Classification of Bravais lattices and crystal structures

Outline

Symmetry group of the Bravais lattice

The classification of Bravais lattices

Symmetry group or space group of a Bravais lattice

- Bravais lattice:
  - Crystal structure obtained by placing a basis of maximum possible symmetry at each lattice point
  - e.g. a rigid sphere
- Symmetry group: set of all rigid operations that transform the lattice into itself
  - a translation by any lattice vector $\boldsymbol{R}$
  - rigid operations that leave a lattice point fixed
  - a combination of both

Symmetry group of the Bravais lattice

Space group

- Any symmetry operation can be obtained as a composition of
  - a translation through a lattice vector $\boldsymbol{R}$, $T_{\boldsymbol{R}}$
  - a rigid operation that leaves a lattice point fixed

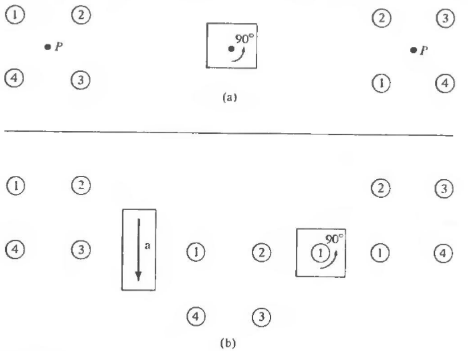
Justification

- Given an operation $\boldsymbol{S}$ that leaves no lattice point fixed
  - $\boldsymbol{O}$ is taken to $\boldsymbol{R}$
- $\boldsymbol{T}_{-\boldsymbol{R}}$ takes $\boldsymbol{R}$ into $\boldsymbol{O}$
- $\boldsymbol{T}_{-\boldsymbol{R}}\boldsymbol{S}$ is also a symmetry operation (group property)
  - leaves the origin fixed
- Therefore
  - $\boldsymbol{S} = \boldsymbol{T}_{\boldsymbol{R}}\boldsymbol{T}_{-\boldsymbol{R}}\boldsymbol{S}$

Symmetry group of the Bravais lattice

Space group

Example



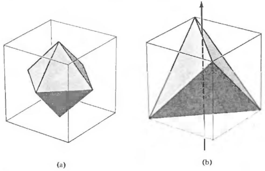
simple cubic lattice

The seven crystal systems

Groups of non-translational symmetry operations

Subgroups of the full symmetry groups

- Any crystal structure belongs to one of seven crystal systems
  - the point group of the underlying Bravais lattice
- Identical point groups:
  - Groups containing the same set of operations
  - e.g. symmetry group of cube and regular octahedron are equivalent
  - e.g. symmetry groups of cube and tetrahedron are different

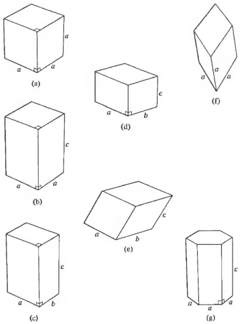


octahedron and tetrahedron inscribed in a cube

The seven crystal systems

Groups of non-translational symmetry operations

Objects with point group symmetries of the seven crystal systems



(a) cube; (b) tetragonal; (c) orthorhombic

(d) monoclinic; (e) triclinic; (f) trigonal; (g) hexagonal

The fourteen Bravais lattices

Space groups of a Bravais lattice

Equivalent space groups

- Symmetry operations of two identical space groups can differ unconsequentially
  - e.g. sc lattices with different lattice constants ($a \neq a'$)
  - e.g. two simple hexagonal lattices with different $\frac{c}{a}$ ratio
- A continuous transformation can be carried out between lattices **1** and **2** that:
  - transform every symmetry operation of **1** to a corresponding of **2**
  - the correspondence is an isomorphism

The seven crystal systems and the fourteen Bravais lattices

Enumeration

Bravais lattices of the cubic crystal system

- Point group: symmetry of the cube (O_h)
  - one lattice constant: a
  - angles of 90°
- Three Bravais lattices with non-equivalent space groups
  - simple cubic (sc)
  - body-centered cubic (bcc)
  - face-centered cubic (fcc)

