Chapter 3
The structure of crystalline solids

Hw: 4, 6, 10, 14, 18, 21, 26, 31, 35, 39, 42, 43, 46, 48, 49, 51, 56, 61 Due Wensday 14/10/2009
Quiz1 on Wensday 14/10/2009

Why study the structure of crystalline solids?

- Properties of some materials are directly related to their crystal structure.
- Significant property differences exist between crystalline and non-crystalline materials having the same composition.

Crystal structures

Fundamental concepts

- The atoms or ions form a regular repetitive, gridlike pattern, in 3D. These materials are called crystalline materials.
- A material displays a SRO if the special arrangement of the atoms extends only to the atom’s nearest neighbors.
- A glass individual tetrahedral units are joined together in a random manner. Thus beyond the basic unit of tetrahedral, there is no periodicity in their arrangement.
- A lattice: collection of points called lattice points, arranged in a periodic pattern so that the surroundings of each point in the lattice are identical.

Unit Cells

- Atoms arrange themselves into an ordered, 3d pattern called a crystal.
- The small repeating volume within a crystal is called a unit cell.
- Each cell has all geometric features found in the total crystal.

Metallic crystal structures

- The atomic bonding is metallic and thus non-directional in nature
- **Lattice Parameter:** describe the size and shape of the unit cell, include the dimensions of the sides of the unit cell and the angles between the sides (F3.4).

The FCC

- \[ a = 2R\sqrt{2} \]
- Table 3.1: atomic radii and crystal structures of 16 metals
- **FCC:** AL, Cu, Pb, Ag, Ni
- **4 atoms per unit cell**
- **FCC compounds**
  \[ (a_{\text{FCC}})_{\text{NaCl}} = 2(r_{\text{Na}^+} + r_{\text{Cl}^-}) \]
- Coordination Number (CN): the # of atoms touching a particular atom, or the # of nearest neighbors for that particular atom
- For FCC, CN=12
- \[ \text{APF} = \frac{\text{(No. of atoms/cell)(volume of each atom)}}{\text{volume of unit cell}} \]
- APF for FCC = 0.74
- Metals typically have relatively large APF to max the shielding provided by the free electron cloud.

BCC

- 2 atoms/unit cell.
  \[ a = \frac{4r}{\sqrt{3}} \]
- CN = 8
- APF = 0.68

Hexagonal Closed-Packed Structure (HCP)

- See F3.16.
Example 3.1: calculate the volume of an FCC in terms of the atomic radius \( R \)

Example 3.2: show that APF for FCC is 0.74

**Density**

\[
\text{Density} = \frac{(\text{No. of atoms/cell})(\text{atomic mass})}{(\text{volume of unit cell})(N_A)}
\]

\[
= \frac{(\text{atoms})(\text{g/mole})}{(\text{cm}^3)(\text{atoms/mole})} = \frac{\text{g}}{\text{cm}^3}
\]

Example 3.3: Cu, \( R = 0.128\text{nm} \), FCC, A=63.5g/mole. Compute theoretical density and compare with the measured density.

**Allotropic or Polymorphic Transformations**

- Polymorphism: Materials that can have more than one crystal structure.
- When found in pure elements the condition is termed Allotropy.
- A volume change may accompany the transformation during heating or cooling.
- This volume change may cause brittle ceramic materials to crack and fail.
- Ex: zirconia (ZrO\(_2\)). At 25\(^{\circ}\)C is monoclinic. At 1170\(^{\circ}\)C, monoclinic zirconia transforms into a tetragonal structure. At 2370\(^{\circ}\)C, it transforms into a cubic form.
- Ex: Fe has BCC at RT which changes to FCC at 912C

**Crystal systems**
• 7 possible systems (T3.2) and (F3.4).

Crystallographic Points, Directions, and Planes

Point Coordinates (F3.5)
• Example 3.4 and 3.5

Crystallographic Directions
• Metals deform in directions along which atoms are in closest contact.
• Many properties are directional.
• Miller indices are used to define directions.

