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

- Translational symmetry is by far the most important for general theory of solids
- However Bravais lattices do fall into categories on the basis of symmetries other than translational
  - crystallography makes such distinctions systematic
- Bravais lattice: viewed as a 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 (preserve distances) operations that transform the lattice into itself
  1. translations by any lattice vector $\boldsymbol{R}$
  2. rigid operations that leave a lattice point fixed
  3. operations obtained by successive applications of the above

Symmetry group of the Bravais lattice

The classification of Bravais lattices

Examples of symmetry operations (other than translations)

- For a cubic Bravais lattice, the following are symmetry operations:
  - rotation through 90° around the $< 100 >$ direction of lattice points
  - rotation through 120° around the $< 111 >$ direction of lattice points
  - reflection of all points in a 100 lattice plane
- For a simple hexagonal Bravais lattice, the following are symmetry operations:
  - rotation through 60° around a direction $\parallel$ to the $\boldsymbol{c}$ axis
  - reflection in a lattice plane $\perp$ to the $\boldsymbol{c}$ axis

Symmetry group of the Bravais lattice

The classification of Bravais lattices

- 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

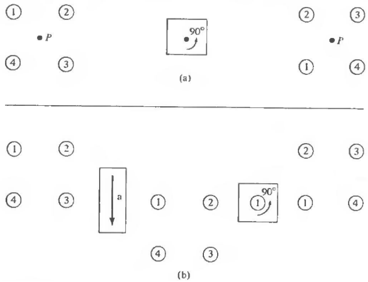
- Given an operation $\boldsymbol{S}$ that leaves no lattice points fixed
  - suppose the origin $\boldsymbol{O}$ is taken to $\boldsymbol{R}$
- $\boldsymbol{T}_{-\boldsymbol{R}}$ takes $\boldsymbol{R}$ into $\boldsymbol{O}$
- $\boldsymbol{T}_{-\boldsymbol{R}}\boldsymbol{S}$ is also a symmetry operation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

Symmetry group of the Bravais lattice

The classification of Bravais lattices

Example

- A sc lattice is carried into itself by a rotation of 90° about an axis passing through P and $\perp$ to the page
- The same result is obtained through:
  - translation by the lattice vector $\boldsymbol{a}$
  - rotation of 90° about an axis passing through 1 and $\perp$ to the page

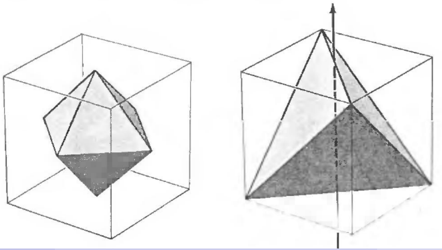


The seven crystal systems

Groups of non-translational symmetry operations

The point group of the Bravais lattice

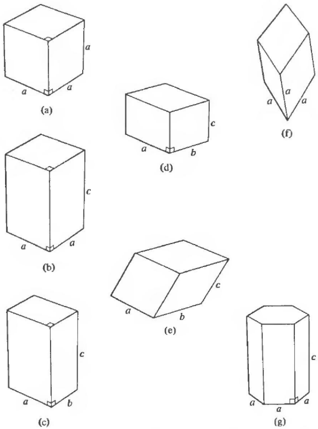
- Any Bravais lattice belongs to one of seven crystal systems
  - point group of the underlying Bravais lattice: group of all symmetry operations that leave one lattice point fixed
- Point group of cube and regular octahedron are equivalent (contain the same set of operations)
  - however symmetry groups of cube and tetrahedron are different (cube has more symmetry ops)



The seven crystal systems

Groups of non-translational symmetry operations

Objects with point group symmetries of the seven crystal systems



(a) cubic; (b) tetragonal; (c) orthorhombic (d) monoclinic; (e) triclinic; (f) trigonal; (g) hexagonal

The fourteen Bravais lattices

Space group (full symmetry group) of a Bravais lattice

There are only fourteen distinct space groups that a Bravais lattice can have.

