MME131: Lecture 7

Packing sequences in crystals

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Today’s topics

- Packing sequences in crystals
- Properties inferred to crystal by its atomic packing

References:
Principles of atomic packing

- Many crystals structures can be described as stacking arrangements atoms in 2-D lattices or, nets.

- Structures based on the square net
  - Simple cubic
  - Body-centred cubic

- Structures based on the close-packed net
  - Face-centred cubic
  - Hexagonal close-packed

16 lattice points in shaded area
18.475 lattice points in shaded area

more efficient packing in the closed-packed net
1. Bottom layer: “A"
2. Place successive layers over the “B” or “C” positions
Structures based on close-packed net

Hexagonal Close-Packed (HCP) Cell

Face-Centred Cubic (FCC) Cell
Why are we interested in packing sequence of crystals?

- It is easier for crystal lattice deformation to occur in the direction that is close packed.
- The number and direction of close-packed planes vary according to packing sequence of crystal.

Density of crystals

1. Theoretical bulk density of crystal
2. Planar density of atoms in a plane of crystal
3. Linear density of atoms along a direction of crystal
Theoretical bulk density of crystals

\[ \rho = \frac{\text{mass of atoms}}{\text{cell volume}} = \frac{n M}{V_C} = \frac{n A}{V_C N_A} \]

- \(\rho\): bulk density
- \(n\): number of atoms per unit cell
- \(M\): atomic weight (g/mol)
- \(V_C\): volume of unit cell (cm\(^3\)/unit cell)
- \(A\): atomic weight (g/mol)
- \(N_A\): Avogadro's number (6.023 x 10\(^{23}\) atoms/mol)

Example
Determining the Density of FCC Copper

Copper has an atomic radius of 0.128 nm, an FCC crystal structure, and an atomic weight of 63.5 g/mol. Compute its bulk density.

\[ \rho = \frac{n A_{Cu}}{V_C N_A} = \frac{n A_{Cu}}{a^3 N_A} = \frac{n A_{Cu}}{(2\sqrt{2} r)^3 N_A} \]

\[ = \frac{[4 \text{ atoms/cell} \times [63.5 \text{ g/mol}]}{[2\sqrt{2} (1.28 \times 10^{-8}) \text{ cm}^3/\text{unit cell}]^3 \times [6.023 \times 10^{23} \text{ atoms/mol}]} \]

\[ = 8.89 \text{ g/cm}^3 \]
### Characteristics of Selected Elements at 20C

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>At. Weight (amu)</th>
<th>Density (g/cm³)</th>
<th>Crystal Structure</th>
<th>Atomic radius (nm)</th>
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<tbody>
<tr>
<td>Aluminum</td>
<td>Al</td>
<td>26.98</td>
<td>2.71</td>
<td>FCC</td>
<td>0.143</td>
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<tr>
<td>Argon</td>
<td>Ar</td>
<td>39.95</td>
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<tr>
<td>Barium</td>
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<td>137.33</td>
<td>3.5</td>
<td>BCC</td>
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<td>Beryllium</td>
<td>Be</td>
<td>9.012</td>
<td>1.85</td>
<td>HCP</td>
<td>0.114</td>
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<tr>
<td>Boron</td>
<td>B</td>
<td>10.81</td>
<td>2.34</td>
<td>Rhomb</td>
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<tr>
<td>Bromine</td>
<td>Br</td>
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<tr>
<td>Cadmium</td>
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<td>Calcium</td>
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<td>Carbon</td>
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<td>2.25</td>
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<td>Cesium</td>
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<td>BCC</td>
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<td>7.19</td>
<td>BCC</td>
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<td>Cobalt</td>
<td>Co</td>
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<td>HCP</td>
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<tr>
<td>Copper</td>
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<td>8.94</td>
<td>FCC</td>
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<tr>
<td>Flourine</td>
<td>F</td>
<td>19.00</td>
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<tr>
<td>Gallium</td>
<td>Ga</td>
<td>69.72</td>
<td>5.90</td>
<td>Ortho.</td>
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<tr>
<td>Germanium</td>
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<td>72.59</td>
<td>5.32</td>
<td>Dia. cubic</td>
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<tr>
<td>Gold</td>
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<tr>
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<tr>
<td>Hydrogen</td>
<td>H</td>
<td>1.008</td>
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</table>

### Why \( \rho_{\text{metals}} \geq \rho_{\text{ceramics}} \geq \rho_{\text{polymers}} \)?

- Metals have...
  - close-packing (metallic bonding)
  - large atomic masses

- Ceramics have...
  - less dense packing (covalent bonding)
  - often lighter elements (oxygen, carbon)

- Polymers have...
  - poor packing (often amorphous)
  - lighter elements (C, H, O)

- Composites-average values
Interstitial sites in crystals

- These are the small holes between the “normal” atoms or ions in a crystal into which another - usually impurity - atom or ion is placed.

