Chapter One  Crystal Structure

Drusy Quartz in Geode    Tabular Orthoclase Feldspar    Encrusting Smithsonite

Peruvian Pyrite

http://www.rockhounds.com/rockshop/xtal
Snow crystals

the Beltsville Agricultural Research Center
Solid: Crystal vs. Amorphous (glassy)

Ordered array of atoms  Disordered arrangement

Competition between attractive (binding) force and repulsive force.

Regular array lowers system energy.

Complicated! -- difficult to predict the structure of materials
Importance: structure plays a major role in determining physical properties of solids.

Determination: X-ray and neutron scattering are key tools for determining crystal structures. (bulk) Also microscopic techniques such as SEM, TEM, STM, AFM… (surface)

Deviations: There is no perfect crystal. Many key properties depend on deviation more. Defects – imperfection in crystal. Phonons – lattice vibrations.
Calcite($\text{CaCO}_3$) crystal is made from spherical particles.
Christiaan Huygen, Leiden 1690

A crystal is made from spherical particles.
Robert Hooke, London 1745

depicted by René Haüy,
Paris, 1822
Crystal
periodic array of atoms: point lattice + basis

### Point lattice – mathematical points in space

\[
\vec{r}' = \vec{r} + u_1 \vec{a}_1 + u_2 \vec{a}_2 + u_3 \vec{a}_3
\]

\(u_1, u_2, u_3 \in \text{integer}\)

\(\vec{a}_1, \vec{a}_2, \vec{a}_3 = \text{lattice vectors}\)
Primitive lattice cell

- A cell will fill all space by the repetition of suitable crystal translation operations. ---- A minimum volume cell.
  - One lattice point per primitive cell.
  - The basis associated w/ a primitive cell -- a primitive basis.
  - Not unique.

\[ A_{\text{cell}} = |\vec{a}_1 \times \vec{a}_2| = |\vec{a}_1| |\vec{a}_2| \sin \phi \]

Same for all primitive cells

Uniform mass density

**Wigner-Seitz Primitive cell** -- lattice point is at its center

*the highest symmetry cell possible*
Wigner-Seitz Primitive cell in 2D (or 3D)

- Draw lines to connect a given lattice point to all nearby lattice points.
- Draw bisecting lines (or planes) to the previous lines.
- The smallest area (or volume) enclosed.
Fundamental types of Bravais lattices

Based on symmetries:

1) Translational – same if translate by a vector
\[ \vec{T} = u_1 \vec{a}_1 + u_2 \vec{a}_2 + u_3 \vec{a}_3 \]

2) Rotational – same if lattice is rotated by an angle about a point
- 2-fold by 180°
- 3-fold by 120°
- 4-fold by 90°
- 6-fold by 60°

3) Mirror symmetry – same if reflected about a plane

4) Inversion symmetry – same if reflected through a point (equivalent to rotation 180° and mirror \( \otimes \) rotational axis \( r \) \( \otimes \) \(-r\)

Auguste Bravais
Five Bravais lattices in two dimensions

**Square lattice**

- $a_1 = a_2$, $\phi = 90^\circ$

**Rectangular lattice**

- $a_1 \neq a_2$, $\phi = 90^\circ$
**Oblique lattice**

- $a_1 \neq a_2$, $\phi \neq 60^\circ, 90^\circ$

**Centered Rectangular lattice**

- $a_1 = 2a_2 \cos \phi$

**Symmetry element**

**Unit cell**
Hexagonal lattice: $a_1 = a_2$, $\phi = 60^\circ$

Symmetry elements:
- Twofold axis (dia)
- Threefold axis (triad)
- Fourfold axis (tetrad)
- Sixfold axis (hexad)
- Mirror line
A Bravais lattice is a lattice in which every lattice point has exactly the same environment.

How about a honeycomb lattice?

A honeycomb crystal = A hexagonal lattice + two-pint basis
The seven crystal systems divided into fourteen Bravais lattices

