Crystal Structure

Order

Sit on an atom & around

What do you see?

short range order (liquids, amorphous)

long range order (crystals)

disordered (gas)

We care about crystals

Crystal = solid material with periodic structure

Periodicity is represented by a lattice (Bravais)

Lattice = infinite set of discrete points

Invariant by translation, geometrical points, not necessary atoms

(Bravais lattices)

Sit on a lattice point and look around

Then move to another lattice point, you will see the same thing

Unit cell = a part of volume (surface of 2D lattice)

That if replicated for every lattice point

Covers all the space, once and only one
Lattice points, many different unit cells

\[ = \text{translational vectors} \quad \vec{a}, \vec{b}, \vec{c} \]
\[ = \text{lattice parameter} \]

**In 2D**

3 possible lattices

(a) Square

(b) Rectangular parallelogram,

\[ \phi = 120^\circ \Rightarrow \text{Hexagonal lattice} \]

LATTICE = geometrical set of points needed for translations

TRANSLATION OF WHAT? OF A BASIS \( \overset{\rightarrow}{2} \)

LATTICE + BASIS = CRYSTAL STRUCTURE

**Figure 3.2-2** Three examples of 2-D patterns all created using the same rectangular lattice but each having a different basis: (a) the basis is a single character; (b) the basis contains a repeated character; and (c) the basis contains two characters with different orientations.
COORDINATION NUMBER

The points in a Bravais lattice that are closest to a given point are called its nearest neighbors. Because of the periodic nature of a Bravais lattice, each point has the same number of nearest neighbors. This number is thus a property of the lattice, and is referred to as the coordination number of the lattice. A simple cubic lattice has coordination number 6; a body-centered cubic lattice, 8; and a face-centered cubic lattice, 12. The notion of a coordination number can be extended in the obvious way to some simple arrays of points that are not Bravais lattices, provided that each point in the array has the same number of nearest neighbors.

PRIMITIVE UNIT CELL

A volume of space that, when translated through all the vectors in a Bravais lattice, just fills all of space without either overlapping itself or leaving voids is called a primitive cell or primitive unit cell of the lattice.\textsuperscript{9} There is no unique way of choosing a primitive cell for a given Bravais lattice. Several possible choices of primitive cells for a two-dimensional Bravais lattice are illustrated in Figure 4.10.

![Figure 4.10](image)

Several possible choices of primitive cell for a single two-dimensional Bravais lattice.

A primitive cell must contain precisely one lattice point (unless it is so positioned that there are points on its surface). It follows that if \( n \) is the density of points in the lattice\textsuperscript{9} and \( v \) is the volume of the primitive cell, then \( n v = 1 \). Thus \( v = 1/n \). Since

---

\textsuperscript{9} Translations of the primitive cell may possess common surface points; the nonoverlapping proviso is only intended to prohibit overlapping regions of nonzero volume.

\textsuperscript{9} The density \( n \) of Bravais lattice points need not, of course, be identical to the density of conduction electrons in a metal. When the possibility of confusion is present, we shall specify the two densities with different symbols.
IN 3D

14 different lattices in 7 FAMILIES

Part I Fundamentals

I. Cubic lattices \( a = b = c; \alpha = \beta = \gamma = 90^\circ \)

1) CUBIC

II. Tetragonal lattices \( a = b \neq c; \alpha = \beta = \gamma = 90^\circ \)

2) TETRAGONAL

III. Hexagonal lattices \( a = b = c; \alpha = \beta = 90^\circ; \gamma = 120^\circ \)

3) HEXAGONAL

IV. Orthorhombic lattices \( a \neq b \neq c; \alpha = \beta = \gamma = 90^\circ \)

4) ORTHORHOMBIC

V. Rhombohedral lattices \( a = b = c; \alpha = \beta = \gamma = 90^\circ \)

5) RHOMBOHEDRAL

VI. Monoclinic lattices \( a \neq b \neq c; \alpha = \gamma = 90^\circ \neq \beta \)

6) MONOCLINIC

VII. Triclinic lattices \( a \neq b \neq c; \alpha \neq \beta \neq \gamma \)

7) TRICLINIC

FIGURE 3.2-3 The 14 Bravais lattices grouped into the 7 lattice types. The restrictions on the lattice parameters \( a, b, \) and \( c \) and the angles between the edges of the unit cell \( \alpha, \beta, \) and \( \gamma \) are listed for each unit cell.

A UNIT CELL IS THE "SMALLEST" POSSIBLE VOLUME WHICH, IF TRANSLATED, COVER ALL THE SPACE.
Some systems can be described with a basis or without basis?

**Example: BCC**

A few sites from a body-centered cubic Bravais lattice. Note that it can be regarded either as a simple cubic lattice formed from the points $A$ with the points $B$ at the cube centers, or as a simple cubic lattice formed from the points $B$ with the points $A$ at the cube centers. This observation establishes that it is indeed a Bravais lattice.

