrightarrow$	# groups = 32

Why?? $\Rightarrow$ Crystallographic restriction theorem

↳ Only certain rotations allowed given translational invariance

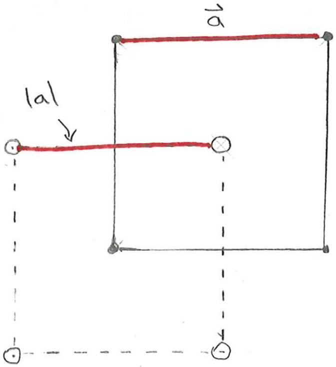
1) Proof (lattice point argument)



8-fold rotation

Displacement vector $\vec{a}$ from 8-fold rotation must apply to all lattice points

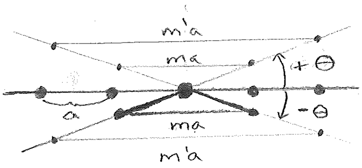
Superimposing lattice w/ translation vector $\vec{a}$ shows octogon w/ smaller volume $\Rightarrow$ shrinkage

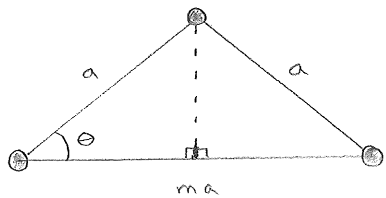


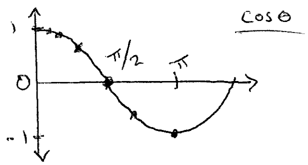
4-fold rotation

no shrinking $\Rightarrow$ acceptable for periodic system (volume preserved)

2) Proof (trig proof)







$$\cos\theta = \frac{\frac{1}{2}ma}{a}$$

$$2a\cos\theta = ma \;;$$

$$\theta = \frac{2\pi}{n}, \quad m \text{ is integer}$$

$$2a\cos\left(\frac{2\pi}{n}\right) = ma$$

$$2\cos\left(\frac{2\pi}{n}\right) = m$$

Possible solns

$n = 2: \; 2\cos(\pi) = -2$ (integer)

$n = 3: \; 2\cos\left(\frac{2\pi}{3}\right) = -1$ (integer)

$n = 4: \; 2\cos\left(\frac{2\pi}{4}\right) = 0$ (integer)

$n = 5: \; 2\cos\left(\frac{2\pi}{5}\right) = 0.618$ (not integer!)

$n = 6: \; 2\cos\left(\frac{2\pi}{6}\right) = 1$ (integer)

$n = 7: \; 2\cos\left(\frac{2\pi}{7}\right) = 1.24$ (not integer!)

...

Only possible rotations

$n = 2, 3, 4, 6$

c) Space group symmetry

Complete symmetry of periodic systems is given by the space group

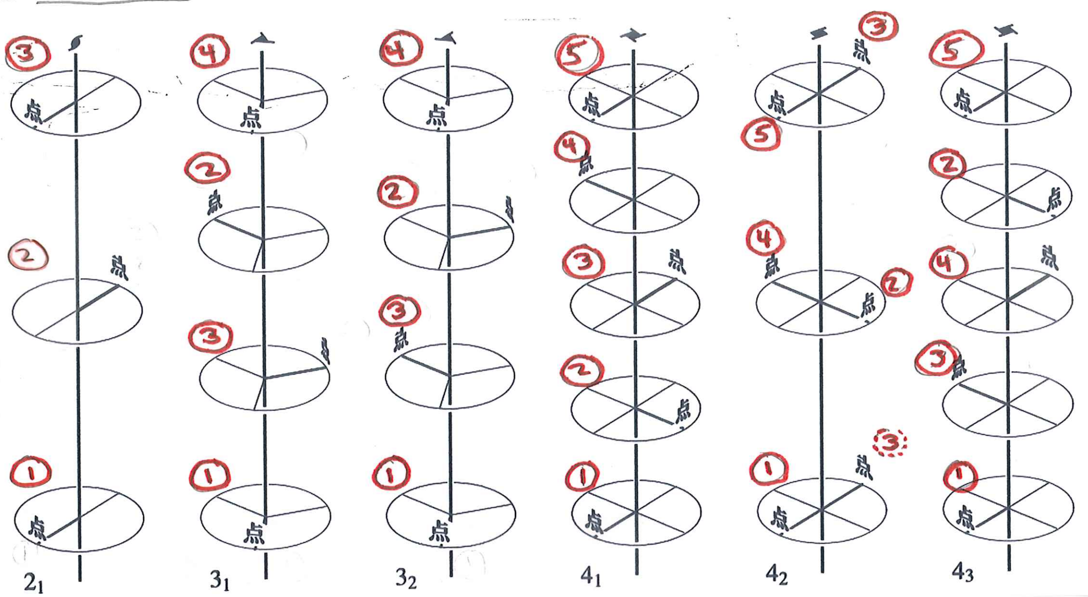
$$\{R\}\{t\} \longrightarrow \text{space group } \{R|t\}$$

$\boxed{230}$ space groups in 3D
- 219 (affine space groups)
- ~~230~~ 11 (enantiomorphs) ⟸ mirror image

Operations

(1) rotations (2) inversion (3) improper rotations (4) screws (rot + translation) (5) glides (mirror + translation)

④ screws



Defn: rotate $\frac{2\pi}{n}$ about an axis and translate parallel to that axis (magnitude d)

periodicity constrains translation lengths

$d \Rightarrow n \cdot d$ must bring you back to the same pt. $\left(\frac{L}{n} = d\right)$

Represented as

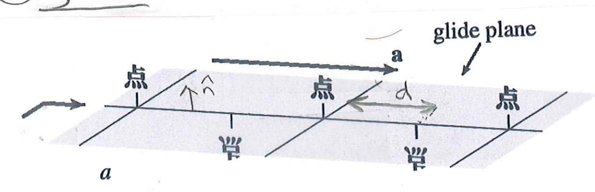
$\boxed{n_d}$

Possibilities in crystallography

$2_1, 3_1, 3_2, 4_1, 4_2, 4_3, 6_1, 6_2, 6_3, 6_4, 6_5$

enantiomorphs (left-handed) : $3_2, 4_3, 6_4, 6_5$

⑤ glides



Defn: each point is reflected through a mirror plane & translated parallel to it

$\hat{n}$: normal to mirror plane

d : translation distance

special glide operations

$\boxed{a, b, c}$: glide translation along ½ corresponding lattice vec.