<table>
<thead>
<tr>
<th>System</th>
<th>Number of lattices</th>
<th>Unit cell characteristics</th>
<th>Characteristic symmetry elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>1: Simple</td>
<td>$a_1 \neq a_2 \neq a_3$</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha = \beta = \gamma$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monoclinic</td>
<td>2: Simple, Base-Centered</td>
<td>$a_1 \neq a_2 \neq a_3$</td>
<td>One 2-fold rotation axis</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td></td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>4: BCC, FCC Simple, Base-Centered</td>
<td>$a_1 \neq a_2 \neq a_3$</td>
<td>Three mutually orthogonal 2-fold rotation axes</td>
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<tr>
<td></td>
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<td>$\alpha = \beta = \gamma = 90^\circ$</td>
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<tr>
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<td></td>
</tr>
<tr>
<td>Tetragonal</td>
<td>2: Simple, BCC</td>
<td>$a_1 = a_2 \neq a_3$</td>
<td>One 4-fold rotation axis</td>
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<tr>
<td></td>
<td></td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td></td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>Cubic</td>
<td>3: Simple, BCC, FCC</td>
<td>$a_1 = a_2 = a_3$</td>
<td>Four 3-fold rotation axes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trigonal</td>
<td>1: Simple</td>
<td>$a_1 = a_2 = a_3$</td>
<td>One 3-fold rotation axis</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha = \beta = \gamma &lt; 120^\circ \neq 90^\circ$</td>
<td></td>
</tr>
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<tr>
<td>Hexagonal</td>
<td>1: Simple</td>
<td>$a_1 \neq a_2 \neq a_3$</td>
<td>One 3-fold rotation axis</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha = \beta = 90^\circ, \gamma = 120^\circ$</td>
<td></td>
</tr>
</tbody>
</table>
TRICLINIC ($\alpha \neq \beta \neq \gamma$)

三斜晶系

MONOCLINIC ($\beta = \gamma = 90^\circ \neq \alpha$)

單斜晶系
Orthorhombic \((\alpha=\beta=\gamma=90^\circ)\)

正交晶系

Simple

Base-centered

BCC

FCC

\(a_1 \perp a_2 \perp a_3\)
Tetragonal \((\alpha=\beta=\gamma=90^\circ)\)

正方晶系

Simple

BCC
Cubic ($\alpha = \beta = \gamma = 90^\circ$)

立方晶系
### Trigonal
$(\alpha = \beta = \gamma < 120^\circ, \quad \square 90^\circ)$

三角（菱面）晶系

### Hexagonal
$(\alpha = \beta = 90^\circ, \gamma = 120^\circ)$

六角晶系

\[ a_3 \parallel a \]
# Characteristics of cubic lattices

<table>
<thead>
<tr>
<th></th>
<th>Simple</th>
<th>Body-centered</th>
<th>Face-centered</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lattice points/cell</strong></td>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td><strong>Number of nearest neighbors</strong></td>
<td>6</td>
<td>8</td>
<td>12</td>
</tr>
<tr>
<td><strong>Nearest-neighbor distance</strong></td>
<td>$a$</td>
<td>$\frac{\sqrt{3}}{2}a$</td>
<td>$\frac{a}{\sqrt{2}}$</td>
</tr>
<tr>
<td><strong>Packing fraction</strong></td>
<td>$\frac{\pi}{6} = 0.524$</td>
<td>$\frac{\sqrt{3}}{8}\pi = 0.680$</td>
<td>$\frac{\sqrt{2}}{6}\pi = 0.740$</td>
</tr>
</tbody>
</table>

Maximum, same as hexagonal
Crystal – Periodic arrangement of atoms

Bravais lattice + Basis of atom
(Array of point in space) (Arrangement of atoms within unit cell)

2 Dimensions → 5 types
3 Dimensions → 14 types

By symmetry

Crystal may have same or less symmetry than original Bravais lattice.

Basis
Symmetry “4mm”
Introducing new symmetries for basis with multiple atoms:

• Point group symmetries:
  combinations of rotation, inversion, reflection that hold
  one point fixed and return original structure.
  2 Dimensions, 10
  3 Dimensions, 32

• Space group symmetries:
  point group operations + translations that return original structure.
  2 Dimensions, 17
  3 Dimensions, 230

There are many possible types by symmetry but most are never observed.

Real crystals form a few types due to energies of crystal formation.
Table 3  Crystal structures of the elements.

The data given are at room temperature for the most common form, or at the stated temperature in deg K. For further descriptions of the elements see Wyckoff, Vol. 1, Chap. 2. Structures labeled complex are described there.