BCC = Every point is a lattice point

Or without basis

$\Rightarrow$ Cubic + a basis of 2 points

BCC or cubic + basis

$0, \frac{a}{2}(x + y + z) \quad (bcc)$

**Elements**

<table>
<thead>
<tr>
<th>Element</th>
<th>$a$ (Å)</th>
<th>Element</th>
<th>$a$ (Å)</th>
<th>Element</th>
<th>$a$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>5.02</td>
<td>Li</td>
<td>3.49 (78 K)</td>
<td>Ta</td>
<td>3.31</td>
</tr>
<tr>
<td>Cr</td>
<td>2.88</td>
<td>Mo</td>
<td>3.15</td>
<td>Ti</td>
<td>3.88</td>
</tr>
<tr>
<td>Cs</td>
<td>6.05 (78 K)</td>
<td>Na</td>
<td>4.23 (5 K)</td>
<td>V</td>
<td>3.02</td>
</tr>
<tr>
<td>Fe</td>
<td>2.87</td>
<td>Nb</td>
<td>3.30</td>
<td>W</td>
<td>3.16</td>
</tr>
<tr>
<td>K</td>
<td>5.23 (5 K)</td>
<td>Rb</td>
<td>5.59 (5 K)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.6
Three primitive vectors, specified in Eq. (4.3), for the body-centered cubic Bravais lattice. The lattice is formed by taking all linear combinations of the primitive vectors with integral coefficients. The point \( P \), for example, is \( P = -a_1 - a_2 + 2a_3 \).

\[
a_1 = a\hat{x}, \quad a_2 = a\hat{y}, \quad a_3 = \frac{a}{2}(\hat{x} + \hat{y} + \hat{z}).
\]

Figure 4.7
A more symmetric set of primitive vectors, specified in Eq. (4.4), for the body-centered cubic Bravais lattice. The point \( P \), for example, has the form \( P = 2a_1 + a_2 + a_3 \).

\[
a_1 = \frac{a}{2}(\hat{y} + \hat{z} - \hat{x}), \quad a_2 = \frac{a}{2}(\hat{z} + \hat{x} - \hat{y}), \quad a_3 = \frac{a}{2}(\hat{x} + \hat{y} - \hat{z}).
\]
\[ a_1 = \frac{a}{2} (y + z), \quad a_2 = \frac{a}{2} (z + x), \quad a_3 = \frac{a}{2} (x + y). \]

**Figure 4.9**
A set of primitive vectors, as given in Eq. (4.5), for the face-centered cubic Bravais lattice. The labeled points are \( P = a_1 + a_2 + a_3, Q = 2a_2, R = a_2 + a_3, \) and \( S = -a_1 + a_2 + a_3. \)

**Table 4.1**
<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>( a ) (( \text{Å} ))</th>
<th>ELEMENT</th>
<th>( a ) (( \text{Å} ))</th>
<th>ELEMENT</th>
<th>( a ) (( \text{Å} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>5.26 (4.2 K)</td>
<td>Ir</td>
<td>3.84</td>
<td>Pt</td>
<td>3.92</td>
</tr>
<tr>
<td>Ag</td>
<td>4.09</td>
<td>Kr</td>
<td>5.72 (58 K)</td>
<td>( \delta )-Pt</td>
<td>4.64</td>
</tr>
<tr>
<td>Al</td>
<td>4.65</td>
<td>La</td>
<td>5.30</td>
<td>Rh</td>
<td>3.80</td>
</tr>
<tr>
<td>Au</td>
<td>4.08</td>
<td>Ne</td>
<td>4.43 (4.2 K)</td>
<td>Sc</td>
<td>4.54</td>
</tr>
<tr>
<td>Cu</td>
<td>5.38</td>
<td>Ni</td>
<td>3.52</td>
<td>Sr</td>
<td>6.08</td>
</tr>
<tr>
<td>Ce</td>
<td>5.16</td>
<td>Pb</td>
<td>4.95</td>
<td>Th</td>
<td>5.08</td>
</tr>
<tr>
<td>( \beta )-Co</td>
<td>3.55</td>
<td>Pd</td>
<td>3.89</td>
<td>Xe (58 K)</td>
<td>6.20</td>
</tr>
<tr>
<td>Cu</td>
<td>3.61</td>
<td>Pr</td>
<td>5.16</td>
<td>Yb</td>
<td>5.49</td>
</tr>
</tbody>
</table>

**FCC LATTICE, NO BASIS OR CUBIC LATTICE WITH BASIS OF 4!**

\[ 0, \quad \frac{a}{2} (x + y), \quad \frac{a}{2} (y + z), \quad \frac{a}{2} (z + x) \quad \text{(fcc).} \]
SOME IMPORTANT EXAMPLES OF CRYSTAL STRUCTURES AND LATTICES WITH BASES

Diamond Structure

The diamond lattice\(^\text{16}\) (formed by the carbon atoms in a diamond crystal) consists of two interpenetrating face-centered cubic Bravais lattices, displaced along the body diagonal of the cubic cell by one quarter the length of the diagonal. It can be regarded as a face-centered cubic lattice with the two-point basis \(0\) and \((a/4)(\hat{x} + \hat{y} + \hat{z})\). The coordination number is 4 (Figure 4.18). The diamond lattice is not a Bravais lattice,

![Figure 4.18](image)

Conventional cubic cell of the diamond lattice. For clarity, sites corresponding to one of the two interpenetrating face-centered cubic lattices are unshaded. (In the zincblende structure the shaded sites are occupied by one kind of ion, and the unshaded by another.) Nearest-neighbor bonds have been drawn in. The four nearest neighbors of each point form the vertices of a regular tetrahedron.

because the environment of any point differs in orientation from the environments of its nearest neighbors. Elements crystallizing in the diamond structure are given in Table 4.3.