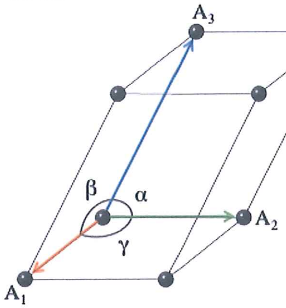
$\boxed{n}$: glide translation along ½ face diagonal

$\boxed{d}$: ¼ face diagonal (diamond)

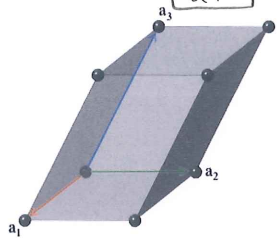
$\boxed{e}$: 2 glides w/ same plane + ½ translation along two diff lattice translations

Space groups split into 7 crystal systems

① Triclinic : $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90°$



aP

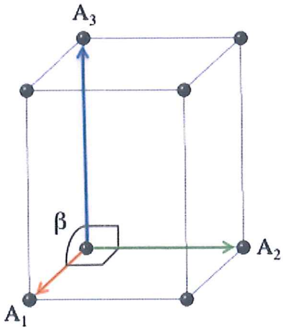


2 space groups

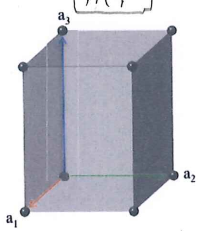
P1 — no symmetry except translation

$\bar{P1}$ — inversion

② Monoclinic : $a \neq b \neq c$, $\alpha = \gamma = 90°$, $\beta \neq 90°$



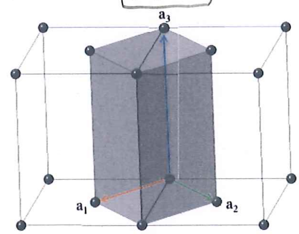
mP



simple monoclinic

8 space groups

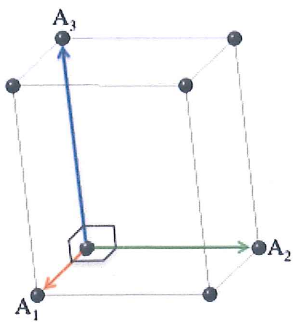
mC



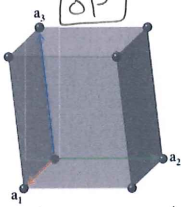
base-centered monoclinic

5 space groups

③ Orthorhombic : $a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$



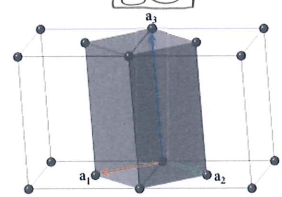
oP



30 space groups

simple orthorhombic

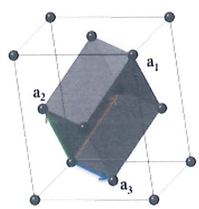
oC



15 space groups

base-centered orthorhombic

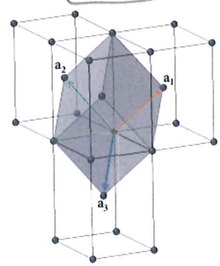
oF



5 space groups

face-centered orthorhombic

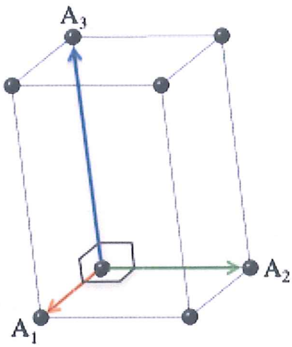
oI



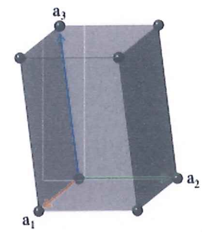
body-centered orthorhombic

9 space groups

(4) Tetragonal : $a = b \neq c$, $\alpha = \beta = \gamma = 90°$



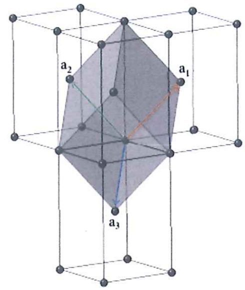
tP



simple tetragonal

49 space groups

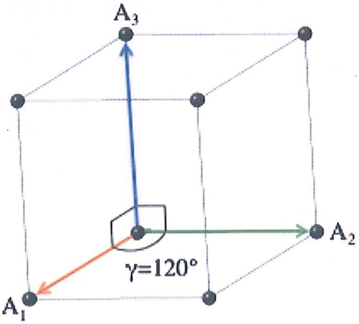
tI



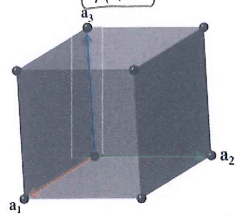
body-centered tetragonal

19 space groups

(5+6) Trigonal/Hexagonal : $a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$



hP

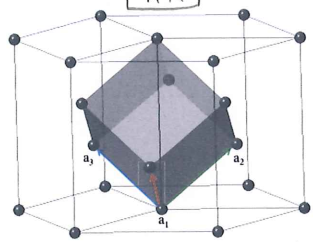


simple hexagonal

trig: 18 space groups

hex: 27 space groups

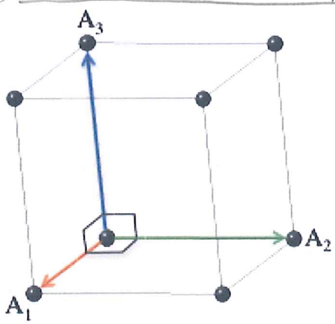
hR



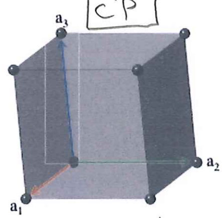
rhombohedral (trig)

7 space groups

(7) Cubic : $a = b = c$, $\alpha = \beta = \gamma = 90°$



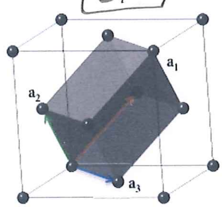
cP



simple cubic

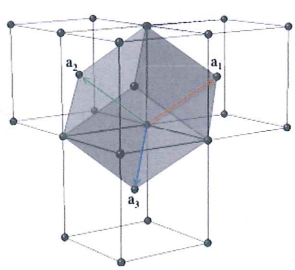
15 space groups

cF



face-centered cubic

11 space groups



cI

body-centered cubic

10 space groups

Space group notations

I) International (Hermann-Mauguin) symbols

$\boxed{\text{Ex}}$ P1, Pmmm, Ibca, $I\bar{4}2m$, I4/mmm, I432, P3

How to read?:

i) first character: centering type for the conventional cell

possible centerings

- ↳ P : primitive
- ↳ C, B, A : base-centered
- ↳ I : body-centered
- ↳ F : face-centered
- ↳ R : rhombohedral

in 3D
capitalized
in 2D
lowercase (only have p, c, h)

ii) subsequent characters: symmetry operation parallel to primary, secondary, tertiary directions of conventional cell

