Outline

1. Classification of Bravais lattices
2. The crystallographic point groups and space groups
3. Examples
1 Classification of Bravais lattices

2 The crystallographic point groups and space groups

3 Examples
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 $R$
  - 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 \( R, T_R \)
  - a rigid operation that leaves a lattice point fixed

Justification

- Given an operation \( S \) that leaves no lattice point fixed
  - \( O \) is taken to \( R \)
  - \( T_{-R} \) takes \( R \) into \( O \)
  - \( T_{-R}S \) is also a symmetry operation (group property)
    - leaves the origin fixed
- Therefore
  - \( S = T_R T_{-R} S \)
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)
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
  - \( sc \rightarrow \text{simple tetragonal} \)
  - \( bcc \text{ and } fcc \rightarrow \text{centered tetragonal} \)
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

Classification of 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 $90^\circ$
- **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
Classification of Bravais lattices

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
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 $a$, $b$, and $c$
- Only one Bravais lattice
  - simple and centered orthorhombic $\rightarrow$ triclinic
  - minimum symmetry ($i$ and $E$)
Bravais lattices of the trigonal crystal system

- Cubic symmetry is reduced by stretching along the body diagonal
  - one lattice constant: $a$
  - 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
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 ($120^\circ$) 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
1 Classification of Bravais lattices

2 The crystallographic point groups and space groups

3 Examples
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 crystallographic 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

<table>
<thead>
<tr>
<th>POINT AND SPACE GROUPS OF BRAVAIS LATTICES AND CRYSTAL STRUCTURES</th>
<th>BRAVAIS LATTICE (BASIS OF SPHERICAL SYMMETRY)</th>
<th>CRYSTAL STRUCTURE (BASIS OF ARBITRARY SYMMETRY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of point groups:</td>
<td>7 (“the 7 crystal systems”)</td>
<td>32 (“the 32 crystallographic point groups”)</td>
</tr>
<tr>
<td>Number of space groups:</td>
<td>14 (“the 14 Bravais lattices”)</td>
<td>230 (“the 230 space groups”)</td>
</tr>
</tbody>
</table>
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
  - unambiguously

- least symmetric of the crystal systems
  - containing all the symmetry operations of the object
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 ⊥ 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
Symmetry operations of the crystallographic point groups

- **Reflections** about some plane
  - mirror plane

- **Inversions**
  - has a single fixed point (origin)
  - \( r \rightarrow -r \)
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: $t_1 + t_2$ 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 restriction theorem

<table>
<thead>
<tr>
<th>$m$</th>
<th>-2</th>
<th>-1</th>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\cos \alpha$</td>
<td>-1</td>
<td>$-\frac{1}{2}$</td>
<td>0</td>
<td>$\frac{1}{2}$</td>
<td>1</td>
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<td>$\alpha$</td>
<td>$\pi$</td>
<td>$\frac{2\pi}{3}$</td>
<td>$\frac{\pi}{4}$</td>
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<td>$n$</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>6</td>
<td>1</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Schoenflies</th>
<th>Hexagonal</th>
<th>Tetragonal</th>
<th>Trigonal</th>
<th>Orthorhombic</th>
<th>Monoclinic</th>
<th>Triclinic</th>
<th>International</th>
</tr>
</thead>
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<tr>
<td>C3</td>
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<td>C3</td>
<td>C2</td>
<td>C1</td>
<td>p</td>
<td>n</td>
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<td>C3v</td>
<td>C3v</td>
<td>C2v</td>
<td>C1v</td>
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<td>n/m</td>
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<td>C3h</td>
<td>C3h</td>
<td>C3’</td>
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<td>D3h</td>
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<td>D3m</td>
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<td>D3m</td>
<td>2</td>
<td>n/m</td>
</tr>
<tr>
<td>D3d</td>
<td>D3d</td>
<td>D3d</td>
<td>D3d</td>
<td>D3d</td>
<td>D3d</td>
<td>2</td>
<td>n/m</td>
</tr>
</tbody>
</table>

* left: Schoenflies name; right: international name
Schoenflies notation for noncubic point groups