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>CUBE SIDE (a) ((\text{Å}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (diamond)</td>
<td>3.57</td>
</tr>
<tr>
<td>Si</td>
<td>5.43</td>
</tr>
<tr>
<td>Ge</td>
<td>5.66</td>
</tr>
<tr>
<td>(\alpha)-Sn (grey)</td>
<td>6.49</td>
</tr>
</tbody>
</table>

Hexagonal Close-Packed Structure

Though not a Bravais lattice, the hexagonal close-packed (hcp) structure ranks in importance with the body-centered cubic and face-centered cubic Bravais lattices; about 30 elements crystallize in the hexagonal close-packed form (Table 4.4).

\(^{16}\) We use the word "lattice," without qualifications, to refer either to a Bravais lattice or a lattice with a basis.
**HEX**

**IS A BRAVAIS LATTICE**

---

Figure 4.19
The simple hexagonal Bravais lattice. Two-dimensional triangular nets (shown in inset) are stacked directly above one another, a distance c apart.

\[ a_1 = a \hat{x}, \quad a_2 = \frac{a}{2} \hat{x} + \frac{\sqrt{3}a}{2} \hat{y}, \quad a_3 = c \hat{z} \]

**PRIMITIVE VECTORS**

---

**HCP IS NOT A BRAVAIS LATTICE**

**HEXAGONAL CLOSED PACKED**

---

**HCP = HEX + BASIS (2)**

---

Figure 4.20
The hexagonal close-packed crystal structure. It can be viewed as two interpenetrating simple hexagonal Bravais lattices, displaced vertically by a distance c/2 along the common c-axis, and displaced horizontally so that the points of one lie directly above the centers of the triangles formed by the points of the other.

**HCP = HEX + BASIS**
Table 4.4
ELEMENTS WITH THE HEXAGONAL CLOSE-PACKED CRYSTAL STRUCTURE

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>(a) (Å)</th>
<th>(c)</th>
<th>(c/a)</th>
<th>ELEMENT</th>
<th>(a) (Å)</th>
<th>(c)</th>
<th>(c/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>2.29</td>
<td>3.58</td>
<td>1.56</td>
<td>Os</td>
<td>2.74</td>
<td>4.32</td>
<td>1.58</td>
</tr>
<tr>
<td>Cd</td>
<td>2.98</td>
<td>5.62</td>
<td>1.89</td>
<td>Pr</td>
<td>3.67</td>
<td>5.92</td>
<td>1.61</td>
</tr>
<tr>
<td>Ce</td>
<td>3.65</td>
<td>5.96</td>
<td>1.63</td>
<td>Re</td>
<td>2.76</td>
<td>4.46</td>
<td>1.62</td>
</tr>
<tr>
<td>a-Co</td>
<td>2.51</td>
<td>4.07</td>
<td>1.62</td>
<td>Ru</td>
<td>2.70</td>
<td>4.28</td>
<td>1.59</td>
</tr>
<tr>
<td>Dy</td>
<td>3.59</td>
<td>5.65</td>
<td>1.57</td>
<td>Sc</td>
<td>3.31</td>
<td>5.27</td>
<td>1.59</td>
</tr>
<tr>
<td>Er</td>
<td>3.56</td>
<td>5.59</td>
<td>1.57</td>
<td>Tb</td>
<td>3.60</td>
<td>5.69</td>
<td>1.58</td>
</tr>
<tr>
<td>Gd</td>
<td>3.64</td>
<td>5.78</td>
<td>1.59</td>
<td>Ti</td>
<td>2.95</td>
<td>4.69</td>
<td>1.59</td>
</tr>
<tr>
<td>He (2 K)</td>
<td>3.57</td>
<td>5.83</td>
<td>1.63</td>
<td>Ti</td>
<td>3.46</td>
<td>5.53</td>
<td>1.60</td>
</tr>
<tr>
<td>Hf</td>
<td>3.20</td>
<td>5.06</td>
<td>1.58</td>
<td>Tm</td>
<td>3.54</td>
<td>5.55</td>
<td>1.57</td>
</tr>
<tr>
<td>Ho</td>
<td>3.58</td>
<td>5.62</td>
<td>1.57</td>
<td>Y</td>
<td>3.65</td>
<td>5.73</td>
<td>1.57</td>
</tr>
<tr>
<td>La</td>
<td>3.75</td>
<td>6.07</td>
<td>1.62</td>
<td>Zn</td>
<td>2.66</td>
<td>4.95</td>
<td>1.86</td>
</tr>
<tr>
<td>Lu</td>
<td>3.50</td>
<td>5.55</td>
<td>1.59</td>
<td>Zr</td>
<td>3.23</td>
<td>5.15</td>
<td>1.59</td>
</tr>
<tr>
<td>Mg</td>
<td>3.21</td>
<td>5.21</td>
<td>1.62</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd</td>
<td>3.66</td>
<td>5.90</td>
<td>1.61</td>
<td>&quot;Ideal&quot;</td>
<td></td>
<td></td>
<td>1.63</td>
</tr>
</tbody>
</table>

\[ c = \left( \frac{4}{\sqrt{6}} \right) a_0 = 1.633a_0 = 3.266r \]

\[ V_{hc}(\text{large HCP}) = \left( \frac{3\sqrt{3}}{2} \right)a_0^2c \]
MILLER INDICES