- ↳ blickrichtung (german) → viewing direction
- ↳ see Table 2.2.4.1 of ITC-A (pg. 18)

| e.g., space group # 17 $P222_1$ |

$\boxed{P\ 2\ 2\ 2_1}$

- P: primitive centering
- first 2: 2-fold rotation axis parallel to [1 0 0]
- second 2: 2-fold rotation axis parallel to [0 1 0]
- 2_1: 2-fold screw axis parallel to [0 0 1]

| e.g., space group # 99 P4mm |

$\boxed{P\ 4\ m\ m}$

- P: primitive centering
- 4: 4-fold rotation axis parallel to [0 0 1]
- first m: mirror plane axis parallel to $\left\{\begin{matrix}[1\,0\,0]\\ [0\,1\,0]\end{matrix}\right\}$
- second m: mirror plane axis parallel to $\left\{\begin{matrix}[1\,\bar{1}\,0]\\ [1\,1\,0]\end{matrix}\right\}$

representation of symmetry elements

↳ symmetry planes: represented by normals ($\hat{n}$)

↳ rotation axis: represented by rotation axis ($\hat{r}$)

special case:

↳ rotation axis and a symmetry plane are parallel, then characters are separated by a slash ("/")

$\boxed{\text{e.g., } P6_3/m}$ or $\boxed{\text{e.g., } P2/m}$

6-fold ~~rotation~~ screw rotation ∥ with mirror plane (along [0 0 1])

2-fold rotation ∥ to mirror plane (along [0 1 0])

Priority rules for symmetry operators

Multiple symmetry elements can be parallel to directions

Rules

1) highest rotational order; pure rotation preferred over screw of same rotational order

   e.g., $2 > 2_1$ and $4 > 4_3$

2) mirror/glide planes: $m > e > (a, b, c) > n$

   ↳ d is always lowest priority

Notes on crystal systems

1) triclinic systems

   ↳ no symmetry direction → just $P1$ and $P\bar{1}$

2) monoclinic systems

   ↳ one symmetry direction (usually b- or c-axis)

   ↳ to distinguish use placeholder "1".

   $\boxed{\text{e.g., } P2}$

   ↳ P121 : unique axis b
   ↳ P112 : unique axis c
   ↳ P211 : unique axis a

   * specifies setting/option

3) orthorhombic, tetragonal, hexagonal, + cubic systems

↳ generally have three symmetry directions

↳ if direction has no symmetry, again use "1"

e.g., P31m, P3m1

↳ if no misinterpretation is possible — "1" at end of space group — "1" can be omitted

e.g., P6 vs P611, $R\bar{3}$ vs $R\bar{3}1$

Short vs full Hermann-Mauguin symbol

↳ generally use short

↳ full specifies setting (useful if non-standard)

↳ short and full differ for:

- monoclinic space groups
- space groups of the following crystal class
  - mmm
  - 4/mmm
  - $\bar{3}m$
  - 6/mmm
  - $m\bar{3}$
  - $m\bar{3}m$

↳ if full symbols contain rotation axis and symmetry plane for each direction → suppress rotation axis when possible

e.g., $P2_1/n\,2_1/m\,2_1/a \rightarrow Pnma$

e.g., $P6_3/m\,2/m\,2/c \rightarrow P6_3/mmc$

e.g., $I4_1/a\,\bar{3}\,2/d \rightarrow Ia\bar{3}d$

2) Schoenflics symbols

Ex C_i^1, D_2^1, T_d^2, O^3, C_s^1, D_{6h}^4

preference to roto-reflection vs roto-inversion

How to read?

i) capital letter

↳ C_n : rotation

C_{nh} : n-fold rotation w/ mirror plane ⊥ to axis (horizontal mirror)

C_{nv} : n-fold rotation w/ mirror plane ∥ to axis (vertical plane)

↳ S_n : n-fold roto-reflection

↳ D_n : (dihedral, two-sided) n-fold rotation + n two-fold axes ⊥ to that axis

↳ T : (tetrahedron) symmetry of tetrahedron

↳ O : (octahedron) symmetry of octahedron (cube)

ii) subscripts

↳ n : rotation axis order

↳ i : inversion

↳ v : vertical mirror (σ) plane (along principle axis)

↳ h : horizontal mirror (σ) plane (⊥ to principle axis)

iii) superscripts

↳ simple enumeration to specify particular space group

See pgs. 74-76 of "Symmetry Relationships between Crystal Structures"

Pitfalls

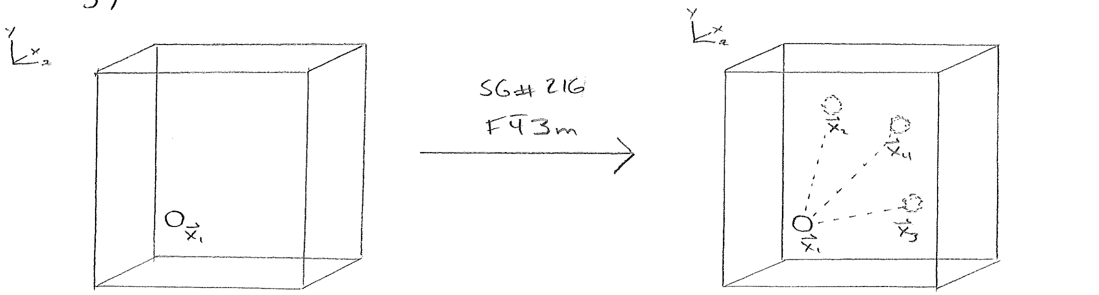
1) no lattice centering
2) no translation info for screw/glides
3) superscript is non-descriptive

3) Hall Symbol : See cci.lbl.gov/sginfo/hall_symbols.html

Symmetry of atoms in the conventional cell $\Rightarrow$ Wyckoff positions

Space group symmetry operators dictate placement of atoms

e.g.,



$\vec{x}_1 = \left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$

$\vec{x}_1 = \left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$
$\vec{x}_2 = \left(\frac{1}{4}, \frac{3}{4}, \frac{3}{4}\right)$
$\vec{x}_3 = \left(\frac{3}{4}, \frac{1}{4}, \frac{3}{4}\right)$
$\vec{x}_4 = \left(\frac{3}{4}, \frac{3}{4}, \frac{1}{4}\right)$

Wyckoff position

A set of symmetrically equivalent points/positions in a conventional unit cell, transformed into one another by the operations of the space group