The seven crystal systems and the fourteen Bravais lattices

Enumeration

Bravais lattices of the tetragonal crystal system

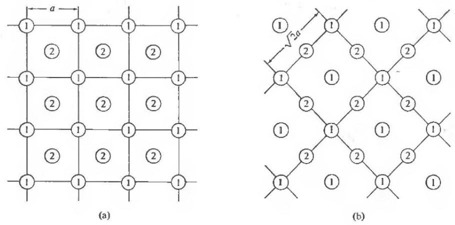
- We look at ways of reducing the symmetry of the cube
  - with a continuous transformation
- Stretch (or shrink) the cube
  - pulling from two opposite faces
- Rectangular prism with a square base
  - two lattice constants: a and $c \neq a$
  - angles of 90°
- Two Bravais lattices with non-equivalent space groups
  - sc → simple tetragonal
  - bcc and fcc → centered tetragonal

The seven crystal systems and the fourteen Bravais lattices

Enumeration

Bravais lattices of the tetragonal crystal system

- Both bcc and fcc are special cases of centered tetragonal
- View (a)
  - points **1**: simple square array
  - bcc when $c = a$



Centered tetragonal lattice viewed along c. **1** lie in a lattice plane $\perp$ c.

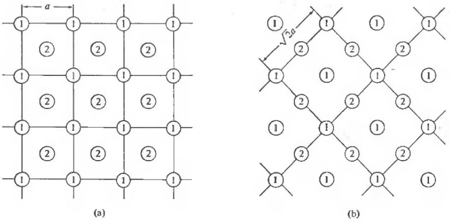
2 lie in a parallel lattice plane at distance $\frac{c}{2}$ away

The seven crystal systems and the fourteen Bravais lattices

Enumeration

Bravais lattices of the tetragonal crystal system

- Both bcc and fcc are special cases of centered tetragonal
- View (b)
  - points **1**: centered square array of side $\sqrt{2}a$
  - fcc when $c = \frac{a}{\sqrt{2}}$



Centered tetragonal lattice viewed along c. **1** lie in a lattice plane $\perp$ c.

2 lie in a parallel lattice plane at distance $\frac{c}{2}$ away

The seven crystal systems and the fourteen Bravais lattices

Enumeration

Bravais lattices of the orthorhombic crystal system

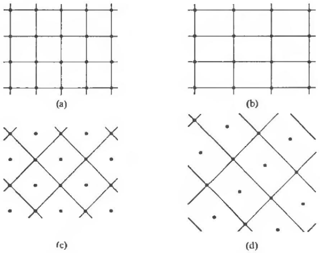
- Tetragonal symmetry is reduced by deformation of the square faces
  - into rectangles
- Object with mutually $\perp$ sides
  - three lattice constants: $a \neq b \neq c$
  - angles of 90°
- Four Bravais lattices with non-equivalent space groups
  - simple tetragonal $\rightarrow$ simple and base-centered orthorhombic
  - centered tetragonal $\rightarrow$ body- and face-centered orthorhombic

The seven crystal systems and the fourteen Bravais lattices

Enumeration

Bravais lattices of the orthorhombic crystal system

- Simple orthorhombic from simple tetragonal: (a)$\rightarrow$ (b)
  - stretching along a side
- Base-centered orthorhombic from simple tetragonal: (c)$\rightarrow$ (d)
  - stretching along a square diagonal



(a) and (c): two ways of viewing a simple tetragonal lattice along c.

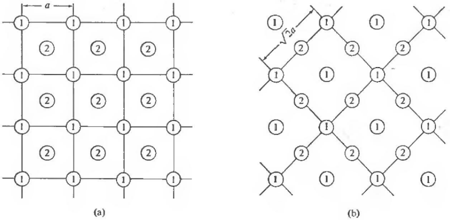
(b) and (d): simple and base-centered orthorhombic lattices obtained from (a) and (c) respectively

The seven crystal systems and the fourteen Bravais lattices

Enumeration

Bravais lattices of the orthorhombic crystal system

- Body-centered orthorhombic from body-centered tetragonal lattice
  - stretching along one set of parallel lines in (***a***)
- face-centered orthorhombic from body-centered tetragonal lattice
  - stretching along one set of parallel lines in (***b***)



Centered tetragonal lattice viewed along c. **1** lie in a lattice plane $\perp$ c.

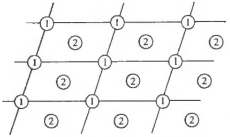
2 lie in a parallel lattice plane at distance $\frac{c}{2}$ away

The seven crystal systems and the fourteen Bravais lattices

Enumeration

Bravais lattices of the monoclinic crystal system

- Orthorhombic symmetry is reduced by deformation of the rectangular faces into parallelograms
  - three lattice constants: $a \neq b \neq c$
  - c is $\perp$ to the plane of a and b
- Two Bravais lattices with non-equivalent space groups
  - simple and base-centered orthorhombic $\rightarrow$ simple monoclinic
  - body- and face-centered orthorhombic $\rightarrow$ centered monoclinic
  - corresponding to the tetragonal ones



Centered monoclinic Bravais lattice viewed along c. **1** lie in a lattice plane $\perp$ c.

2 lie in a parallel lattice plane at distance $\frac{c}{2}$ away

The seven crystal systems and the fourteen Bravais lattices

Enumeration

Bravais lattices of the triclinic crystal system

- Monoclinic symmetry is reduced by tilting the c axis
  - c is no longer $\perp$ to the plane of a and b
  - three lattice constants: $a \neq b \neq c$
  - no special relationships between $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$
- Only one Bravais lattice
  - simple and centered orthorhombic $\rightarrow$ triclinic
  - minimum symmetry ($\boldsymbol{i}$ and $\boldsymbol{E}$)

The seven crystal systems and the fourteen Bravais lattices

Enumeration

Bravais lattices of the trigonal crystal system

- Cubic symmetry is reduced by stretching along the body diagonal
  - one lattice constants: a
  - one angle between either pair of lattice vectors
  - special values of the angle introduces extra symmetry
- Only one Bravais lattice
  - sc, bcc, and fcc $\rightarrow$ trigonal

The seven crystal systems and the fourteen Bravais lattices

Enumeration

Bravais lattices of the hexagonal crystal system

- Right prism with a regular hexagon as base
- Only one Bravais lattice (simple hexagonal)
  - two lattice constants: a, and c
  - one angle (120°) between the primitive vectors of the hexagonal face
- No other Bravais lattice are obtained by distortion of the simple hexagonal:
  - change of angle: $\rightarrow$ base-centered orthorhombic
  - change of angle and $a \neq b$: monoclinic
  - further tilting c axis: triclinic

The crystallographic point groups and space groups

Classification

Symmetry group of a Bravais lattice with a basis of general symmetry

- Consider now a general crystal structure
  - placing an object of arbitrary symmetry at each lattice point
- The symmetry group obtained depends on:
  - the symmetry of the Bravais lattice
  - the symmetry of the object
- A large number of point- and space-groups are obtained:
  - 32 cristallographic point-groups (vs 7 for spherical objects)
  - 230 space groups (vs 14 for spherical objects)

The crystallographic point groups

Classification

Symmetry group of a Bravais lattice with a basis of general symmetry

POINT AND SPACE GROUPS OF BRAVAIS LATTICES AND CRYSTAL STRUCTURES

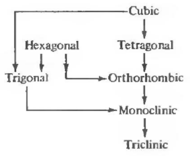
	BRAVAIS LATTICE (BASIS OF SPHERICAL SYMMETRY)	CRYSTAL STRUCTURE (BASIS OF ARBITRARY SYMMETRY)
Number of point groups:	7 ("the 7 crystal systems")	32 ("the 32 crystallographic point groups")
Number of space groups:	14 ("the 14 Bravais lattices")	230 ("the 230 space groups")

The crystallographic point groups and space groups

The 32 crystallographic point groups

Relation to the seven crystal systems

- Obtained by reducing the symmetry of the objects characterized by the seven crystal systems
  - other 25 new groups are obtained
- Each crystallographic point group can be associated to a crystal system
  - unambiguosly
- least symmetric of the crystal systems
  - containing all the symmetry operations of the object



hierarchy of symmetries among the seven crystal systems

The crystallographic point groups and space groups

The 32 crystallographic point groups

Symmetry operations of the crystallographic point groups

- Rotations about some axis of integral multiples of $\frac{2\pi}{n}$
  - n-fold rotation axis
  - n: order
  - only $n = 2, 3, 4, 6$ are allowed by the translational symmetry
- Rotation-reflections.
  - rotation about some axis of integral multiples of $\frac{2\pi}{n}$
  - reflection about a plane $\perp$ to the axis
  - n-fold rotation-reflection axis (e.g. groups S_6 and S_4)
- Rotation-inversions.
  - rotation about some axis of integral multiples of $\frac{2\pi}{n}$
  - inversion in a point belonging to the axis
  - n-fold rotation-inversion axis