- CUBIC, TETRAGONAL, ORTHOROMbic

For all the units with angles $\alpha = \beta = \gamma = 90^\circ$

RIGHT HAND CARTESIAN SYSTEM

Take "RECTANGULAR" unit cell

$a, b, c$ in meters \[\text{[may be } \AA \text{ or } \text{cm}]\]

\((h, k, l)\) = fractional positions of point $P$

with respect to \((a, b, c)\).

POINTS (FRACTIONAL)

negative put a \(\bar{a}\) at the top

\[\text{put numbers in}\]

\[\text{and get}\]

\[(h, k, l)\]

- Maximum common denominator \(\Rightarrow \text{Divide}\)
- Minimum common multiplier \(\Rightarrow \text{Multiply}\)

\[\left(1, \frac{3}{2}, 0\right) \Rightarrow [2 \bar{3} 0]\]

\[\left(\frac{2}{2}, 0\right) \Rightarrow [1 1 0]\]

\(\left[\frac{1}{2} 2 \frac{1}{2}\right] \Rightarrow \text{MILLER INDICES}\)
2) Identify intercepts in \((b, c, d)\) notation (fractional), in the \(x, y, z\) axes.

3) Take reciprocal
\[
\left(\frac{1}{b}, \frac{1}{c}, \frac{1}{d}\right) \rightarrow \left(0, \frac{1}{2}, 1\right)
\]

4) Clear fractions but do not reduce at lower integer
MUST COUNT ONLY LATTICE POINTS (BRAVAIS) NOT ATOM
NECESSARY (UNLESS BASIS = 1 ATOM)

1) PICK 1 DIRECTION, PUT IN MILLER NOTATION
2) COUNT # OF EQUIVALENT LATTICE POINTS #
3) DIVIDE BY THEIR DISTANCE

\[ \frac{1}{|\mathbf{a}|} \quad \text{LENGTH OF LINE CONTAINED IN ONE UNIT CELL} \]
\[ \downarrow \quad \rho_L = \# \text{ OF LATTICE POINTS ALONG ONE UNIT CELL} \]

EQUIVALENT NOTATION, BUT EASIER! (STEFANO'S)

1) PICK 1 DIRECTION FROM ORIGIN (1 POINT 000)
2) MEASURE DISTANCE WITH 1ST EQUIVALENT POINT TO # OF ORIGIN = q

\[ \Rightarrow \quad \rho_L(\text{DIRECTION}) = \frac{1}{q}, \text{DIST} \]

EXAMPLE 3.5.1 (79)

BCC

\[ \begin{array}{c}
\text{along } [111] \\
\alpha = 4r \quad (\text{relation } \frac{r}{\alpha} \text{ lattice parameter for BCC})
\end{array} \]

Start from (000)
go along (111) meet \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) at position \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) distance

\[ = 2r \Rightarrow \rho_L(111) = \frac{1}{2r} \]
Along [110] \[ a\sqrt{3} = 4z \Rightarrow a = 4z/\sqrt{3} \]

Go along [110] meet point (1,1,0) at distance \( a\sqrt{2} \)

\[ \Rightarrow P_L (1101) = \frac{1}{a\sqrt{2}} = \frac{\sqrt{3}}{24\sqrt{2}} = 0.3/2 \]

**Symmetry**

\[ P_L [110] = P_L [101] = P_L [011] = 0.3/2 \]
\[ P_L [111] = 0.5 \]
\[ P_L [100] = P_L [010] = P_L [001] = 0.43/2 \]

Along [100] go along (1,0,0) meet point (1,0,0) @ \( a \)

\[ P_L (1001) = \frac{1}{a} = \frac{\sqrt{3}}{4z} = 0.43/2 \]

**Close Packing Direction**

Is the direction where equivalent points are closest!! (Highest \( P_L \))
FCC

\[ \text{FACE} \]
\[ \Rightarrow a\sqrt{2} = 4r \]
\[ \Rightarrow a = 4r / \sqrt{2} \]

along \([111]\) and \([1\overline{1}1]\) \(\Rightarrow a\sqrt{3} \Rightarrow \)
\[ \rho_l \ [111] = \frac{1}{a\sqrt{3}} = \frac{\sqrt{2}}{4r \sqrt{3}} \approx 0.2 \frac{r}{a} \]

along \([110]\) or \([101]\) or \([011]\)

\[ \text{find} \ (1/2, 1/2, 0) \odot \frac{a\sqrt{2}}{2} = \frac{a}{\sqrt{2}} \Rightarrow \rho_l \ [111] = \frac{\sqrt{2}}{4r} \frac{\sqrt{2}}{2r} \approx 0.06 \frac{r}{a} \]

along \([001]\) or \([010]\) or \([001]\)

\[ \text{find} \ (1,0,0) \odot a \Rightarrow \rho_l \ [001] = \frac{1}{a} = \frac{\sqrt{2}}{4r} \approx 0.35 \frac{r}{a} \]