↳ Tabulated for all 230 spacegroups (ITC-A)

Generally represented with the following

e.g.,	4	c	$\bar{4}3m$	(position)	(position) ...
	①	②	③	④	

① Multiplicity : # of equivalent points per cell for this position

② Wyckoff letter : arbitrary designation for each Wyckoff position

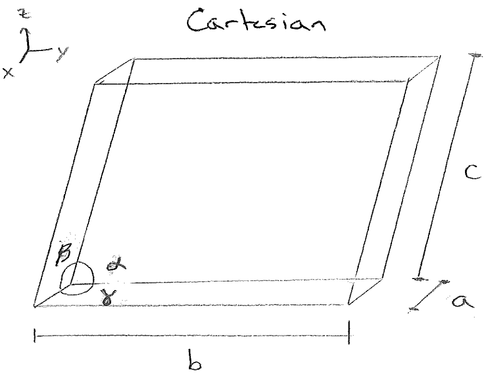
③ Site symmetry : symmetry operations that related the group of equivalent positions

④ positions : coordinates of the equivalent position wrt the conventional cell $\Rightarrow$ FRACTIONAL COORDS.

A little detour....

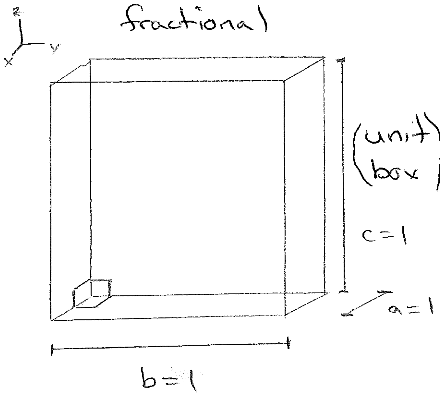
Cartesian vs fractional coordinate systems

Cartesian



$$\underset{f2c}{\overset{c2f}{\rightleftharpoons}}$$

fractional



↳ atoms positions represented in Cartesian (global) coordinates

$\boxed{\text{e.g., } \vec{x}_c = X\hat{x} + Y\hat{y} + Z\hat{z}}$

$\hat{x}, \hat{y}, \hat{z}$: Cartesian directions

X, Y, Z : no restrictions

(generally represented with lattice parameters, a, b, c and angles α, β, γ)

↳ c2f = converting to fractional

$$\vec{x}_f = L^{-1}\vec{x}_c$$

↳ atoms positions represented as fractions of the lattice vectors

$\boxed{\text{e.g. } \vec{x}_f = u\hat{i} + v\hat{j} + w\hat{k}}$

$\hat{i} = (1, 0, 0)$ along a

$\hat{j} = (0, 1, 0)$ along b

$\hat{k} = (0, 0, 1)$ along c

$0 \leq u, v, w < 1$

(in cell)

↳ f2c : converting to Cartesian

$$\vec{x}_c = L\vec{x}_f$$

$$L = \begin{pmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{pmatrix}$$

$\boxed{\text{Most codes use fractional coordinates}}$

* careful : pay attention to row vs column

row major $\tilde{L} = \begin{pmatrix} a_1 & a_2 & a_3 \\ b_1 & b_2 & b_3 \\ c_1 & c_2 & c_3 \end{pmatrix}$

Pearson symbol

Now, we have atoms in the unit cell!

previously for lattices...

- first symbol : crystal system
- second symbol : lattice centering
- number : # of lattice points in the conventional cell

with atoms, the ~~P~~ Pearson symbol is

- first symbol : crystal system (same as before)
  - ↳ a : triclinic
  - ↳ m : monoclinic
  - ↳ o : orthorhombic
  - ↳ t : tetragonal
  - ↳ h : hexagonal/trigonal
  - ↳ c : cubic
- second symbol : lattice centering (same as before)
  - ↳ P : primitive
  - ↳ C (~~A~~ or S) : base-centered
  - ↳ I : body-centered
  - ↳ F : face-centered
  - ↳ R : rhombohedral
- number : # of atoms in the conventional cell
  - ↳ $\sum_i (\text{Wyckoff multiplicities})_i$

e.g., zincblende (sg # 216, cF)

Wyckoff positions

$$\left.\begin{array}{llll} Zn: 4 & a & \bar{4}3m & (0,0,0) \\ S: 4 & c & \bar{4}3m & (\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4}) \end{array}\right\} \sum(\text{mult}) = 4+4 = 8 \quad \boxed{cF8}$$

The International Tables for Crystallography A (ITC-A)

↳ A complete tabulation of the 230 space groups and the Wyckoff positions
↳ Reference for all things related to crystallography

Contents of a particular space group page

1. Short Hermann-Mauguin symbol
2. Schoenflies symbol
3. Crystal class (i.e., crystallographic point group)
4. Crystal system
5. Space group number
6. Full Hermann-Mauguin symbol
7. Patterson symmetry
   - ↳ Gives symmetry of Patterson function $P(x,y,z)$

     $$P(x,y,z) = \frac{1}{V}\sum_h \sum_k \sum_l |F_{hkl}|^2 e^{-2\pi i(hx+ky+lz)}$$

     i.e., Fourier transform of intensities (rather than structure factor)
   - ↳ space group of Patterson function is identical to that of the "vector set" of the structure (always centrosymmetric + symmorphic)
     - → symmorphic : apart from translations, leaves one point fixed
     - → centrosymmetric : contains inversion center
   - ↳ Deduce from space group by
     1) Glides → mirrors, screws → rotations (remove translations)
     2) Add ~~cente~~ inversion symmetry if missing

⑧ Space group diagrams

↳ shows relative placement of symmetry ~~elements~~ axes/plane in unit cell

↳ projections along a, b, and c directions (some others)

↳ see pgs. 7 – 10 of ITC-A

⑨ Origin of the unit cell

↳ centered on particular site symmetry

↳ if centrosymmetric (contains inversion), two choices

1) inversion

2) other high symmetry site

e.g., sg #227 $Fd\bar{3}m$
option 1: $\bar{4}3m$
option 2: $\bar{3}m$

distance btwn site symmetries is also given.

⑩ Asymmetric Unit

↳ Smallest closed part of space that when operated on by symmetry operations of the space group, fills the space

↳ aka: fundamental region/domain

⑪ Symmetry operations

↳ Enumerated symmetry operations for the space group

↳ For centered cells (C, I, F, R (hexagonal axis)) additional subheadings indicate the symmetry operations w/ centerings

↳ Interpretation

- first symbol: type of symmetry (n-fold rot, mirror, glide, screw)

• if glide/screw: translation given in parentheses

• +, – on rotation indicates counterclockwise + clockwise ~~[illegible]~~, respectively

- <u>coordinate triplet</u>: location + orientation of symmetry element
    - ↳ roto-inversions include inversion pt.