• Procedure of finding Miller indices:
  a. Using a RH coordinate system, find coordinates of 2 points that lie along the direction.
  b. Subtract tail from head.
  c. Clear fractions.
  d. Enclose the No’s in [ 634 ], -ve sign (bar above no.)
• A direction and its –ve are not identical.
• A direction and its multiple are identical.
• Example 3.6 and 3.7

Families of directions
• Identical directions: any directional property will be identical in these directions.

<111> = [111], [111], [111], [111], [111], [111], [111], [111]
• Ex: all parallel directions possess the same indices. Sketch rays in the [120] direction that pass through locations: 0,0,0, and 0,1,0 and ½,1,1
• Directions in cubic crystals having the same indices without regard to order or sign are equivalent

Miller-Bravais indices for hexagonal unit cells
• Directions in HCP: 3-axis or 4-axis system.
• We determine No. of lattice parameters we must move in each direction to get from tail to head of direction, while for consistency still making sure that \( h + k = -i \).
• Conversion from 3 axis to 4 axis:
  ▪ \( h = \frac{n}{3}(2h` - k`) \)
  ▪ \( k = \frac{n}{3}(2k` - h`) \)
  ▪ \( i = -\frac{n}{3}(h` + k`) \)
  ▪ \( l = nl` \)
• \( h`, k`, \) and \( l` \) are the indices in the 3 axis system.
• After conversion, clear fraction or reduce to lowest integer for the values of \( h, k, i, \) and \( l \).
• Example.

**Crystallographic planes**
- Crystal contains planes of atoms that influence properties and behavior of a material.
- Metals deform along planes of atoms that are most tightly packed together.
- The surface energy of different faces of a crystal depends upon the particular crystallographic planes.

**Calculation of planes:**
  a. Identify points at which plane intercepts \( x, y, z \) coordinates. If plane passes in origin of coordinates; system must be moved.
  b. Take reciprocals of intercepts
  c. Clear fractions but do not reduce to lowest integer ( ).

**Note:**
- Planes and their –ve are identical
- Planes and their multiple are not identical.
- For cubic crystals, planes and directions having the same indices are perpendicular to one another
Example 3.8 and Example 3.9
Atomic arrangements and Families of planes 
- 2 or more planes may belong to the same family of planes (all have the same planner density)
- In cubic system only, planes having the same indices irrespective of order and sign are equivalent.
  
  \[ \{100\} = (100), (010), (001), (\bar{1}00), (0\bar{1}0), (00\bar{1}) \] in simple cubic
- Ex: \{111\} is a family of planes that has 8 planes.

Repeat Distance, Linear density, and Packing Fraction
- Repeat distance: distance between lattice points along the direction
- Repeating dist betw equiv sites differs from direction to direction.
- Ex: in the [111] of a BCC metal, lattice site is repeated every 2R.
  
  \[ \text{Ex: repeating dist in } [110] \text{ for a BCC is } a\sqrt{2}, \text{ but } \frac{a}{\sqrt{2}} \text{ for FCC.} \]
- Linear density is the No of atoms per unit length along the direction.
- Equivalent directions have identical LDs
- With regard to the number of atoms, it is necessary to take into account the sharing of atoms with adjacent unit cells
- In general, LD equals to the reciprocal of the repeat distance
- Example: find linear density along [110] for FCC.

Planner densities of atoms
- Need for plastic deformation
  
  Planner density = \[ \frac{\text{No. of atoms}}{\text{unit area}} \]
- Planar packing fraction: fraction of area of the area of a plane actually covered by atoms.
• In cubic systems, a direction that has the same indices as a plane is perpendicular to that plane.
• **Ex:** how many atoms per mm\(^2\) are there on the (100) and (111) planes of lead (FCC)
• **LD and PD are important considerations relative to the process of slip.**
  • Slip is the mechanism by which metals plastically deform.
  • Slip occurs on the most closely packed planes along directions having the greatest LD.