CLOSE-PACKING DIRECTION FOR FCC = \([110]\)

C13
PLANAR DENSITY

PLANAR DENSITY IS THE DENSITY OF POINTS PER UNIT AREA

\[ \rho_p (\text{plane}) = \frac{\# \text{ of points lattice}}{\text{area of the surface considered}} \]

(PICK SURFACE INSIDE UNIT CELL FOR SIMPLICITY BUT NOT NECESSARY)

AS FOR LINEAR DENSITY, SUBSTITUTE POINTS WITH SPHERES OF RADIUS \( \frac{a}{2} \) SO YOU CAN COMPARE DIFFERENT STRUCTURES (AND YOU ARE READY TO RUN IF THE BASIS IS HOMOATOMIC!)

FCC

**Figure 3.5-2** (a) The portion of the (1 1 1) plane contained within a single FCC unit cell is sketched in 3-D; (b) the same plane sketched in 2-D; (c) the portion of the (1 1 0) plane contained within a single FCC unit cell is sketched in 3-D; (d) the same plane sketched in 2-D.

**Exercise 3.5-2**

\[ T = \frac{4}{3} \Rightarrow \frac{4}{3} = \frac{\sqrt{2}}{a^2} \Rightarrow a = \frac{2}{\sqrt{8}} = \frac{1}{2} \]

Along (1 1 1)

\[ \rho_p (\text{1 1 1}) = \frac{4}{a^2} = \frac{2}{\sqrt{8}} = \frac{1}{2} \]

\[ \rho_p (\text{1 1 0}) = \frac{2}{a \sqrt{2} \cdot \frac{2}{a}} = \frac{1}{\sqrt{2}} \]

\[ \rho_p (\text{1 0 0}) = \frac{2}{a \sqrt{2} \cdot \frac{2}{a}} = \frac{1}{\sqrt{2}} \]

\[ \rho_p (\text{1 0 0}) = \frac{2}{a \sqrt{2} \cdot \frac{2}{a}} = \frac{1}{\sqrt{2}} \]

**Nice Box**

CIV
HIGHEST DENSITY PLANE

CLOSE-PACKED PLANE

\[ \rho_p(111) = \frac{1}{21\sqrt{2}} \]

HIGHEST DENSITY PLANE

\[ \rho_p(110) = \frac{3}{8\sqrt{2}} \]

92% \( \rho_p(\overline{1}11) \)

\[ \rho_p(2\overline{1}0) \]

\[ \rho_{BC} \]

BC is NOT CLOSE-PACKED

FOR SOME \( \rho_{BC}(100), \rho_{BC}(1\overline{1}1), \rho_{BC}(2\overline{1}0) \) ? FAST

FCC is THE HIGHEST DENSITY PLANE

\[ \rho_{C} \]

BC is NOT C.P.

FCC is C.P. FOR 
plan(1\overline{1}1)

CLOSE-PACKED IF \( \rho_{MAX} = \frac{1}{21\sqrt{2}} \)

HCP \[ = \text{HEX} + \text{BASIS} \]

\[ \text{is C.P. on the basal plane} \]

SEE LATER.
**FCC**

For simplicity, we take
CUBIC UNIT CELL

Vol = \# of lattice point
UNIT VOLUME

1) Put points as special atoms
2) Count them in UNIT CELL (TAKE one easy one)
3) \( \rho_v = \# / \text{Volume} \)

- **Corners**
  - Have 8 spheres with \( 1/8 \) value each
  - \( 1/8 \)
  - \( \Rightarrow \) \# of atoms = \( 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4 \)

- **Value**
  - \( a^3 \Rightarrow a = \frac{\sqrt{2}a}{2} \)
  - \( \rho_v = \frac{4 \times 2^{3/2}}{4 \times \frac{\sqrt{2}}{2} a^3} \)
  - \( \frac{\text{Re}}{\rho_v} = \frac{1}{4\sqrt{2} a^3} \)

**HCP is same**
\( \rho_v = \frac{1}{4\sqrt{2} a^3} \)

If \( \% = 1.6 \) theoretical one

**HCP & FCC are both CLOSE PACKED STRUCTURE**
ATOMIC PACKING FACTOR

$\text{APF}$ measures the empty volume of the cell!!

$\text{APF} \uparrow \text{empty volume} \downarrow$

\[ = \text{occupied fraction of volume} \]

\[ \text{APF} = \frac{\text{Volume of atoms (in octahedron)}}{\text{Volume of cell}} \]

Each atom sphere is $\frac{4\pi r^3}{3}$

\[ \text{ATOMS/CUBIC CELL} \]

\[ a \rightarrow 2 \pi \text{ relation} \]

\[ \frac{1}{8} \times 4 \times \frac{4\pi r^3}{3} = 0.52 \]

\[ \text{SIMPLE CUBIC} \]

\[ 8 \times \frac{1}{8} = 1 \]

\[ a = 2r \]

\[ \text{BCC} \]

\[ 8 \times \frac{1}{8} + 1 = 2 \]

\[ a = \frac{4r}{\sqrt{3}} \]

\[ \text{FCC} \]

\[ 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4 \]

\[ a = \frac{4r}{\sqrt{2}} \]

\[ \text{HCP (ideal } c/a = 1.6) \]

\[ 4 \times \frac{1}{6} + 4 \times \frac{1}{12} + 1 = 2 \]

\[ c = 1.633a \]

\[ = 3.266r \text{ IDEAL} \]

\[ \text{HCP} = \text{HEX} + \text{BASIS} (2) \]

\[ \text{EXTRA ATOM (1 in 18)} \]

\[ c = (\frac{4}{16})a = 1.633 \]

\[ \text{HCP} \quad \text{DENSE!!} \]

\[ \text{CUBE} \]

\[ \frac{1}{2} \quad \frac{1}{6} \]
CLOSE PACKED STRUCTURES

FCC & HCP are the most DENSE STRUCTURES

they are very SIMILAR

FCC in [111] direction is an HEX LATTICE + BASIS
HCP in [110] direction is an HEX LATTICE + BASIS

Part I Fundamentals

FCC

HCP

FCC is HEX + Basis of 3

Cubic close packing

HCP is HEX + Basis of 2

Hexagonal close packing
3.6.2 Interstices in the BCC Structure

Like the FCC structure, the BCC structure also contains both octahedral and tetrahedral sites. As shown in Figure 3.6–1c, the octahedral sites are located in the center of each face and the center of each edge, giving a total of six sites per unit cell. The diameter of the octahedral site cannot be determined by examination of the face diagonal. The BCC structure is not a close-packed structure, and the atoms that surround the interstitial site are not all equidistant neighbors. When the largest possible atom occupies the octahedral position, the atoms touch only along (1 0 0) as measured from one central atom to
CRYS TALS WITH 2 ATOMS/CELL

SODIUM CHLORIDE STRU CT.  PROTOTYPE NO CC  BOD K SALT

IONIC

BLACK ATOMS FORM FCC LATTICE
WHITE ATOMS ARE SECOND ATOM
IN BASIS

OR VICE VERSA

SODIUM CHLORIDE STRUCTURE =

FCC + BASIS(2)

FCC(=)

\[ a_1 = \frac{a}{2} (1+2) \]
\[ a_2 = \frac{a}{2} (2+0) \]
\[ a_3 = \frac{a}{2} (0+1) \]

\((0, 0, 0)\) Na
\([^1/2, 1/2, 1/2]_{\text{CL}}\)

SEE PHOTOCOPY FOR EXAMPLE

OR YOU CAN CONSIDER AS

2 INTERPENETRATING FCC LATTICES

\[ a \times 2 \]

ALONG [100] DIR
FACE CENTRED
The Sodium Chloride Structure

We are forced to describe the hexagonal close-packed and diamond lattices as lattices with bases by the intrinsic geometrical arrangement of the lattice points. A lattice with a basis is also necessary, however, in describing crystal structures in which the atoms or ions are located only at the points of a Bravais lattice, but in which the crystal structure nevertheless lacks the full translational symmetry of the Bravais lattice because more than one kind of atom or ion is present. For example, sodium chloride (Figure 4.24) consists of equal numbers of sodium and chlorine ions placed at alternate points of a simple cubic lattice, in such a way that each ion has six of the other kind of ions as its nearest neighbors. This structure can be described as a face-centered cubic Bravais lattice with a basis consisting of a sodium ion at 0 and a chlorine ion at the center of the conventional cubic cell, \((a/2)(\hat{x} + \hat{y} + \hat{z})\).

![Figure 4.24](image)

The sodium chloride structure. One type of ion is represented by black balls, the other type by white. The black and white balls form interpenetrating fcc lattices.