- **C\textsubscript{n}**: cyclic groups of order \( n \)
  - only \( n \)-fold rotation axis (principal or vertical)
- **C\textsubscript{nv}**
  - an additional mirror plane containing the axis (vertical)
  - plus additional vertical planes due to \( C\textsubscript{n} \)
- **C\textsubscript{nh}**
  - \( n \)-fold rotation axis
  - mirror plane \( \perp \) to the axis (horizontal)
- **S\textsubscript{n}**
  - only \( n \)-fold rotation-reflection axis
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 $C_2$s 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 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
- \( C_n \rightarrow n \)
- \( C_{nv} \rightarrow nmm \)
  - \( mm \) 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

- $D_{nh} = D_n \times C_{1h}$
- $D_{nh} \rightarrow \frac{n}{m} \frac{2}{m} \frac{2}{m}$
  - abbreviated as $n/m/m$
  - $2/m/m \rightarrow 2/m/m$
  - exception: $D_{3h} \rightarrow \bar{6}2m$
- $D_{nd} \rightarrow \bar{n}2m$
  - $\bar{n}$ with $\perp C_2$ and vertical $m$
  - $D_{3h} \rightarrow \bar{6}2m$
  - $n = 3 \rightarrow \bar{3}m$

- 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 $\times$ 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

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>NUMBER OF POINT GROUPS</th>
<th>NUMBER OF BRAVAIS LATTICES</th>
<th>PRODUCT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>5</td>
<td>3</td>
<td>15</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>7</td>
<td>2</td>
<td>14</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>3</td>
<td>4</td>
<td>12</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>3</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>Triclinic</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>7</td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td>Trigonal</td>
<td>5</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>Totals</td>
<td>32</td>
<td>14</td>
<td>61</td>
</tr>
</tbody>
</table>
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 **nonsymmmorphic**
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 $c$. Lattice planes are separated by $\frac{c}{2}$

dashed line: glide plane; axis through the central dot: screw axis
1. Classification of Bravais lattices

2. The crystallographic point groups and space groups

3. Examples
Examples among the elements

Elements with trigonal Bravais lattices

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>(a) (Å)</th>
<th>(\theta)</th>
<th>ATOMS IN PRIMITIVE CELL</th>
<th>BASIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg (5 K)</td>
<td>2.99</td>
<td>70°45′</td>
<td>1</td>
<td>(x = 0)</td>
</tr>
<tr>
<td>As</td>
<td>4.13</td>
<td>54°10′</td>
<td>2</td>
<td>(x = \pm 0.226)</td>
</tr>
<tr>
<td>Sb</td>
<td>4.51</td>
<td>57°6′</td>
<td>2</td>
<td>(x = \pm 0.233)</td>
</tr>
<tr>
<td>Bi</td>
<td>4.75</td>
<td>57°14′</td>
<td>2</td>
<td>(x = \pm 0.237)</td>
</tr>
<tr>
<td>Sm</td>
<td>9.00</td>
<td>23°13′</td>
<td>3</td>
<td>(x = 0, \pm 0.222)</td>
</tr>
</tbody>
</table>
Examples among the elements

Elements with centered tetragonal Bravais lattices

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>BASIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>4.59</td>
<td>4.94</td>
<td>At face-centered positions of the conventional cell</td>
</tr>
<tr>
<td>Sn (white)</td>
<td>5.82</td>
<td>3.17</td>
<td>At 000, 0 1/4, 1/2 0 3/4, 1/2 1/2, with respect to the axes of the conventional cell</td>
</tr>
</tbody>
</table>

described as simple tetragonal with a basis
Examples among the elements

Elements with orthorhombic Bravais lattices

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga</td>
<td>4.511</td>
<td>4.517</td>
<td>7.645</td>
</tr>
<tr>
<td>P (black)</td>
<td>3.31</td>
<td>4.38</td>
<td>10.50</td>
</tr>
<tr>
<td>Cl (113 K)</td>
<td>6.24</td>
<td>8.26</td>
<td>4.48</td>
</tr>
<tr>
<td>Br (123 K)</td>
<td>6.67</td>
<td>8.72</td>
<td>4.48</td>
</tr>
<tr>
<td>I</td>
<td>7.27</td>
<td>9.79</td>
<td>4.79</td>
</tr>
<tr>
<td>S (rhombic)</td>
<td>10.47</td>
<td>12.87</td>
<td>24.49</td>
</tr>
</tbody>
</table>

* NOTES: