International School on Fundamental Crystallography

and

Workshop on Structural Phase Transitions

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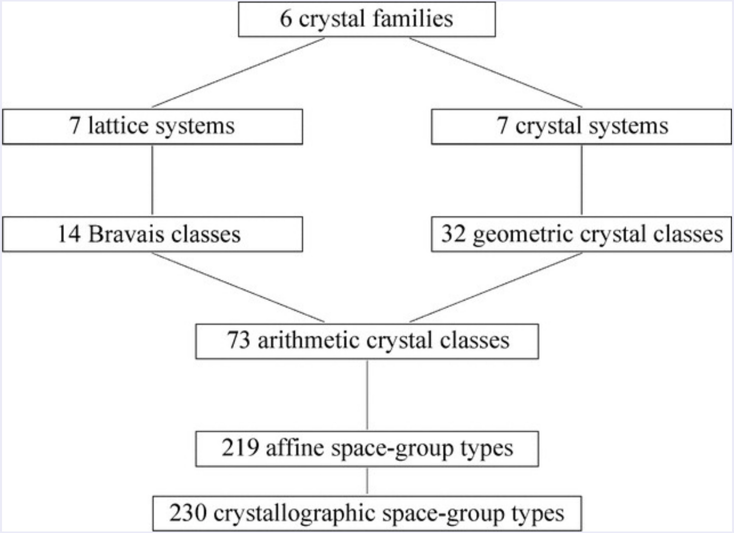
Crystallographic space groups.

Classification of space groups

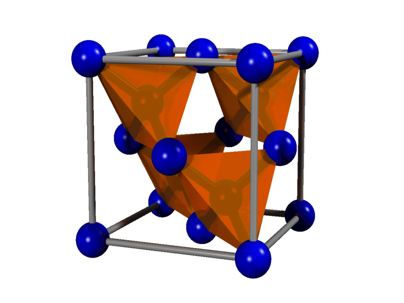


A motivation for changing the coordinate system

Group-subgroup pairs

- For each space group $\mathcal{G}$ a conventional setting is defined, which is a canonical choice of coordinate system in which the group is usually considered.
- For a space group $\mathcal{G}$ in conventional setting, a subgroup $\mathcal{H} < \mathcal{G}$ may not be in its conventional setting and a change of coordinate system is required to transform it to its conventional setting.
- For a phase transition in which the symmetry of a crystal structure is changed from $\mathcal{G}$ to $\mathcal{H}$, one wants to use the same coordinate system both for $\mathcal{G}$ and $\mathcal{H}$
  $\Rightarrow$ consider $\mathcal{G}$ (or $\mathcal{H}$) in two different coordinate systems (conventional for $\mathcal{G}$ or for $\mathcal{H}$).
- With respect to different coordinate systems, an element $g \in \mathcal{G}$ has different matrix-column pairs.

Similar crystal structures



- The elements carbon and silicon both crystallize in the *diamond structure* with face-centred cubic unit cell, but with different cell parameters: 3.5668Å for carbon and 5.4310Å for silicon.
- Described in the same coordinate system, the two structures have different space groups, since the translation vectors have different lengths.
- If the basis vectors are rescaled by the factor $5.4310/3.5668$ for silicon, the space groups of the two structures become the same.

Space-group types

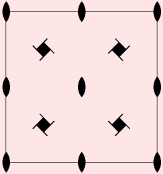
Two space groups $\mathcal{G}$ and $\mathcal{G}'$ belong to the same affine space-group type if $\mathcal{G}'$ can be obtained from $\mathcal{G}$ by a change of the coordinate system.
If the coordinate transformation can be chosen orientation-preserving, i.e. with $\det \mathbf{P} > 0$ for $\mathbf{P}$ the basis transformation, the space groups belong to the same (crystallographic) space-group type.

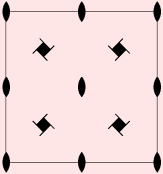
Chirality makes the difference

- There are 219 affine space-group types and 230 crystallographic space-group types in 3D, 11 affine space-group types split into 11 pairs of crystallographic space-group types.
- Two space groups $\mathcal{G}$ and $\mathcal{G}'$ that belong to the same affine space-group type, but to different crystallographic space-group types, are said to form an *enantiomorphic pairs*, they just differ by their handedness.
- Example: $P4_1$ (right-handed 4-fold screw) and $P4_3$ (left-handed 4-fold screw)

Quick quiz

Changing the coordinate system by the orientation-reversing reflection m_{001} turns the space-group diagram on the left into that on the right (direction of 4-fold screw rotations reversed).





The space groups with these diagrams clearly belong to the same affine space-group type, but do they also belong to the same crystallographic space-group type?

Answer

Yes, a translation by $\frac{1}{2}\mathbf{a}$ or $\frac{1}{2}\mathbf{b}$ transforms the left diagram into the right and translations are orientation-preserving.