↳ Examples

$\boxed{1)\ a\ \ x, y, \tfrac{1}{4}}$

↳ glide reflection w/ component $(\tfrac{1}{2}, 0, 0)$ through the $x, y, \tfrac{1}{4}$ plane

$\boxed{2)\ \bar{4}^{+}\ \ \tfrac{1}{4}, \tfrac{1}{4}, z;\ \tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4}}$

↳ 4-fold roto-inversion; counter-clockwise 90° about $\tfrac{1}{4}, \tfrac{1}{4}, z$ line w/ an inversion through pt. $\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4}$

(12) Generators

↳ Sequence of symmetry operators that generate all symmetrically equivalent points of the general Wyckoff position

↳ Only need finite subset of operations (based on crystal class of space group)

→ see ~~pg.~~ Table 8.3.5.1 of ITCA (pg. 737)

↳ $\boxed{\text{Ex}}$ sg # 14, P12$_1$/c1

(13) Positions

↳ Wyckoff positions
- → Multiplicity
- → Letter
- → Site symmetry
- → Coordinates
    - • Centered cells include additional "sets"

↳ Includes general + special positions

→ General position

↳ Set of symmetrically equivalent pts. only left invariant by identity operation (no other symmetry operation of the space group)

→ Special position(s)

↳ Set of symmetrically equivalent pts. left invariant by identity + at least one other symmetry operation of the space group

↳ site symmetry directions ⇒ same as for space group (i.e., same primary, secondary, tertiary dirs.)

- Here, a "." indicates no symmetry element contributes to that direction

↳ Ex sg # 94 $P4_22_12$

- $\boxed{4\ f\ ..2}$: 2-fold rotation along one tertiary dir
- $\boxed{4\ b\ 2.22}$: 2-fold rot along primary, 2-fold along both tertiary directions

(14) Reflection conditions

↳ Non-zero intensity in diffraction pattern ("conditions of occurrence")

↳ General vs special

→ General: conditions occur for all Wyckoff positions

→ Special: extra conditions for particular Wyckoff

↳ Ex http://pd.chem.ucl.ac.uk/pdnn/symm4/hklcond.html

(15) Symmetry of special projects

↳ Two-dimensional symmetry projection along given directions

(16) Maximal non-isomorphic subgroups

↳ direct subgroups of space group

I: translationengleiche (t subgroups)

↳ same translation group

↳ lower crystal class

II: klassengleiche (k subgroup)

↳ same crystal class

↳ fewer translations

IIa: Conventional cells of G and subgroup H are the same

IIb: Conventional cell of subgroup H is larger than G

(17) Maximal isomorphic space groups

↳ same space group

(18) Minimal non-isomorphic space group

↳ direct supergroups of space group

A) Space group setting choices

1) monoclinic systems

↳ unique axis - b

↳ unique axis - c

, where unique axis is parallel to m

$\boxed{\text{Ex sg \#14}}$

2) rhombohedral systems

↳ rhombohedral setting

↳ hexagonal setting (x3)

$\boxed{\text{Ex sg \#146}}$

3) centrosymmetric systems

↳ origin on inversion site

↳ origin on other high symmetry site

$\boxed{\text{Ex sg \#227}}$

B) Enantiomorphic space groups

See "AFLOW library of crystallographic prototypes: pt 2" pgs. 58-59

Important symmetry groups

1) Point groups

↳ rotations, roto-inversions, inversion = $\boxed{\{R\}}$

↳ Important types:

A) Point group of the lattice

↳ symmetry of lattice pts

B) Point group of the crystal

↳ symmetry of crystal face normals

↳ considers atomic basis

C) Point group of the reciprocal lattice

↳ symmetry of the Brillouin zone

↳ dual/reciprocal of lattice in real space

D) ~~Point group~~ Dual of the point group of the crystal

↳ symmetry of the irreducible Brillouin zone

↳ dual/reciprocal of crystal face normals

2) Space groups

↳ rotations, inversions, roto-inversions, screw, glides : $\{R \mid T+t\}$

→ T: lattice translations

→ t: internal translations

$$\boxed{\begin{aligned}&\{R \mid T+t\}\\ &= \{R_1, R_2, \dots R_n \mid T+t\}\end{aligned}}$$

3) Factor groups

↳ cosets of the subgroup of lattice translations (T)

$$\equiv \{I \mid 0\}\{I \mid T\}, \{R_1 \mid t_1\}\{I \mid T\}, \{R_2 \mid t_2\}\{I \mid T\}, \dots \{R_n \mid t_n\}\{I \mid T\}$$

- subgroup = $\{I \mid T\}$ ⇒ ~~the~~ lattice translation subgroup

- coset representatives: $\{I \mid 0\}, \{R_1 \mid t_1\}, \{R_2 \mid t_2\}, \dots \{R_n \mid t_n\} \equiv$ $\boxed{\text{unit cell symmetry}}$

↳ NOTE: The coset representatives do not necessarily form a group!!! Closure (A1) violated! (e.g., screw translation eventually leaves unit cell)

↳ Multiplying the cosets returns the space group $\{R|T+t\}$

↳ Relationship to point group of the crystal

- if primitive cell : coset representative is isomorphic to point group of the crystal

- if conventional cell (or any non-primitive) : coset representative is homomorphic to point group of the crystal (integer multiple)

4) Site point group

↳ point group symmetry when centered on a particular atom or site

↳ local symmetry environment, same for all Wyckoff positions

↳ use-case = phonons

Crystal-spin symmetry

- Include magnetic moment as symmetry-breaking feature
- General relation:

$$\boxed{\text{crystal symmetry} \geq \text{crystal-spin symmetry}}$$

Magnetic point/space groups

- Consider spin-flip symmetry
- Outside scope of this class
- Time reversal symmetry!

Representation of symmetry operators

Types of transformations

1) translations
2) fixed-point
3) fixed-point free (combo of 1) + 2) ≡ screw and glides)

1) translations

↳ 3x1 vectors

$$\vec{t} = \begin{pmatrix} t_1 \\ t_2 \\ t_3 \end{pmatrix}$$

(Cartesian or fractional coordr.)