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 in the language of group theory

The seven crystal systems and the fourteen Bravais lattices

Enumeration: A. Bravais (1845)

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: A. Bravais (1845)

Bravais lattices of the tetragonal crystal system

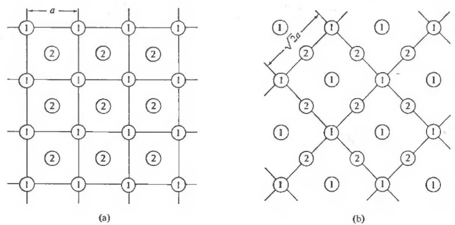
- We look at ways of reducing the symmetry of the cube with a continuous transformation:
    - stretch (or shrink) the cube pulling from two opposite faces
- We obtain a rectangular prism with a square base
    - two lattice constants: a and $c \neq a$
    - angles of 90°
- Two Bravais lattices with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

The seven crystal systems and the fourteen Bravais lattices

Enumeration: A. Bravais (1845)

Bravais lattices of the tetragonal crystal system

- Both bcc and fcc are special cases of centered tetragonal
- View (a), along the c-axis:
  - points **1**: simple square array
  - we obtain bcc when $c = a$
  - viewed as a result of stretching the bcc lattice along the c-axis



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

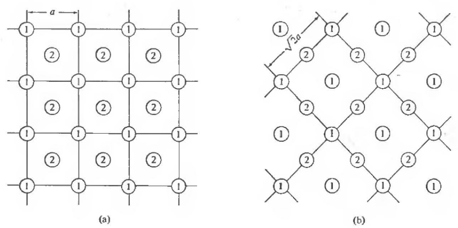
2 lie in a parallel lattice plane at distance $\frac{c}{2}$ away

The seven crystal systems and the fourteen Bravais lattices

Enumeration: A. Bravais (1845)

Bravais lattices of the tetragonal crystal system

- Both bcc and fcc are special cases of centered tetragonal
- View (b), along the c-axis:
  - points $\mathbf{1}$: centered square array of side $\sqrt{2}a$
  - fcc when $c = \frac{a}{\sqrt{2}}$
  - viewed as a result of stretching the fcc lattice along the c-axis



Centered tetragonal lattice viewed along the c-axis. $\mathbf{1}$ lie in a lattice plane $\perp$ c.

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

The seven crystal systems and the fourteen Bravais lattices

Enumeration: A. Bravais (1845)

Bravais lattices of the orthorhombic crystal system

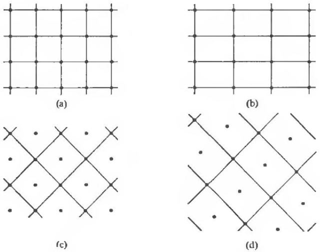
- Tetragonal symmetry is reduced by deformation of the square faces into rectangles
- We obtain an object with mutually $\perp$ sides
  - three lattice constants: $a \neq b \neq c$
  - angles of 90°
- Four Bravais lattices with non-equivalent space groups
  - simple tetragonal $\rightarrow$ simple and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

The seven crystal systems and the fourteen Bravais lattices

Enumeration: A. Bravais (1845)

Bravais lattices of the orthorhombic crystal system

- Simple orthorhombic from simple tetragonal: (a)$\rightarrow$ (b)
  - stretching along one of the *a* axis
- Base-centered orthorhombic from simple tetragonal: (c)$\rightarrow$ (d)
  - stretching along a square diagonal in (a) or a side in (c)



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

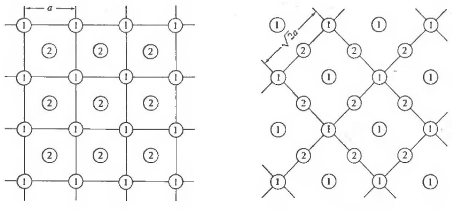
(b) and (d): simple and base-centered orthorhombic lattices obtained from (a) and (c) respectively

The seven crystal systems and the fourteen Bravais lattices

Enumeration: A. Bravais (1845)

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: A. Bravais (1845)