<table>
<thead>
<tr>
<th>Element</th>
<th>Structure</th>
<th>a [Å]</th>
<th>b [Å]</th>
<th>Crystal Structure</th>
<th>b [Å]</th>
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<tbody>
<tr>
<td>Li</td>
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<td>3.75</td>
<td>6.12</td>
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<td>2.27</td>
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<td>Mg</td>
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<td>4.225</td>
<td>3.21</td>
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<td>Na</td>
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<td>5.21</td>
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<td>4.09</td>
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<td>5.430</td>
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<tr>
<td>As</td>
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<td>5.430</td>
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<td>Se</td>
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<tr>
<td>Br</td>
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<tr>
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<td>5.66</td>
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<tr>
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<td>5.33</td>
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<tr>
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<td>5.73</td>
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<tr>
<td>Mo</td>
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<td>5.15</td>
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<tr>
<td>Tc</td>
<td>hcp</td>
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<td>4.44</td>
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<tr>
<td>Ru</td>
<td>fcc</td>
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<td>4.28</td>
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<tr>
<td>Rh</td>
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<td>4.09</td>
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<tr>
<td>Pd</td>
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<td>4.62</td>
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<tr>
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<td>5.52</td>
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<tr>
<td>I</td>
<td>fcc</td>
<td>3.34</td>
<td>3.34</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Ce      | fcc       | 5.16  | 3.67  |                   |       |
| Pr      | hex.      | 3.66  | 3.66  |                   |       |
| Nd      | hex.      | 4.58  | 4.58  |                   |       |
| Pm      | bcc       | 3.63  | 3.63  |                   |       |
| Sm      | hcp       | 3.60  | 3.60  |                   |       |
| Eu      | hcp       | 3.59  | 3.59  |                   |       |
| Gd      | hcp       | 3.59  | 3.59  |                   |       |
| Tb      | hcp       | 3.59  | 3.59  |                   |       |
| Dy      | hcp       | 3.59  | 3.59  |                   |       |
| Ho      | hcp       | 3.59  | 3.59  |                   |       |
| Er      | hcp       | 3.59  | 3.59  |                   |       |
| Tm      | hcp       | 3.59  | 3.59  |                   |       |
| Yb      | hcp       | 3.59  | 3.59  |                   |       |
| Lu      | hcp       | 3.59  | 3.59  |                   |       |
| Th      | fcc       | 5.08  | 3.92  |                   |       |
| Pa      | complex   | 3.24  | 3.24  |                   |       |
| U       | complex   | 3.64  | 3.64  |                   |       |
| Np      | complex   | 3.64  | 3.64  |                   |       |
| Pu      | complex   | 3.64  | 3.64  |                   |       |
| Am      | hex.      | 3.64  | 3.64  |                   |       |
| Cm      | fcc       | 3.34  | 3.34  |                   |       |
| Bk      | ABAC      |       |       |                   |       |
| Cf      | ABAC      |       |       |                   |       |
| Es      | ABAC      |       |       |                   |       |
| Fm      | ABAC      |       |       |                   |       |
| Md      | ABAC      |       |       |                   |       |
| No      | ABAC      |       |       |                   |       |
| Lr      | ABAC      |       |       |                   |       |
Directions and planes in crystals

Useful to develop a notation for describing directions and identifying planes of atoms in crystals

Consider lattice defined by \( \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \)

Vector direction \( \vec{r} = u_1 \mathbf{a}_1 + u_2 \mathbf{a}_2 + u_3 \mathbf{a}_3 \) is described as \([u_1 \; u_2 \; u_3]\)

where \( u_1, u_2, \) and \( u_3 \) are the lowest reduced integers.

Note:

- \([8 \ 6 \ 0]\) same as \([4 \ 3 \ 0]\)
- use \( \bar{u} \) instead of \(-u\) \([1\bar{2}1]\)
- \([u_1 \; u_2 \; u_3]\) not as the same as Cartesian coordinate direction except for simple cubic crystal
Cubic has highest symmetric directions

By symmetry, [1 0 0], [0 1 0], [0 0 1] are equivalent

\[ \{1 0 0\} \equiv \text{set of equivalent directions} \]
Crystal planes – atoms fall on planes labeled by “Miller indices”

Note:

- Find the intercepts on the axes in terms of $a_1$, $a_2$, and $a_3 \parallel h' k' \ell'$
- Take reciprocals and make integers $\left( \frac{1}{h'}, \frac{1}{k'}, \frac{1}{\ell'} \right) \times h' k' \ell'$
- Reduce to smallest three integers
- If the plane does not intersect one of the crystal axes, that intercept is taken to be infinitely far from the origin and the corresponding index is zero.