The crystallographic point groups and space groups

The 32 crystallographic point groups

Symmetry operations of the crystallographic point groups

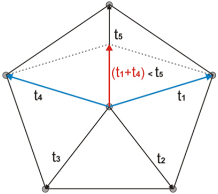
- Reflections about some plane
  - mirror plane
- Inversions
  - has a single fixed point (origin)
  - $\boldsymbol{r} \rightarrow -\boldsymbol{r}$

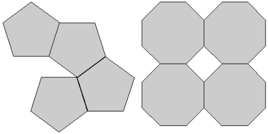
The crystallographic point groups and space groups

The 32 crystallographic point groups

The restriction theorem

- Only rotation axes with order $n = 2, 3, 4, 6$ are allowed by the translational symmetry



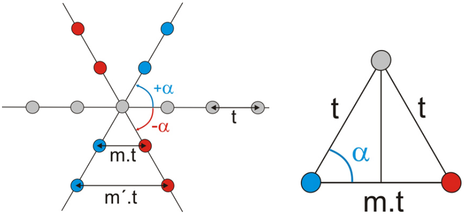


left: $\boldsymbol{t}_1 + \boldsymbol{t}_2$ is not a lattice vector; right: pentagonal and octagonal tiles cannot fill completely the space

The crystallographic point groups and space groups

The 32 crystallographic point groups

The restriction theorem



proof of the relation $\cos\alpha = \frac{m}{2}$

The crystallographic point groups and space groups

The 32 crystallographic point groups

The restriction theorem

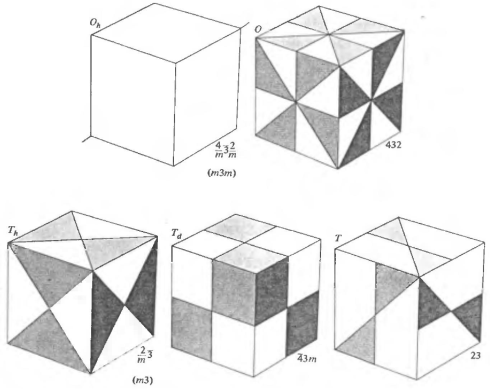
m	-2	-1	0	1	2
$\cos\alpha$	-1	$-\frac{1}{2}$	0	$\frac{1}{2}$	1
α	π	$\frac{2\pi}{3}$	$\frac{\pi}{4}$	$\frac{\pi}{3}$	0
n	2	3	4	6	1

The crystallographic point groups and space groups

The 32 crystallographic point groups

The five cubic crystallographic point groups

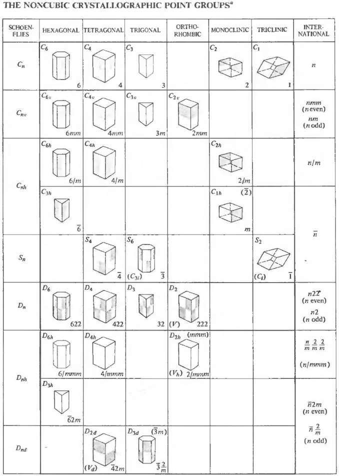
OBJECTS WITH THE SYMMETRY OF THE FIVE CUBIC CRYSTALLOGRAPHIC POINT GROUPS[a]



left: Schoenflies name; right: international name

The crystallographic point groups and space groups

The noncubic crystallographic point groups



THE NONCUBIC CRYSTALLOGRAPHIC POINT GROUPS[a]

SCHOENFLIES	HEXAGONAL	TETRAGONAL	TRIGONAL	ORTHORHOMBIC	MONOCLINIC	TRICLINIC	INTERNATIONAL
C_n	C_6 6	C_4 4	C_3 3		C_2 2	C_1 1	n
C_{nv}	C_{6v} $6mm$	C_{4v} $4mm$	C_{3v} $3m$	C_{2v} $2mm$			nmm (n even) nm (n odd)
C_{nh}	C_{6h} $6/m$	C_{4h} $4/m$			C_{2h} $2/m$		n/m
	C_{3h} $\bar{6}$				C_{1h} $(\bar{2})$ m		$\bar{n}$
S_n		S_4 $\bar{4}$	S_6 (C_{3i}) $\bar{3}$			S_2 (C_i) $\bar{1}$	
D_n	D_6 622	D_4 422	D_3 32	D_2 (V) 222			$n22$ (n even) $n2$ (n odd)
D_{nh}	D_{6h} $6/mmm$	D_{4h} $4/mmm$		D_{2h} (mmm) (V_h) $2/mmm$			$\frac{n}{m}\frac{2}{m}\frac{2}{m}$ (n/mmm)
	D_{3h} $\bar{6}2m$						$\bar{n}2m$ (n even)
D_{nd}		D_{2d} (V_d) $\bar{4}2m$	D_{3d} $(\bar{3}m)$ $\bar{3}\frac{2}{m}$				$\bar{n}\frac{2}{m}$ (n odd)

left: Schoenflies name; right: international name

The crystallographic point groups and space groups

The 32 crystallographic point groups: nomenclature

Schoenflies notation for noncubic point groups

- C_n: cyclic groups of order n
  - only n-fold rotation axis (principal or vertical)
- C_{nv}
  - an additional mirror plane containing the axis (vertical)
  - plus additional vertical planes due to C_n
- C_{nh}
  - n-fold rotation axis
  - mirror plane $\perp$ to the axis (horizontal)
- S_n
  - only n-fold rotation-reflection axis

The crystallographic point groups and space groups

The 32 crystallographic point groups: nomenclature

Schoenflies notation for noncubic point groups

- D_n: dihedral groups of order n
  - n-fold rotation axis
  - 2-fold axis $\perp$ to the C_n axis
  - plus additional C_2s due to C_n
- D_{nh}
  - an additional mirror plane $\perp$ to the C_n axis
- D_{nd}
  - elements of D_n
  - plus mirror planes bisecting the angles between the C_2 axes (diagonal)

The crystallographic point groups and space groups

The 32 crystallographic point groups: nomenclature

Schoenflies notation for the cubic point groups

- O_h
  - full symmetry group of the cube (or regular octahedron)
  - includes improper operations admitted by the *h* plane
  - improper:odd number of inversions or mirroring
- O
  - cubic without improper operations
- T_d
  - full symmetry group of the regular tetrahedron
  - includes all improper operations
- T
  - symmetry group of the regular tetrahedron
  - excluding all improper operations
- T_h
  - inversion is added to T

The crystallographic point groups and space groups

The 32 crystallographic point groups: nomenclature

International notation for noncubic point groups

- Treats the 3-fold axis as a special case
- $\mathrm{C}_n \rightarrow n$
- $\mathrm{C}_{nv} \rightarrow nmm$
  - mm denotes two different types of vertical mirror planes
  - $(2j+1)$-fold axis takes v into $2j+1$ others
  - $(2j)$-fold axis takes v into j others plus j bisecting adjacent angles in the first set
  - objects 2mm, 4mm and 6mm vs 3m
  - $\mathrm{C}_{3v} \rightarrow 3m$
- $\mathrm{D}_n \rightarrow n22$
  - 22 denotes two different types of two-fold axes
  - see discussion above

The crystallographic point groups and space groups

The 32 crystallographic point groups: nomenclature

International notation for noncubic point groups

- $C_{nh} \to n/m$ except
  - $C_{3h} \to \bar{6}$ (rotation-inversion axis)
  - note that $\sigma \to \bar{2}$
  - $C_{1h} \to 1/m \to m$
- $\bar{n}$
  - contains a n-fold rotation-inversion axis
  - $S_4 \to \bar{4}$
  - $S_6 \to \bar{3}$
  - $S_2 \to \bar{1}$