<table>
<thead>
<tr>
<th>CRYSTAL</th>
<th>(a) (Å)</th>
<th>CRYSTAL</th>
<th>(a) (Å)</th>
<th>CRYSTAL</th>
<th>(a) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>4.02</td>
<td>RbF</td>
<td>5.64</td>
<td>CsS</td>
<td>5.69</td>
</tr>
<tr>
<td>LiCl</td>
<td>5.13</td>
<td>RbCl</td>
<td>6.58</td>
<td>CsSe</td>
<td>5.91</td>
</tr>
<tr>
<td>LiBr</td>
<td>5.50</td>
<td>RbBr</td>
<td>6.85</td>
<td>CsTe</td>
<td>6.34</td>
</tr>
<tr>
<td>LiI</td>
<td>6.00</td>
<td>RbI</td>
<td>7.34</td>
<td>SrO</td>
<td>5.16</td>
</tr>
<tr>
<td>NaF</td>
<td>4.62</td>
<td>CaF</td>
<td>6.01</td>
<td>SrS</td>
<td>6.02</td>
</tr>
<tr>
<td>NaCl</td>
<td>5.64</td>
<td>AgF</td>
<td>4.92</td>
<td>SrSe</td>
<td>6.23</td>
</tr>
<tr>
<td>NaBr</td>
<td>5.97</td>
<td>AgCl</td>
<td>5.55</td>
<td>SrTe</td>
<td>6.47</td>
</tr>
<tr>
<td>NaI</td>
<td>6.47</td>
<td>AgBr</td>
<td>5.77</td>
<td>BaO</td>
<td>5.52</td>
</tr>
<tr>
<td>KF</td>
<td>5.35</td>
<td>MgO</td>
<td>4.21</td>
<td>BaS</td>
<td>6.39</td>
</tr>
<tr>
<td>KCl</td>
<td>6.29</td>
<td>MgS</td>
<td>5.20</td>
<td>BaSe</td>
<td>6.60</td>
</tr>
<tr>
<td>KBr</td>
<td>6.60</td>
<td>MgSe</td>
<td>5.45</td>
<td>BaTe</td>
<td>6.99</td>
</tr>
<tr>
<td>KI</td>
<td>7.07</td>
<td>CaO</td>
<td>4.81</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Cesium Chloride Structure

Similarly, cesium chloride (Figure 4.25) consists of equal numbers of cesium and chlorine ions, placed at the points of a body-centered cubic lattice so that each ion

\(^{17}\) For examples see Table 4.5.
Cesium Chloride Structure: Motivic CsCl

Ionic

2 Interpenetrating Cubic

CSCL = Eubic + Basis (2)

\[ a_1 = a \hat{x}, \quad a_2 = a \hat{y}, \quad a_3 = a \hat{z} \]

\[ \frac{a}{2} (0, 0, 0), \quad \frac{a}{2} (1, 1, 1) \]

C22

Can be seen as BCC with black/white alternating atoms.
Some Important Examples of Crystal Structures and Lattices with Bases

has eight of the other kind as its nearest neighbors. The translational symmetry of this structure is that of the simple cubic Bravais lattice, and it is described as a simple cubic lattice with a basis consisting of a cesium ion at the origin \(0\) and a chlorine ion at the cube center \((a/2)(x + y + z)\).

Figure 4.25
The cesium chloride structure. One type of ion is represented by black balls, the other type by white. The black and white balls form interpenetrating simple cubic lattices.

<table>
<thead>
<tr>
<th>Table 4.6</th>
<th>SOME COMPOUNDS WITH THE CESIUM CHLORIDE STRUCTURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRYSTAL</td>
<td>(a (\text{Å}))</td>
</tr>
<tr>
<td>Cesium</td>
<td>4.12</td>
</tr>
<tr>
<td>Chlorine</td>
<td>4.29</td>
</tr>
<tr>
<td>Strontium</td>
<td>4.57</td>
</tr>
</tbody>
</table>

The Zincblende Structure

Zincblende has equal numbers of zinc and sulfur ions distributed on a diamond lattice so that each has four of the opposite kind as nearest neighbors (Figure 4.18). This structure is an example of a lattice with a basis, which must be so described both because of the geometrical position of the ions and because two types of ions occur.

<table>
<thead>
<tr>
<th>Table 4.7</th>
<th>SOME COMPOUNDS WITH THE ZINCBLENDE STRUCTURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRYSTAL</td>
<td>(a (\text{Å}))</td>
</tr>
<tr>
<td>CuF</td>
<td>4.26</td>
</tr>
<tr>
<td>CuCl</td>
<td>5.41</td>
</tr>
<tr>
<td>CuBr</td>
<td>5.69</td>
</tr>
<tr>
<td>CuI</td>
<td>6.04</td>
</tr>
<tr>
<td>AgI</td>
<td>6.47</td>
</tr>
<tr>
<td>BeS</td>
<td>4.85</td>
</tr>
<tr>
<td>BeSe</td>
<td>5.07</td>
</tr>
<tr>
<td>BeTe</td>
<td>5.54</td>
</tr>
<tr>
<td>MnS (red)</td>
<td>5.60</td>
</tr>
<tr>
<td>MnSe</td>
<td>5.82</td>
</tr>
</tbody>
</table>

\footnote{For examples see Table 4.6.}

\footnote{For examples see Table 4.7.}
**Diamond & Zinc Blende**

Table 4.3

<table>
<thead>
<tr>
<th>Element</th>
<th>Cube Side $a$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (diamond)</td>
<td>3.57 $\pm$ 0.04</td>
</tr>
<tr>
<td>Si</td>
<td>5.43</td>
</tr>
<tr>
<td>Ge</td>
<td>5.66</td>
</tr>
<tr>
<td>α-Sn (grey)</td>
<td>6.49</td>
</tr>
</tbody>
</table>