$\left( h, k, \ell \right)$ is called Miller index of the plane

Miller indices specify a vector normal to the plane, and not a specific plane: all parallel planes have the same indices
Schematic illustrations of lattice planes
Lines in two dimensional crystals

Low index plane: more dense and more widely spaced
High index plane: Less dense and more closely spaced
Most common crystal structures:

Simple Cubic lattice: \textit{Po} conventional cell: 1 atom/cube

Body Centered Cubic lattice:

Conventional cell: 2 atoms/ cube

Not a primitive lattice

8 nearest neighbors

Alkali metals: Li, Na, K, Rb, Cs
Ferromagnetic metals: Cr, Fe
Transition metals: Nb, V, Ta, Mo, W

- BCC lattice + single atom basis
- SC lattice + basis of 2 atoms at (0,0,0) and (1/2,1/2,1/2)
Body Centered Cubic lattice

\[ \mathbf{a}_1 = \frac{a}{2} (\hat{x} + \hat{y} - \hat{z}) \]

\[ \mathbf{a}_2 = \frac{a}{2} (-\hat{x} + \hat{y} + \hat{z}) \]

\[ \mathbf{a}_3 = \frac{a}{2} (\hat{x} - \hat{y} + \hat{z}) \]
Body-centered Cubic lattice

Primitive cell:
Rhombohedron
w/.
1. edge $\frac{\sqrt{3}}{2}a$
2. the angle between two adjacent edges is $109^\circ 28'$
Face Centered Cubic lattice:

Conventional cell: 4 atoms/cube

Not a primitive lattice

12 nearest neighbors

Noble metals: Cu, Ag, Au
Transition metals: Ni, Pd, Pt,
Inert gas solids: Ne, Ar, Kr, Xe

• FCC lattice + single atom basis
• SC lattice + basis of 4 atoms at (0,0,0), (1/2,1/2,0), (1/2,0,1/2), and (0,1/2,1/2)
Face Centered Cubic lattice

Rhombohedral Primitive cell

The angle between two adjacent edges: $60^\circ$

Edge: $\frac{\sqrt{2}}{2}a$

\[
\vec{a}_1 = \frac{a}{2}(\hat{x} + \hat{y})
\]
\[
\vec{a}_2 = \frac{a}{2}(\hat{y} + \hat{z})
\]
\[
\vec{a}_3 = \frac{a}{2}(\hat{x} + \hat{z})
\]
Hexagonal Close-Packed lattice

\[ |a_1| = |a_2|, \text{ with an included angle } 120^\circ \]
\[ |c| = 1.633|a_1| \]

\( a_1, a_2, \text{ and } c \) do not construct a primitive lattice

\( a_1, a_2, \text{ and } a_3 \) construct a primitive lattice

\[ |a_1| = |a_2| = |a_3| \]

12 nearest neighbors

Transition metals: Sc, Y, Ti, Zr, Co…

IIA metals: Be, Mg

Hexagonal lattice + basis of 2 atoms at \((0,0,0)\) and \((2/3,1/3,1/2)\)
HCP lattice

A B A B A B …

FCC lattice

A B C A B C A B C …
Diamond structure: two FCC displaced from each other by $\frac{1}{4}$ of a body diagonal

FCC lattice + basis of 2 atoms at (0,0,0) and (1/4,1/4,1/4)

Tetrahedral bonding: 4 nearest neighbors
12 next nearest neighbors

The maximum packing fraction = 0.34

Si, Ge, Sn, C, ZnS, GaAs, …
Some atoms form multiple stable structures: for example, C → diamond or graphite (hexagonal)

An STM image of a graphite surface clearly shows the interconnected 6-membered rings of graphite
graphite

diamond
Many crystals undergo structural changes with $T$, $P$: for example,

- **Fe**
  - $\delta$-ferrite: BCC at 910°C, FCC at 1400°C, BCC at 2100°C
  - $\alpha$-ferrite: Liquid

- **Na**
  - HCP at 36K, FCC at 371K
  - Liquid
Compounds

**NaCl structures**
- NaCl, NaF, KCl, AgCl, MgO, MnO, …
- FCC lattice + basis of two atoms
- Cl (0,0,0), Na (1/2,1/2,1/2)
- SC w/. alternating atoms

**CsCl structures**
- CsCl, BeCu, ZnCu(brass), AlNi, AgMg, …
- SC lattice + basis of two atoms
- Cs (0,0,0), Cl (1/2,1/2,1/2)
- BCC w/. alternating atoms
ZnS structures

ZnS, CuF, CuCl, … compounds
CdS Photoconductor
GaAs, GaP, InSb, … III-V semiconducting compounds

- FCC lattice + basis of two atoms
  - Zn (0,0,0), S (1/4,1/4,1/4)
  - Ga(0,0,0), As(1/4,1/4,1/4)

diamond w/. alternating atoms
Zinc Blende underlying lattice is fcc

Wurtzite underlying lattice is hcp

GaAs

CdS

[1,1,1] axis

(a)

(b)

c-axis
High Tc superconductors

Orthorhombic 
O(I) (Pmmm)

Tetragonal 
T (P4/mmm)

Orthorhombic 
O(II) (Cmmm)
C-60
“Bucky balls”
BuckminsterFullurene