The crystallographic point groups and space groups

The 32 crystallographic point groups: nomenclature

International notation for noncubic point groups

- $\mathrm{D}_{nh} = D_n \times C_{1h}$
- $\mathrm{D}_{nh} \rightarrow \frac{n}{m}\frac{2}{m}\frac{2}{m}$
  - abbreviated as n/mmm
  - $2/mmm \rightarrow 2mmm$
  - exception: $\mathrm{D}_{3h} \rightarrow \bar{6}2m$
- $\mathrm{D}_{nd} \rightarrow \bar{n}2m$
  - $\bar{n}$ with $\perp$ C_2 and vertical m
  - $\mathrm{D}_{3h} \rightarrow \bar{6}2m$
  - $n = 3 \rightarrow \bar{3}m$
- cubic groups: contain 3 as a second number
  - C_3 is contained in all cubic point groups

The crystallographic point groups and space groups

The 230 space groups

Symmorphic space groups

- Some 61 space groups are easily constructed:
  - Nr. of crystallographic point groups × nr. of Bravais lattices
- other 5 obtained by placing a trigonal object in a simple hexagonal lattice
- other 7 from cases of different orientations within the same Bravais lattice

ENUMERATION OF SOME SIMPLE SPACE GROUPS

SYSTEM	NUMBER OF POINT GROUPS	NUMBER OF BRAVAIS LATTICES	PRODUCT
Cubic	5	3	15
Tetragonal	7	2	14
Orthorhombic	3	4	12
Monoclinic	3	2	6
Triclinic	2	1	2
Hexagonal	7	1	7
Trigonal	5	1	5
Totals	32	14	61

The crystallographic point groups and space groups

The 230 space groups

Non symmorphic space groups

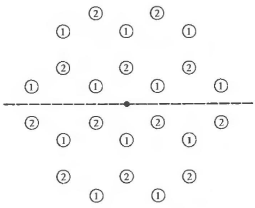
- Contain two new types of operations that bring into coincidence a crystal structure
- Screw axes
  - translation through a vector not in the Bravais lattice followed by
  - rotation about the axis defined by the vector
- Glide planes
  - translation through a vector not in the Bravais lattice followed by
  - reflection in a plane containing the vector
- Requires special relations btw the dimensions of the basis and Bravais lattice
- Most space-groups are nonsymmorphic

The crystallographic point groups and space groups

Nonsymmorphic space groups

Hexagonal close-packed structure

- two basis (**1** and **2**) separated by $\frac{c}{2}$
- contains glide planes and screw axes



hcp structure viewed along c. $\perp$ lattice planes are separated by $\frac{c}{2}$

dashed line: glide plane; axis through the central dot: screw axis

Examples among the elements

Elements with trigonal Bravais lattices

ELEMENTS WITH RHOMBOHEDRAL (TRIGONAL) BRAVAIS LATTICES[a]

ELEMENT	a (Å)	θ	ATOMS IN PRIMITIVE CELL	BASIS
Hg (5 K)	2.99	70°45′	1	$x = 0$
As	4.13	54°10′	2	$x = \pm 0.226$
Sb	4.51	57°6′	2	$x = \pm 0.233$
Bi	4.75	57°14′	2	$x = \pm 0.237$
Sm	9.00	23°13′	3	$x = 0, \pm 0.222$

Examples among the elements

Elements with centered tetragonal Bravais lattices

ELEMENTS WITH TETRAGONAL BRAVAIS LATTICES[a]

ELEMENT	a (Å)	c (Å)	BASIS
In	4.59	4.94	At face-centered positions of the conventional cell
Sn (white)	5.82	3.17	At 000, $0\frac{1}{2}\frac{1}{4}$, $\frac{1}{2}0\frac{3}{4}$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, with respect to the axes of the conventional cell

described as simple tetragonal with a basis

Examples among the elements

Elements with orthorhombic Bravais lattices

ELEMENTS WITH ORTHORHOMBIC BRAVAIS LATTICES[a]

ELEMENT	a (Å)	b (Å)	c (Å)
Ga	4.511	4.517	7.645
P (black)	3.31	4.38	10.50
Cl (113 K)	6.24	8.26	4.48
Br (123 K)	6.67	8.72	4.48
I	7.27	9.79	4.79
S (rhombic)	10.47	12.87	24.49