Bravais lattices of the monoclinic crystal system

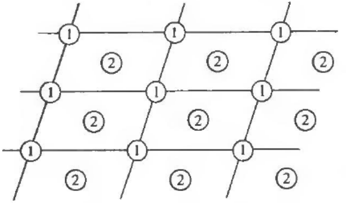
- Orthorhombic symmetry is reduced by deformation of the rectangular faces into parallelograms
  - three lattice constants: $a \neq b \neq c$
  - c is $\perp$ to the plane of a and b
- Two Bravais lattices with non-equivalent space groups
  - simple and base-centered orthorhombic $\rightarrow$ simple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

The seven crystal systems and the fourteen Bravais lattices

Enumeration: A. Bravais (1845)

Bravais lattices of the monoclinic crystal system

- The two Bravais lattices correspond to the two tetragonal ones:
  - rectangular and centered rectangular nets have distinct 2D symmetry groups
  - square and centered square nets belong to the same 2D symmetry group (as for parallelogram and centered parallelogram net)



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 and directly above the centers of the parallelograms formed by **1**

The seven crystal systems and the fourteen Bravais lattices

Enumeration: A. Bravais (1845)

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 the three primitive vectors
- Only one Bravais lattice is obtained:
  - simple and centered monoclinic $\rightarrow$ triclinic
  - minimum point-group symmetry of the Bravais lattice (operations $\boldsymbol{i}$ and $\boldsymbol{E}$)

The seven crystal systems and the fourteen Bravais lattices

Enumeration: A. Bravais (1845)

Bravais lattices of the trigonal crystal system

- Cubic symmetry is reduced by stretching the cube along a body diagonal
  - one lattice constants: a
  - equal angle between each pair of lattice vectors
  - special values of the angle introduce extra symmetry (giving some of the cubic system)
- Only one Bravais lattice
  - sc, bcc, and fcc $\rightarrow$ trigonal

The seven crystal systems and the fourteen Bravais lattices

Enumeration: A. Bravais (1845)

Bravais lattices of the hexagonal crystal system

- Right prism with a regular hexagon as the 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 btw the primitive vectors $\perp$ to the c-axis: $\rightarrow$ base-centered orthorhombic lattice
  - change of angle btw the primitive vectors $\perp$ to the c-axis and their magnitude: monoclinic
  - tilting of the 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 (lattice with a basis)
  - obtained by translating an object of arbitrary symmetry through all $\boldsymbol{R} \in \mathcal{R}$
- The possible symmetry groups so obtained depend on:
  - the symmetry of the Bravais lattice
  - the symmetry (if any) of the object
- A large number of point- and space-groups are obtained
- 32 cristallographic point-groups (vs 7 for spherical objects)
  - point groups: set of symmetry operations (satisfying the properties of the algebraic structure of group) that take the crystal structure into itself while leaving one point fixed
- 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

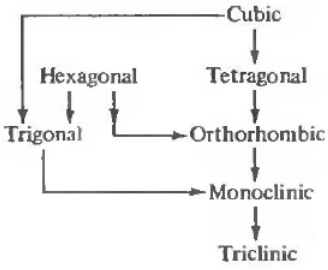
Relation to the seven crystal systems

- Obtained by reducing the symmetry of the objects characterized by the seven crystal systems
- Other 25 new groups are obtained
- Each new crystallographic point group can be associated to one of the seven crystal systems, unambiguously, according to the rule:
  - groups constructed by reducing the symmetry of an object characterized by a particular crystal system still belongs to it until the symmetry has been reduced so far that the remaining symmetry operations of the resulting object are found in a less symmetrical crystal system.
  - then it is assigned to the less symmetric crystal system
- The crystal system of a crystallographic point group is that of the least symmetric of the 7 Bravais lattice point groups still containing every symmetry operation of the crystallographic point group

The crystallographic point groups and space groups

The 32 crystallographic point groups

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

The crystallographic point groups and space groups

The 32 crystallographic point groups

Symmetry operations of the crystallographic point groups

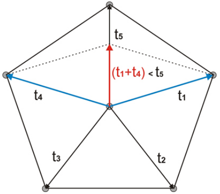
- Reflections about some plane
  - symmetry element: mirror plane
- Inversions
  - has a single fixed point (inversion center)
  - if taken as the origin, $\boldsymbol{r} \rightarrow -\boldsymbol{r}$