- **Cubic site** - An interstitial position that has a coordination number of eight, that is, it touches eight neighbouring atoms or ions. Usually found in SC structure.

- **Octahedral site** - An interstitial position that has a coordination number of six (3 atoms in two adjacent planes). Occurs in BCC, FCC and HCP structures.

- **Tetrahedral site** - An interstitial position that has a coordination number of four (3 in one plane, 1 in the adjacent plane). Occurs in BCC, FCC and HCP structures.

The location of the interstitial sites in cubic unit cells. Only representative sites are shown.
FCC structure showing tetrahedral and octahedral position

Tetrahedral hole

Octahedral hole

Tetrahedral interstice

Octahedral interstice
Why do we care about the holes in crystal lattices?

- Alloying elements/impurities can fit in the holes
  - In steels, C atoms fit into the holes in the Fe lattice
  - Most metals are permeable to hydrogen and helium

- Ceramic crystals are made with one ion forming the lattice, and the other ion in the holes

- The ions need to fit snugly, so they squeeze into holes that are not quite big enough
  - Funny things happen if the hole size is bigger than the size of inclusion atom!! (as in barium titanate)

Example
Calculation of octahedral interstitial site

From the figure,

\[ 2(2R)^2 = (2R + 2r)^2 \]
\[ 2R\sqrt{2} = 2R + 2r \]
\[ r = (\sqrt{2} - 1)R \]
\[ r/R = 0.414 \]
We wish to produce a radiation-absorbing wall composed of 10,000 lead balls, each 3 cm in diameter, in a face-centered cubic arrangement.

We decide that improved absorption will occur if we fill interstitial sites between the 3-cm balls with smaller balls.

Design the size of the smaller lead balls and determine how many are needed.

### Example

**Design of a radiation-absorbing wall**

We wish to produce a radiation-absorbing wall composed of 10,000 lead balls, each 3 cm in diameter, in a face-centered cubic arrangement.

We decide that improved absorption will occur if we fill interstitial sites between the 3-cm balls with smaller balls.

Design the size of the smaller lead balls and determine how many are needed.
SOLUTION

First, we can calculate the diameter of the octahedral sites located between the 3-cm diameter balls. Figure shows the arrangement of the balls on a plane containing an octahedral site.

\[
AB = 2R + 2r = 2R\sqrt{2} \\
r = \sqrt{2R} - R = (\sqrt{2} - 1) R \\
r/R = 0.414
\]

Since \( r/R = 0.414 \), the radius of the small lead balls is:

\[
r = 0.414 \times R = (0.414)(3 \text{ cm}/2) = 0.621 \text{ cm}
\]

Now, there are four octahedral sites in the FCC arrangement, which also has four lattice points. Therefore, we need the same number of small lead balls as large lead balls, or 10,000 small balls.

Single crystals vs. polycrystals

- Some engineering applications require single crystals:
  - Gems
  - Diamond single crystals for abrasives
  - Ni-base alloys single crystals for turbine blade

- When the repeated arrangement of atoms in a crystalline solid extends throughout the entirety of the specimen without interruption, the result is a single crystal.

- If the extremities of a single crystal are permitted to grow without any external constraint, the crystal will assume a regular geometric shape having flat faces.

- Within the past few years, single crystals have become extremely important in many of our modern technologies.
Most engineering materials are **polycrystals**.

They are composed of a collection of many small crystals or **grains**; each grain is itself a single crystal, which is typically range from 1 nm to 2 cm (from a few to $10^8$ atomic layers).

Initially, small crystals or nuclei form at various positions. These have **random crystallographic orientations**.

There exists some atomic mismatch within the region where two grains meet; this area is called a **grain boundary**.

Properties of **single crystal** vary with direction, resulting "**anisotropic**" material.

Properties of **polycrystal** may or may not vary with direction.

For randomly oriented grains (resulted during casting, for example), properties are "**isotropic**" ($E \approx 210$ GPa).