2) fixed-point

↳ rotations, inversions, improper rotations (roto-inversions)

↳ Elements of the orthogonal group ≡ $O(n)$

→ $O(n)$

- norm preserving group (distances in object are preserved)

↳ Elements represented by 3x3 matrix (in 3D)

$$U = \begin{pmatrix} u_{11} & u_{12} & u_{13} \\ u_{21} & u_{22} & u_{23} \\ u_{31} & u_{32} & u_{33} \end{pmatrix}$$

→ $\det(u) = \pm 1$

→ Cartesian or fractional

if lattice

$$L = \begin{pmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{pmatrix}$$

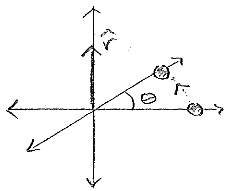
$$\boxed{\begin{aligned} U_f &= L^{-1} U_c L \\ U_c &= L U_f L^{-1} \end{aligned}}$$

Other representations for <u>pure</u> rotations

1) axis-angle

$\hat{r} = (r_1, r_2, r_3)$

$\theta = \frac{2\pi}{n}$ (magnitude of rotation)



Rodrigues's formula

$$\vec{p}_{rot} = \vec{p}\cos\theta + (\hat{r} \times \vec{p})\sin\theta + \hat{r}(\hat{r}\cdot\vec{p})(1-\cos\theta)$$

Rotations form subgroup of $O(n) \Rightarrow SO(n)$

<u>$SO(n)$:</u> special orthogonal group

↳ $\det = +1$

↳ a <u>Lie group</u>

Lie group

↳ group whose elements are continuous and smooth

↳ differentiable manifolds

↳ infinitesimal form ⇒ Lie algebra

Lie algebra

↳ local/linearized version of Lie group

↳ called "infinitesimal group"

So,

$SO(3) \equiv$ pure rotations $(u) \Rightarrow$ Lie group

$so(3) \equiv$ matrix generator $(G) \Rightarrow$ Lie algebra

2) Matrix generator

↳ Lie algebra so(3) (pure rotations only)

↳ skew symmetric matrix

$$G = \begin{pmatrix} 0 & -r_3 & r_2 \\ r_3 & 0 & -r_1 \\ -r_2 & r_1 & 0 \end{pmatrix}$$, where r_1, r_2, r_3 components of $\hat{r}$

↳ recover U (SO(3)) via matrix exponential

$$\boxed{U = \exp(\theta G) = \sum_k^{\infty} \frac{(\theta G)^k}{k!}}$$ ⇒ connection btwn Lie group + Lie algebra

↳ useful for combining multiple symmetry operators

e.g., $U_1 \cdot U_2 = \exp(\theta_1 G_1)\exp(\theta_2 G_2) = \underline{\exp(\theta_1 G_1 + \theta_2 G_2)}$

Note: only if matrices commute

↳ decompose on L_x, L_y, L_z

$$\boxed{G = xL_x + yL_y + zL_z}$$

$$L_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}$$

$$L_y = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix}$$

$$L_z = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

3) Quaternion

↳ $\boxed{\vec{q} = (q_0, q_1, q_2, q_3)}$

$$\left.\begin{aligned} q_0 &= \cos(\theta/2) \\ q_1 &= r_1 \sin(\theta/2) \\ q_2 &= r_2 \sin(\theta/2) \\ q_3 &= r_3 \sin(\theta/2) \end{aligned}\right\} \text{Euler angles}$$

↳ recast into SU(2) matrix (2x2)

$$\boxed{C = \begin{pmatrix} q_0 + q_3 i & q_2 + q_1 i \\ -q_2 + q_1 i & q_0 - q_3 i \end{pmatrix}}$$

SU(n)
special unitary group

↳ Lie group

→ decompose on Pauli matrices (σ_i)

$$C = q_0 I + q_1 i \sigma_1 + q_2 i \sigma_2 + q_3 i \sigma_3$$

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

↳ corresponding Lie algebra su(2) of SU(2)

$$\boxed{g = \frac{i}{2} \begin{pmatrix} r_3 & r_1 - r_2 i \\ r_1 + r_2 i & -r_3 \end{pmatrix}}$$

→ decompose onto Pauli matrices

$$g = x\sigma_1 + y\sigma_2 + z\sigma_3$$

$$x = \left(\frac{i}{2}\right) r_1, \quad y = \left(\frac{i}{2}\right) r_2, \quad z = \left(\frac{i}{2}\right) r_3$$

Matrix exponential connects back to C

$$C = \exp(\theta g)$$

↳ 4x4 quaternion matrix

$$Q = \begin{pmatrix} q_0 & q_1 & q_2 & q_3 \\ -q_1 & q_0 & -q_3 & q_2 \\ -q_2 & q_3 & q_0 & -q_1 \\ -q_3 & -q_2 & q_1 & q_0 \end{pmatrix}$$

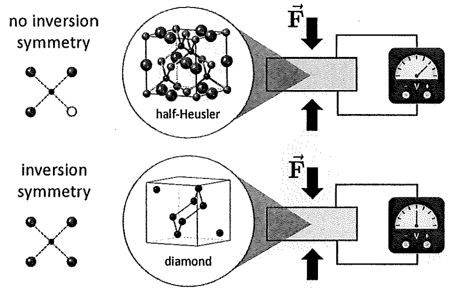
→ allows matrix-vector multiplication versus quaternion algebra

AFLOW - SYM

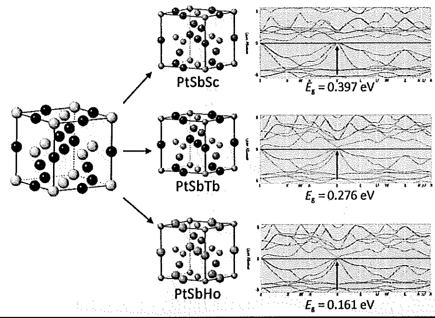
Structure vs properties

understanding structure to guide materials design

e.g., symmetry and piezoelectricity



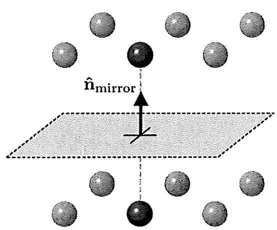
e.g., prototype structures

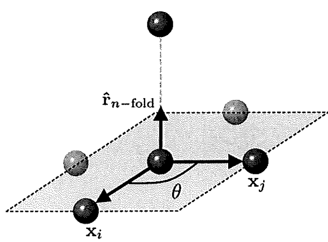


Hahn, Kluwer Academic Publishers (2002); Zou, Tang, and Pan, Proc. Royal Soc. Lond. A **469**, 2012075 (2013) 1

AFLOW-SYM

AFLOW-SYM tests invariance of crystal under transformations





descriptions:

space group	Bravais lattice	conventional cell	…
Pearson symbol	Wyckoff positions	primitive cell	