**Closed Packed Planes and directions**
• In HCP, close packed planes are (0001) and (0002) named basal planes.
• An HCP unit cell is built up by stacking together CPPs in a …ABABAB… stacking sequence (F3.27).
• Atoms in plane B (0002) fit into the valleys between atoms on plane A (0001).
• The center atom in a basal plane is touched by 6 other atoms in the same plane, 3 atoms in a lower plane, and 3 atoms in an upper plane. Thus, CN of 12.
• In FCC, CPPs are of the form \{111\} (F3.28).
• When parallel (111) planes are stacked, atoms in plane B fit over valleys in plane A and atoms in plane C fit over valleys in both A and B. the 4\(^{th}\) plane fits directly over atoms in A. Therefore, a stacking sequence …ABCABCABC… is produced using the (111) plane. CN is 12.
• Unlike the HCP unit cell, there are 4 sets of nonparallel CPPs: (111), (111\^`), (11\^`1), and (1\^`11) in the FCC.

**LRO**
• Single crystal materials. The properties of single crystal materials depend upon the chemical composition and specific directions within the crystal.
• Polycrystalline material. Many properties of polycrystalline materials depend upon the physical and chemical char of both grains and grain boundaries.
• Liquid crystals (LC): polymeric materials that have a special type of order. LC polymers behave as amorphous materials in one state. When an external stimulus is provide some polymer molecules undergo alignment and form small regions that are crystalline.

3.2 Amorphous Materials
• A material that exhibits only a SRO of atoms or ions, non-crystalline one. Ex: silicate glass.
• Crystallization of glasses can be controlled by deliberately nucleating ultrafine crystals into amorphous glasses. The resultant materials, known as glass ceramics can be made up to 99.9% crystalline and are quite strong.
• Many plastics are also amorphous.
• Metallic glasses: liquid metals cooled at a very high cool rate of  > 10^6 °C/s.

Isotropic and Anisotropic behavior
• A material is anisotropic if its properties depend on the crystallographic direction along which the property is measured.
• If the properties are identical in all directions, the material is isentropic.
• Most polycrystalline materials will exhibit isotropic properties.

Inter-planar spacing:
• Distance between adjacent parallel planes of atoms with the same Miller indices, d_{hkl}. In cubic cells, it’s given by

\[
d_{hkl} = \frac{a_o}{\sqrt{h^2 + k^2 + l^2}}
\]
• **Ex:** calc dist between adj (111) planes in gold which has a lattice constant of 4.0786Å.

**X-ray diffraction**

• X-rays is electromagnetic radiation with wavelengths between 0.1Å and 100Å, typically similar to the inter-atomic distances in a crystal.

X-ray diffraction is an important tool used to:

• Identify phases by comparison with data from known structures
• Quantify changes in the cell parameters, orientation, crystallite size and other structural parameters
• Determine the (crystallographic) structure (i.e. cell parameters, space group and atomic coordinates) of novel or unknown crystalline materials.

**Bragg’s law**

• An X-ray incident upon a sample will either:

  1. Be transmitted, in which case it will continue along its original direction
  2. Be scattered by the electrons of the atoms in the material. We are primarily interested in the peaks formed when scattered X-rays constructively interfere.

• When two parallel X-rays from a coherent source scatter from two adjacent planes their path difference must be an integer number of wavelengths for constructive interference to occur.

Path difference = \( n \lambda = 2d \sin \theta \)

\[ \lambda = 2 \ d_{hkl} \sin \theta_{hkl} \]

• The angle between the transmitted and Bragg diffracted beams is always equal to 2θ as a consequence of the geometry of the Bragg condition. This angle is readily obtainable in experimental situations
and hence the results of X-ray diffraction are frequently given in terms of $2\theta$.