If grains are textured (using rolling, etc.), anisotropy resulted.
Polymorphic and allotropic transformations

- Some materials may exist in more than one crystal structure in the solid state. This is called polymorphism.
  Example: Iron, carbon, steels, silica, zirconia.

- If the material is an elemental solid, it is called allotropic material.
  Example: Fe, C.

- The mechanisms and kinetics of the phase transformation (in the solid state) is vitally important in materials science and engineering for modifying the properties of material.

Example: Calculating volume changes in polymorphs of zirconia

Calculate the percent volume change as zirconia transforms from a tetragonal to monoclinic structure.

The lattice constants for the monoclinic unit cells are:

\[ a = 5.156, \quad b = 5.191, \quad c = 5.304 \text{ Å} \]

The angle \( \beta \) for the monoclinic unit cell is 98.9°.

The lattice constants for the tetragonal unit cell are:

\[ a = 5.094, \quad c = 5.304 \text{ Å} \]

Does the zirconia expand or contract during this transformation? What is the implication of this transformation on the mechanical properties of zirconia ceramics?
SOLUTION

The volume of a tetragonal (TG) unit cell is given by
\[ V = a^2c = (5.094)^2 (5.304) = 134.33 \text{ Å}^3. \]

The volume of a monoclinic (MC) unit cell is given by
\[ V = abc \sin \beta = (5.156) (5.191) (5.304) \sin(98.9) = 140.25 \text{ Å}^3. \]

Thus, there is an expansion of the unit cell as ZrO$_2$ transforms from a TG to MC form.

The percent change in volume
\[ \frac{\text{final volume} - \text{initial volume}}{\text{initial volume}} \times 100 = \frac{140.25 - 134.33}{140.25} \times 100 = 4.21\%. \]

Most ceramics are very brittle and cannot withstand more than a 0.1% change in volume. The conclusion here is that

ZrO$_2$ ceramics cannot be used in their monoclinic form

since, when zirconia does transform to the tetragonal form, it will most likely fracture. Therefore, ZrO$_2$ is often stabilized in a cubic form using different additives such as CaO, MgO, and Y$_2$O$_3$.

Example

Designing a sensor to measure volume change

To study how iron behaves at elevated temperatures, we would like to design an instrument that can detect (with a 1% accuracy) the change in volume of a 1-cm$^3$ iron cube when the iron is heated through its polymorphic transformation temperature.

At 911°C, iron is BCC, with a lattice parameter of 0.2863 nm. At 913°C, iron is FCC, with a lattice parameter of 0.3591 nm. Determine the accuracy required of the measuring instrument.
The volumes of BCC and FCC iron unit cells before transforming are:

\[ V_{\text{BCC}} = a_0^3 = (0.2863 \text{ nm})^3 = 0.023467 \text{ nm}^3 \]
\[ V_{\text{FCC}} = a_0^3 = (0.3591 \text{ nm})^3 = 0.046307 \text{ nm}^3 \]

But this is the volume occupied by 4 iron atoms, as there are 4 atoms per FCC unit cell. Therefore, we must compare two BCC cells (with a volume of \(2(0.023467) = 0.046934 \text{ nm}^3\)) with each FCC cell.

The percent volume change during transformation is:

\[
\text{Volume change} = \left( \frac{0.046307 - 0.046934}{0.046934} \right) \times 100 = -1.34\%
\]

The 1-cm\(^3\) cube of iron contracts to \((1 - 0.0134) = 0.9866 \text{ cm}^3\) after transforming; therefore, to assure 1% accuracy, the instrument must detect a change of:

\[ \Delta V = (0.01)(0.0134) = 0.000134 \text{ cm}^3 \]

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**Diffraction technique for crystal structure analysis**

- **Diffraction** - The constructive interference, or reinforcement, of a beam of x-rays or electrons interacting with a material. The diffracted beam provides useful information concerning the structure of the material.

- **Bragg's law** - The relationship describing the angle at which a beam of x-rays of a particular wavelength diffracts from crystallographic planes of a given interplanar spacing.

- **In a diffractometer** a moving x-ray detector records the 20 angles at which the beam is diffracted, giving a characteristic diffraction pattern
(a) Destructive and (b) constructive interactions between x-rays and the crystalline material.

Reinforcement occurs at angles that satisfy Bragg’s law:

\[ d = \frac{n \lambda}{2 \sin \theta} \]
Next Class

MME131: Lecture 8

Imperfections in atomic arrangement