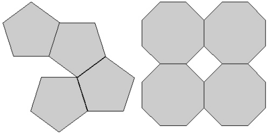
The crystallographic point groups and space groups

The 32 crystallographic point groups

The restriction theorem

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



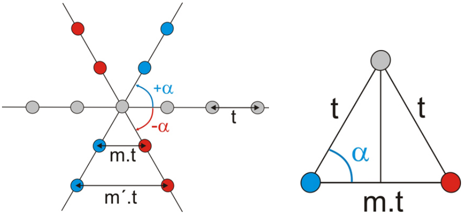


left: $\boldsymbol{t}_1 + \boldsymbol{t}_2$ is not a lattice vector; right: pentagonal and octagonal tiles cannot fill completely the space

The crystallographic point groups and space groups

The 32 crystallographic point groups

The restriction theorem



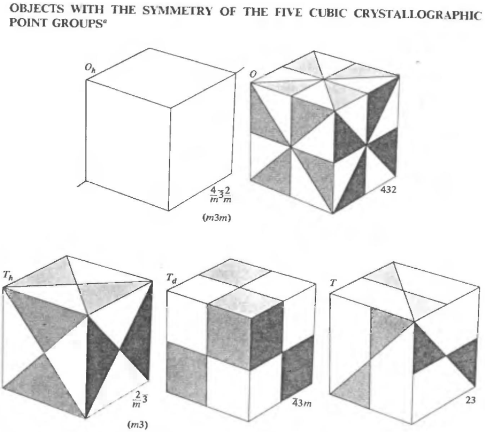
proof of the relation $\cos\alpha = \frac{m}{2}$

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

The crystallographic point groups and space groups

The 32 crystallographic point groups

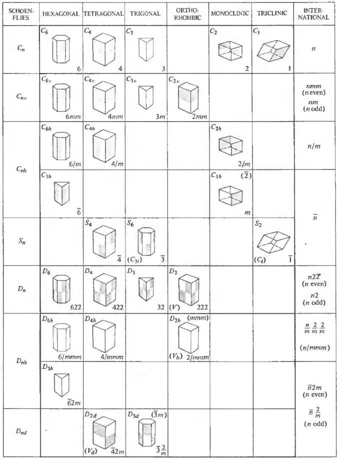
The five cubic crystallographic point groups



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) $\bar{n}\frac{2}{m}$ (n odd)
D_{nd}		D_{2d} (V_d) $\bar{4}2m$	D_{3d} ($\bar{3}m$) $\bar{3}\frac{2}{m}$				

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 group 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
- $C_n \rightarrow n$
- $C_{nv} \rightarrow nmm$
  - *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
  - $C_{3v} \rightarrow 3m$
- $D_n \rightarrow n22$
  - 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

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

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
  - $2/mmm \rightarrow mmm$
  - 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 of the systems
- 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

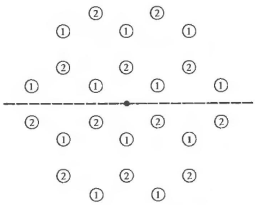
- Contain two new types of operations that bring a crystal structure into coincidence with itself
- Screw axes
  - translation through a vector not in the Bravais lattice followed by
  - rotation about the axis defined by the translation
- Glide planes
  - translation through a vector not in the Bravais 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

hcp structure: two-point basis (**1** and **2**) separated by $\frac{c}{2}$

- contains glide planes and screw axes
  - invariant under a translation of $\frac{c}{2}$ followed by rotation of 60° around the screw axis
  - invariant under a translation of $\frac{c}{2}$ followed by reflection in the glide plane of 60°



hcp structure viewed along the c axis. lattice planes ⊥ to c are separated by $\frac{c}{2}$ and contain alternatively **1** and **2**

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

Examples among the elements

Elements with trigonal Bravais lattices

- a is the common length of the primitive vectors, θ is the angle btw them
- basis points at coordinates $x(\boldsymbol{a}_1 + \boldsymbol{a}_2 + \boldsymbol{a}_3)$

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

- Most commonly described as simple tetragonal with a basis

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

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