- The diffracting plane might not be parallel to the surface of the sample in which case the sample must be tilted to fulfill this condition.

**Powder diffraction**

- A powder is a polycrystalline material in which there are all possible orientations of the crystals so that similar planes in different crystals will scatter in different directions.

- In single crystal X-ray diffraction there is only one orientation. This means that for a given wavelength and sample setting relatively few reflections can be measured: possibly zero, one or two.
- As other crystals are added with slightly different orientations, several diffraction spots appear at the same $2\theta$ value and spots start to appear at other values of $2\theta$.
- Rings consisting of spots and then rings of even intensity are formed.
- A powder pattern consists of rings of even intensity from each accessible reflection at the $2\theta$ angle defined by Bragg's Law.
The **diffractometer** is an apparatus used to determine angles at which diffraction occurs for powdered specimens; Fig 3.3W. A specimen S in the form of a flat plate is supported so that rotations about the axis labeled O are possible.

As the counter moves at constant angular velocity, a recorder automatically plots diffracted beam intensity as a function of $2\theta$. Fig 3.4W shows a diffraction pattern for a powdered specimen of lead.

The high-intensity peaks result when the Bragg diffraction condition is satisfied by some set of crystallographic planes. These peaks are plane-indexed in the figure.

The unit cell size and geometry may be resolved from the angular positions of the diffraction peaks.

Arrangement of atoms within the unit cell is associated with the relative intensities of these peaks.
EXAMPLE PROBLEM 3.1W
For BCC iron, compute (a) the inter-planar spacing, and (b) the diffraction angle for the (220) set of planes. The lattice parameter for Fe is 0.2866 nm (2.866 Å). Also, assume that monochromatic radiation having a wavelength of 0.1790 nm (1.790 Å) is used, and the order of reflection is 1.

Ex: chromium radiation of $\lambda = 2.291\text{Å}$ produced a diffracted line on a film at $2\theta = 58.2^\circ$. What is the inter-planner spacing of crystallographic plane that produced the diffracted line?

Coordination number
- Refers to no. of 1st neighbors that an atom has.
- 2 factors affect CN:
  1. Covalence: no. of covalent bonds around an atom depends on no. of its valence electrons. Ex: $\text{O}_2$, CN = 2
  2. Efficient atomic packing in ionic bonds: ionic compounds generally have high CN (as many neighbors as possible without introducing the strong mutual repulsion forces between ions of like charges).

3.6 Interstitial Sites
- See F3.29.
- Interstitial atoms or ions whose radii are slightly larger than the radius of the interstitial site may enter that site, pushing the surrounding atoms slightly apart.
- Atoms whose radii are smaller than the radius of the hole are not allowed to fit into the interstitial site, because the ion would rattle around in the site.
• If the interstitial atom becomes too large, it prefers to enter a site having a larger CN (T3.6).
• Example

**T3.6: The CN and the Radius Ratio**

<table>
<thead>
<tr>
<th>CN</th>
<th>Interstitial</th>
<th>r/R</th>
<th>Coordination Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Linear</td>
<td>0-0.155</td>
<td></td>
</tr>
<tr>
<td>3-fold</td>
<td>Center of triangle</td>
<td>0.155-0.225</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Center of tetrahedron</td>
<td>0.225-0.414</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Center of octahedron</td>
<td>0.414-0.732</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Center of cube</td>
<td>0.732-1</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

Example: show that 0.15 is the min ratio for a CN of 3.