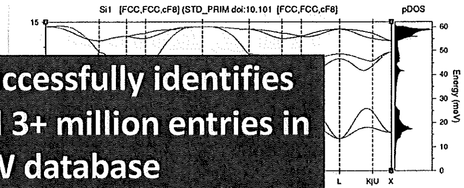
Hicks *et al.*, Acta Cryst. A74, 184 (2018) 2

X33

Symmetry is ubiquitous

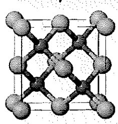
Brillouin zones/kpaths/
band structures

phonon calculations



AFLOW-SYM successfully identifies symmetry for all 3+ million entries in AFLOW database (no human-intervention)

generation/classification



characterization

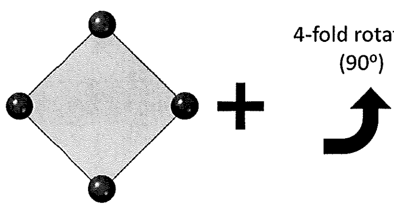
AFLOW
Automatic - FLOW for Materials Discovery

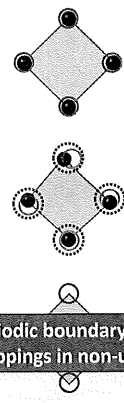
Hicks *et al.*, Acta Cryst. A**74**, 184 (2018), Setyawan and Curtarolo, Comp. Mat. Sci. **49**, 299 (2010)

Identifying symmetry elements

attempt symmetry operation

4-fold rotation (90°)





✓ mapped

✓ mapped

radius ϵ
(threshold for mappings)

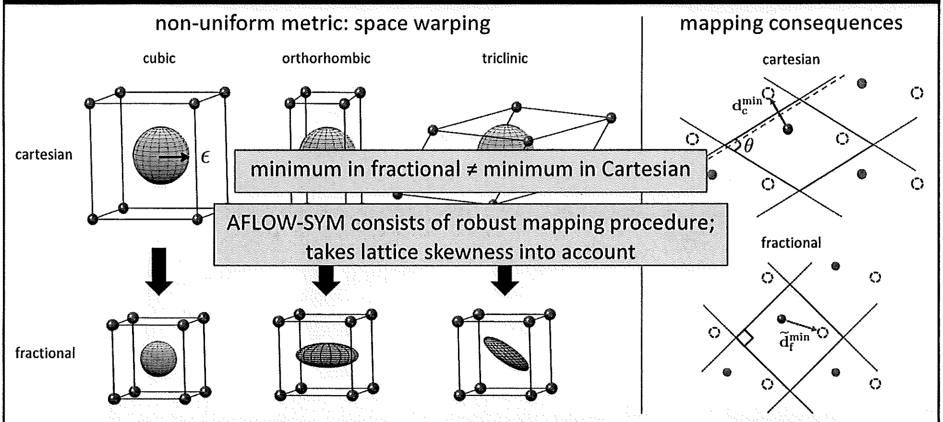
1. periodic boundary conditions
2. mappings in non-uniform metric spaces

$$\left|\left|\mathbf{x}_{\mathrm{orig}} - \mathbf{x}_{\mathrm{transformed}}\right|\right| \leq \epsilon$$

Hicks *et al.*, Acta Cryst. A**74**, 184 (2018)

X34

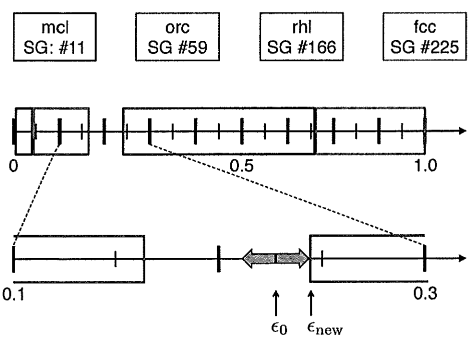
Tolerance: Cartesian and fractional spaces



Hicks *et al.*, Acta Cryst. A74, 184 (2018)

Automatic adaptive tolerance

self-consistent tolerance scan



system-specific tolerance

$$\boxed{\epsilon_{\text{tight}} = d_{\text{nn}}^{\text{min}}/100}$$

$$\boxed{\epsilon_{\text{loose}} = d_{\text{nn}}^{\text{min}}/10}$$

single global tolerance

Hicks *et al.*, Acta Cryst. A74, 184 (2018)

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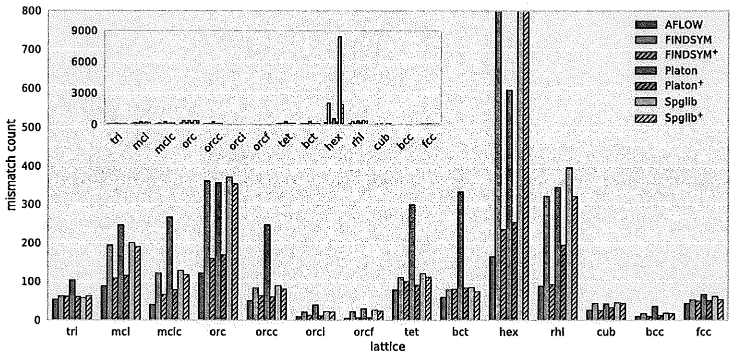
Benchmark with existing packages



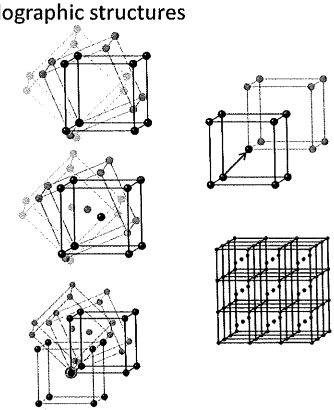
Mismatch with respect to space group listed in description of experimental structure in ICSD

Hicks *et al.*, Acta Cryst. A**74**, 184 (2018)

Crystallographic symmetry

Calculates the relevant symmetry groups for crystallographic structures

- lattice point group
- reciprocal lattice point group (BZ symmetry)
- factor group (unit cell symmetry)
- crystallographic point group
- dual of crystallographic point group (IBZ symmetry)
- space group
- site point group (atom point symmetry)



Hicks *et al.*, Acta Cryst. A**74**, 184 (2018)