Merging space-group types to larger classes

Disregarding information leads to coarser classifications

- A space-group $\mathcal{G}$ is determined by three ingredients:
  (1) the translation lattice $\mathbf{L}$ giving rise to the translation subgroup $\mathcal{T}$;
  (2) the point group $\mathcal{P}$ acting on $\mathbf{L}$;
  (3) the translation parts $\mathbf{w}$ of coset representatives $(\mathbf{W}, \mathbf{w})$ of $\mathcal{G}$ relative to $\mathcal{T}$ determine how $\mathcal{T}$ and $\mathcal{P}$ are combined to form $\mathcal{G}$.
- dropping information about (3): arithmetic crystal classes
- dropping information about (1) and (3): geometric crystal classes
- dropping information about (2) and (3): Bravais classes

Arithmetic crystal classes

A space group $\mathcal{G}$ is assigned to a symmorphic space group in a canonical way by changing the translation parts $\mathbf{w}$ of coset representatives relative to $\mathcal{T}$ to $\mathbf{o}$.
Two space groups $\mathcal{G}$ and $\mathcal{G}'$ belong to the same arithmetic crystal class if they are assigned to symmorphic space groups of the same space-group type in this way.

Properties of this classification level

- There are 73 symmorphic space-group types in 3D, and thus also 73 arithmetic crystal classes.
- Transformation of the Hermann-Mauguin symbol of $\mathcal{G}$ to that of the corresponding symmorphic space-group type:
  - screw axis $N_m \to$ rotation axis N
  - glide plane a, b, c, d, e, $n \to$ mirror plane m
- Example: space-group types in the arithmetic crystal class containing the symmorphic space-group type $P4mm$:
  $P4mm$, $P4bm$, $P4_2cm$, $P4_2nm$, $P4cc$, $P4nc$, $P4_2mc$, $P4_2bc$

Geometric crystal classes

Two space groups $\mathcal{G}$ and $\mathcal{G}'$ with point groups $\mathcal{P}$ and $\mathcal{P}'$ belong to the same geometric crystal class if $\mathcal{P}'$ can be obtained from $\mathcal{P}$ by a basis transformation.

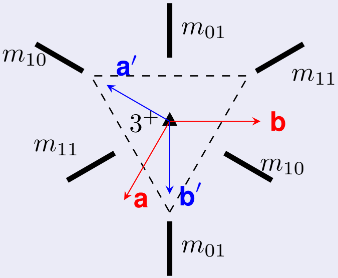
Properties of this classification level

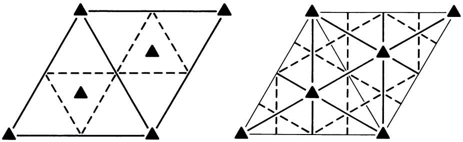
- There are 32 geometric crystal classes in 3D, corresponding to the 32 point-group types.
- Point groups of space groups in the same geometric crystal class are conjugate matrix groups: $\mathcal{P}' = \mathbf{P}^{-1}\mathcal{P}\mathbf{P} = \{\mathbf{P}^{-1}\mathbf{W}\mathbf{P} \mid \mathbf{W} \in \mathcal{P}\}$.
- Whereas basis changes between point groups in the same geometric crystal class are arbitrary, within arithmetic crystal classes they have to preserve the translation lattice.
- Arithmetic crystal classes within the same geometric crystal class represent the actions of the same point group on different types of lattices.

Example: point group mmm

The arithmetic crystal classes of $Pmmm$, $Cmmm$, $Fmmm$ and $Immm$ correspond to the action of a point group of type mmm on primitive, one-face-centred, all-face-centred and body-centred orthorhombic lattices and therefore belong to the same geometric crystal class.

Example: point group $3m$





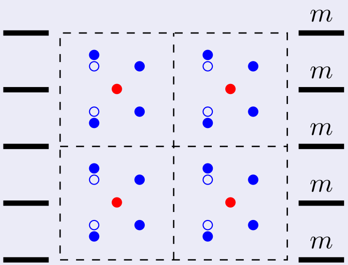
different arithmetic crystal classes depending on lattice basis

- blue: basis vectors in mirror planes → $P31m$
- red: basis vectors not in mirror planes → $P3m1$

Metric specialization

- The point group $\mathcal{P}$ gives a lower bound for the symmetry of the translation lattice $\mathbf{L}$.
- Example: if $\mathcal{P}$ contains a 4-fold rotation, the lattice must be tetragonal or cubic.
- $\mathbf{L}$ may have higher symmetry than is required by $\mathcal{P}$, since the contents of the unit cell may reduce the symmetry.

Example in 2D



- square lattice, would allow 4-fold rotation, but symmetry is broken by contents of the unit cell
- point group m only requires rectangular lattice, symmetry remains unchanged when lattice is rescaled in $\mathbf{a}$- or $\mathbf{b}$-direction
- often due to phase transitions, moving $\bullet$ to $\circ$ gives full tetragonal symmetry

Bravais arithmetic crystal classes

- Each lattice $\mathbf{L}$ has associated with it its full symmetry group (Bravais group) $\mathcal{B}$.
- Forming the symmorphic space group $\mathcal{G}$ with translation lattice $\mathbf{L}$ and point group $\mathcal{B}$ gives for each of the 14 types of Bravais lattices a corresponding symmorphic space group:
  - triclinic: $P\bar{1}$,
  - monoclinic: $P2/m$, $C2/m$,
  - orthorhombic: $Pmmm$, $Cmmm$, $Fmmm$, $Immm$,
  - tetragonal: $P4/mmm$, $I4/mmm$,
  - hexagonal: $P6/mmm$, $R\bar{3}m$,
  - cubic: $Pm\bar{3}m$, $Fm\bar{3}m$, $Im\bar{3}m$
- The arithmetic classes of these symmorphic space groups are called Bravais arithmetic crystal classes.
- A geometric crystal class containing a Bravais arithmetic crystal class is called a holohedry.