**3.7 Crystal structures of ionic materials**

• Many ionic crystals can be viewed as being generated by closed packing of larger anions. Anions form tetrahedral or octahedral, allowing the cations (smaller ions) to fit into their appropriate interstitial sites of the closed packed anions.
• The ratio of the sizes of the ionic radii of anions and cations influences both the manner of packing and the CN (T3.6).
• As a general rule, anions are larger than cations.
• The radii of cations and anions also depend upon the CN. Ex: the radius of Al$^{+3}$ is 0.39Å when the CN is 4. However, the radius of Al$^{+3}$ is 0.53Å when the CN is 6.
• The CN for cations is the # of nearest anions and vice versa.
**Electrical Neutrality**

- For a valence of 1 for both the cation and anion, the formula for the compound is AX.
- If the valence of the cation is +2 and that of the anion is -1, then twice as many anions must be present and the formula is AX₂.
- The structure of the AX₂ compound must assure that the CN of the cation is twice the CN of the anion.

**Connection between anion polyhedra**

- The coordination polyhedra will share corners, as opposed to faces or edges. This is because in corner sharing polyhedra electrostatic repulsion between cations is reduced considerably and this leads to the formation of a more stable crystal structure.
- The lattice constants of ceramic materials tend to be larger than those for metallic materials because electrostatic repulsion between ions prevents close packing of both anions and cations
- See (F3.31).

**Cesium Chloride Structure**

- CsCl is SC (F3.32a), with the cubic interstitial site filled by Cl⁻ anion.
- The radius ratio \( \frac{r_{Cs}^+}{r_{Cl}^-} = \frac{0.167 \text{nm}}{0.181 \text{nm}} = 0.92 \), dictates that the CsCl has a CN of 8.
- 2 ions: one Cs⁺ and one Cl⁻ associated with each lattice point (basis of 2).

**NaCl Structure**
$\frac{r_{Na}^+}{r_{Cl}^-} = \frac{0.097 nm}{0.181 nm} = 0.536$. Therefore, each anion and cation must have a CN of 6.

- With the FCC structure, Cl$^-$ ions at FCC positions and Na$^+$ at the 4 octahedral sites (F3.32b).
- We can consider this structure to be FCC with 2 ions: one Na$^{+1}$ and Cl$^{-1}$ associated with each lattice point.

**Zinc Blend Structure**
- Although Zn ions have a charge of +2 and S ions have a charge of -2, ZnS cannot have the NaCl structure, because $\frac{r_{Zn}^{+2}}{r_{S}^{-2}} = \frac{0.074 nm}{0.184 nm} = 0.402$.
- Therefore, CN of 4, which means that the S ions enter tetrahedral sites in a unit cell (F3.33).
- The FCC structure, with Zn cations at the normal lattice points and S anions at half of the tetrahedral sites, can accommodate the restrictions of both charge balance and CN.

**Fluorite Structure**
- The fluorite structure is FCC, with anions located at all 8 of the tetrahedral positions (F3.34).
- Thus, there are 4 cations and 8 anions per cell and the ceramic compound must have the formula AX$_2$.
- The CN of Ca ion is 8, but that of the fluoride ions is 4.

**3.8 Covalent Structures**

**Diamond Cubic structure**
- Carbon bonded by 4 covalent bonds and produce a tetrahedron.
- The CN for each atom is only 4.
- As these tetrahedral groups are combined, a large cube can be constructed (F3.38b).
• This large cube contains 8 smaller cubes that are the size of the tetrahedral cube. However, only 4 of the cubes contain tetrahedral.
• The large cube is the diamond cube (DC) unit cell.
• The atoms on the corners of the tetrahedral cubes provide atoms at the regular FCC lattice points. However, 4 additional atoms are present within the DC unit from the atoms in the center of the tetrahedral cubes.
• We can describe DC crystal structure as an FCC lattice with 2 atoms associated with each lattice point (basis of 2). Therefore, there must be 8 atoms per unit cell.

**Allotropic transformation**

• Materials that can have more than one crystal structure are called allotropic or polymorphic.
• Ex: iron is bcc at RT, FCC at high temp.

**Ex:** calculate change in volume that occurs when bcc iron is heated and changes to fcc iron. At the transformation temp, \( a_o \) of bcc is 2.863A and \( a_o \) of fcc is 3.591A.