**Fcc ($\vec{a}_1, \vec{a}_2, \vec{a}_3$) + Basis (Z)**

$\mathbf{Zn}^{++}$ $\mathbf{S}^{--}$

**Ionic $\leftrightarrow$ ZnS**

Basis

$\frac{a}{4} (111)$ **Sulfur**

$\frac{a}{4} (111)$ **Zinc**

which $\rightarrow$ **GaAs** *(semiconductor)*

Can be (quantum dots)*

**C2v**

**Assignment**

- Electrospun (92)
- Crystobalite (92-93)
- Methane Solid (99)
- Polyethylene (95-95)

**Liquid Crystals**

(Long molecules tilted with external fields (electric))
 Fluorite - Antifluorite

**Fluorite**

\[ = \text{FCC} + \text{Interstitial} \]
\[ = \text{FCC} + \text{Basis} \]

Twice as many interstitials:

- \( \text{CaF}_2 \), \( \text{Al}_2 \text{O}_3 \), \( \text{MX}_2 \)
  - \( \text{Metal} \)

**Antifluorite**

Some \( \text{Fluorite} \)

But Metal Inverted

\( \text{Li}_2 \text{O} \)

- C2S
**PEROVSKITE STRUCTURE**

Usually $\text{ABO}_3$

- $A, B$ metals
- $O$ anions

Oxygen $5\times 4$; all $O^2-$
- One metal gives 4
- Other gives 2

A total of 6 electrons must come from the metals

---

**CUBIC CALCIUM (A) STRUCTURE**

- Calcium in the faces (6) = Octahedra
- Metal Titanium (B) in the centre

---

**BARIUM TITANATE**

Offset between top plane of $\text{Ba}^+$ ions and top center $O^2-$ ion

Offset between $\text{Ti}^{4+}$ and midplane

---

**Figure 3.7-8** The tetragonal unit cell of $\text{BaTiO}_3$ shown (a) in 3-D, and (b) in 2-D.

---

**C26**
Many ceramic materials are also in the form of polycrystalline solids. With some inorganic solids, such as silica, it can be relatively easy to cool the material sufficiently quickly that crystal formation does not occur. Hence, these materials may be either crystalline or noncrystalline (amorphous), depending on thermal history. The structures of noncrystalline and partially crystalline materials will be discussed in Chapter 6.

Polymers are unique in that because of the nature of long-chain molecules, they can form structures that are entirely crystalline. Hence, polymers are either semicrystalline or amorphous. Although there are no commercial single-crystal polymers, Spectra® is one of the strongest materials known, has a structure similar to that of a single crystal. Spectra consists of long polyethylene chains that are processed in such a way that the molecules are highly aligned. Crystallinity is very high, and defects, principally ends, are randomly dispersed through the continuous crystal.

Few materials are used in a single-crystal form; however, those few are commercially significant. Single-crystal materials have no grain boundaries, so they offer unique chemical, optical, and electrical properties. Single-crystal quartz (SiO₂) and perovskites are used as transducers in a variety of applications, such as in high quality receivers and pickups (phonograph cartridges). Single-crystal germanium and silicon are used extensively in the microelectronics industry. Single-crystal nickel alloys are used in turbine blades in high-performance jet aircraft. Sapphire (Al₂O₃) and diamond (C) single crystals are precious stones.

3.10 ALLOTROPY AND POLYMORPHISM

Many materials can exhibit crystal structures that change from one unit cell to another under certain conditions, a phenomenon described as allotropy or polymorphism.

C27
X-ray Diff (Light)

in phase + in phase → constructive interference

out of phase → destructive

Phase or antiphase: depends on the distance travelled

On a crystal, planes reflect like mirrors

\[ \sqrt{V} = \frac{2 \lambda d \sin \theta}{\sin \phi} \]

\( d \sin \theta = n \lambda \) → positive interference

Bragg Law
But which plane am I toting?
DUNNO!

\[ \text{powder} \rightarrow \text{crystal} \rightarrow \text{powder} \]

For \( (111) \)

\[ d_{(111)} = \frac{a\sqrt{2}}{3} \]

For Fcc

\[ d_{(hke)} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} \]

\[ \text{intensity} (100) \quad (110) \quad (200) \quad (210) \]

One for every plane

IF SOMETHING IS MISSING?
WHAT ABOUT MISSING LINES

EXAMPLE

TAKE CUBIC \( \odot \) \( 0,0,0 \) YOU HAVE LINE \( \text{for } d(100) \)

\[ \begin{array}{c}
\text{Positive} \\
\text{second ray has extra path}
\end{array} \]

\[ \Rightarrow \text{second ray has extra path} = \frac{1}{m}h \]

3 ray has extra \( \frac{1}{m}h \)
but 2 ray has \( \frac{1}{2}m \frac{1}{2} \)

\[ \Rightarrow \text{DESTRUCTIVE DIFFRACTION} \]

same for FCC \( ^{(100)} \)

\[ \Rightarrow \text{RULES BCC: } (h+k+2) \text{ even } \Rightarrow \text{LINE } (h,k,2) \]

FCC: \( h,k,l \) all even or one odd \( (h,k,l) \)

---

All X-RAY TECHNOLOGY IS AN EVOLUTION OF THESE IDEAS

\[ \Rightarrow \text{EXTREMELY POWERFUL} \]

---

\( C30 \)