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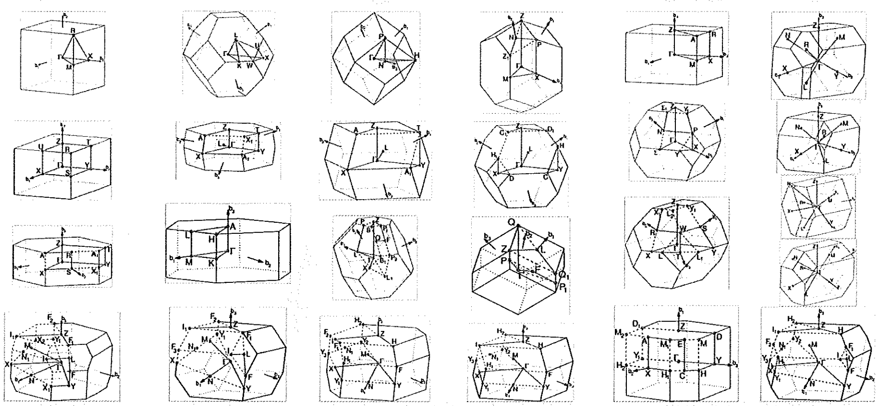
AFLOW Brillouin zones

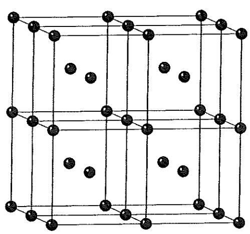


Setyawan and Curtarolo, Comp. Mat. Sci. **49**, (2010)

Crystal-spin symmetry

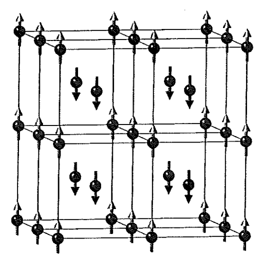
crystal symmetry

$\mathrm{Im\bar{3}m}\ \#229$



crystal-spin symmetry

$\mathrm{Pm\bar{3}m}\ \#221$



spin – degree of freedom that can break symmetry

$\boxed{\text{crystal symmetry} \geq \text{crystal-spin symmetry}}$

Hicks *et al.*, Acta Cryst. **A74**, 184 (2018)

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Symmetry descriptions

representations for each symmetry element

operator information	AFLOW-SYM	Spglib
operator type	✓	
Hermann-Mauguin	✓	
Schönflies	✓	
transformation matrix (cartesian)	✓	
transformation matrix (fractional)	✓	✓
generator matrix	✓	
so(3) coefficients (L_x, L_y, L_z)	✓	
angle	✓	
axis	✓	
quaternion (vector)	✓	
quaternion (2 × 2 matrix)	✓	
quaternion (4 × 4 matrix)	✓	
su(2) coefficients (Pauli)	✓	
inversion boolean	✓	
internal translation (cartesian)	✓	
internal translation (fractional)	✓	✓
atom index map	✓	
atom type map	✓	
lattice translation (cartesian)	✓	
lattice translation (fractional)	✓	

$$U_{3\text{-fold}} = \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ 1 & 0 & 0 \end{pmatrix}$$

$$A = \begin{pmatrix} 0.0 & -1.2092 & -1.2092 \\ 1.2092 & 0.0 & -1.2092 \\ 1.2092 & 1.2092 & 0.0 \end{pmatrix}$$

$$\hat{r} = (0.57735, -0.57735, 0.57735)$$

$$\theta = 120^\circ$$

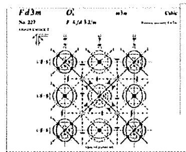
$$q = (0.5, 0.5, -0.5, 0.5)$$

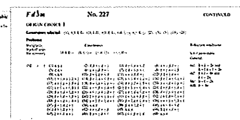
$$C = \begin{pmatrix} 0.5 + 0.5i & -0.5 + 0.5i \\ 0.5 + 0.5i & 0.5 - 0.5i \end{pmatrix}$$

$$Q = \begin{pmatrix} 0.5 & 0.5 & -0.5 & 0.5 \\ -0.5 & 0.5 & -0.5 & -0.5 \\ 0.5 & 0.5 & 0.5 & -0.5 \\ -0.5 & 0.5 & 0.5 & 0.5 \end{pmatrix}$$

consistent with International Tables for Crystallography (ITC)

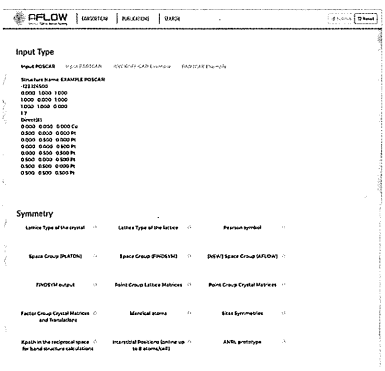
- standard space group label
- space group setting
- Wyckoff positions
  - multiplicity
  - letter designation
  - site symmetry
  - coordinates



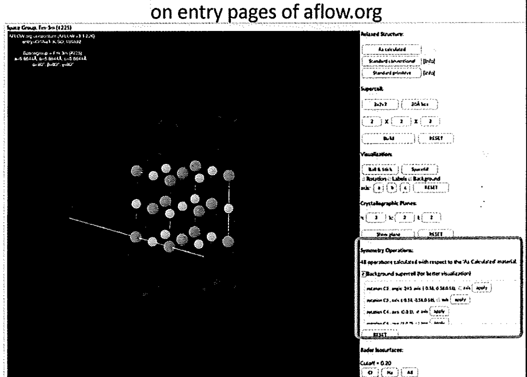


AFLOW-SYM: online

online functionality



visualize symmetry operations on entry pages of aflow.org



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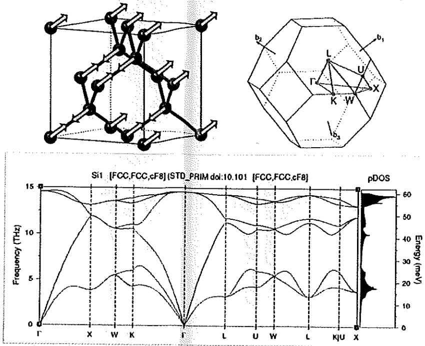
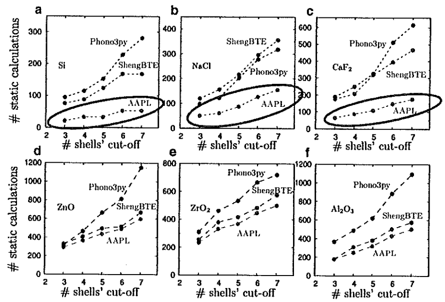
Symmetry reduced phonon calculations

lattice vibrations (phonons) :
APL (harmonic) and AAPL (anharmonic)



robust symmetry = more efficient than competitors



Toher *et al.*, in *Handbook of Materials Modeling*. Springer, Cham (2018); Plata *et al.*, NPJ Computational Materials 3, 45 (2017)

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Next time

- Put into practice
  - Calculate crystallographic symmetries with AFLOW-SYM
    - Tutorial
    - Exercises
- Bring your laptop
  - Install AFLOW software on you computer
  - Set up account on our research computer
  - Operating system?

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