Assignment of an arbitrary space group to a lattice type

- A space group $\mathcal{G}$ with point group $\mathcal{P}$ is assigned to the Bravais arithmetic crystal class with point group of minimal order such that $\mathcal{P}$ is a subgroup of a point group in this class.
- In this way, $\mathcal{G}$ is associated with the lattice type of lowest symmetry (corresponding to this Bravais arithmetic crystal class) which is compatible with the point group $\mathcal{P}$ of $\mathcal{G}$.
- The lattice $\mathbf{L}$ of $\mathcal{G}$ may actually have higher symmetry, due to metric specialization.

Bravais classes

Two space groups $\mathcal{G}$ and $\mathcal{G}'$ belong to the same Bravais class if they are assigned to the same Bravais arithmetic crystal class.
There are 14 Bravais classes in 3D, corresponding to the 14 types of lattices.

Lattice systems

- Two lattices belong to the same lattice system if their Bravais groups are point groups belonging to the same geometric crystal class which necessarily is a holohedry.
- Two space groups $\mathcal{G}$ and $\mathcal{G}'$ belong to the same lattice system if the Bravais arithmetic crystal classes to which they are assigned lie in the same holohedry.

The hexagonal/rhombohedral exception

- In general, lattice systems join a primitive lattice with its centrings.
- The hexagonal lattice and its rhombohedral centring belong to different lattice systems, since their holohedries have point groups of type $6/mmm$ and $\bar{3}m$ (subgroup of index 2 in $6/mmm$), respectively.

Crystal systems

Two space groups $\mathcal{G}$ and $\mathcal{G}'$ belong to the same crystal system if the point groups in their geometric crystal classes act on the same types of lattices.

The hexagonal/trigonal exception

- In general, crystal systems join a holohedry with its subgroups not having lattices of lower symmetry (i.e. with more free parameters).
- A point group containing a 3-fold rotation but no 6-fold rotation or rotoinversion acts both on a hexagonal lattice and on a rhombohedral lattice. The geometric crystal classes with point groups of this kind form the trigonal crystal system.
- A point group containing a 6-fold rotation or rotoinversion only acts on a hexagonal but not on a rhombohedral lattice. The geometric crystal classes with point groups of this kind form the hexagonal crystal system.

Overview of the hexagonal case

Crystal system	Geometric class	Lattice system: Hexagonal	Lattice system: Rhombohedral
Hexagonal	$6/mmm$	$P6/mmm$, $P6/mcc$, $P6_3/mcm$, $P6_3/mmc$	
	$\bar{6}2m$	$P\bar{6}m2$, $P\bar{6}c2$, $P\bar{6}2m$, $P\bar{6}2c$	
	$6mm$	$P6mm$, $P6cc$, $P6_3cm$, $P6_3mc$	
	622	$P622$, $P6_122$, $P6_522$, $P6_222$, $P6_422$, $P6_322$	
	$6/m$	$P6/m$, $P6_3/m$	
	$\bar{6}$	$P\bar{6}$	
	6	$P6$, $P6_1$, $P6_5$, $P6_2$, $P6_4$, $P6_3$	
Trigonal	$\bar{3}m$	$P\bar{3}1m$, $P\bar{3}1c$, $P\bar{3}m1$, $P\bar{3}c1$	$R\bar{3}m$, $R\bar{3}c$
	$3m$	$P3m1$, $P31m$, $P3c1$, $P31c$	$R3m$, $R3c$
	32	$P312$, $P321$, $P3_112$, $P3_121$, $P3_212$, $P3_221$	$R32$
	$\bar{3}$	$P\bar{3}$	$R\bar{3}$
	3	$P3$, $P3_1$, $P3_2$	$R3$

The final step

- Lattice systems contain full Bravais classes, but the geometric crystal classes in the trigonal crystal system are distributed over the hexagonal and the rhombohedral lattice systems.
- Crystal systems contain full geometric crystal classes, but the Bravais classes in the hexagonal lattice system are distributed over the hexagonal and trigonal crystal system.
- It is desirable to have a further classification level consisting of full Bravais classes and full geometric crystal classes.

Crystal families

- The crystal family of a space group $\mathcal{G}$ is the union of all geometric crystal classes containing a space group $\mathcal{G}'$ in the same Bravais class as $\mathcal{G}$.
- The hexagonal crystal family joins the hexagonal and trigonal crystal systems,
  all other crystal families coincide with single crystal systems.

Crystallographic space groups.

Classification of space groups