CRYSTALLOGRAPHY IV: PLANES

Plane (hkl)

i. Find intercept with a, b, c

ii. Intercept = 1/h, 1/k, 1/l

(Planes parallel to axis have an intercept at ∞)

ii. Take reciprocal of intercepts

iii. Clear any common integer

iv. Plane (hkl)
CRYSTALLOGRAPHY IV: PLANE

(001) Plane referenced to the origin at point O

Other equivalent (001) planes

(a)

(110) Plane referenced to the origin at point O

Other equivalent (110) planes

(b)

(111) Plane referenced to the origin at point O

Other equivalent (111) planes

(c)

Figure 3.9. Representations of a series each of (a) (001), (b) (110), and (c) (111) crystallographic planes.
Examples

Plane A
Intercepts
  x: $\frac{1}{2}$
  y: $-\frac{1}{2}$
  z: $\infty$

Plane: $(2\bar{2}0)$

Clear common integer
Plane: $(1\bar{1}0)$

Instead of writing “-” sign in crystallographic notation
We use a “bar” over the number

$(2\bar{2}0)$ “Two two bar zero”
CRYSTALLOGRAPHY IV: PLANES

Specific plane: (hkl)

Families of planes: \{hkl\}

\{100\} : (100), (\bar{1}00), (010), (0\bar{1}0), (001), (00\bar{1})
Hexagonal:

\[ |a| = a \]
\[ |b| = a \]
\[ |c| = c \]
\[ \alpha = \beta = 90^\circ \]
\[ \gamma = 120^\circ \]

Two crystallographic conventions: three-index and four-index

\[
[u'v'w'] \rightarrow [uvtw]
\]

\[
u = \frac{n}{3}(2u' - v')
\]

\[
v = \frac{n}{3}(2v' - u')
\]

\[
i = -(h + k)
\]

\[
t = -(u + v)
\]

\[
w = nw'
\]
CRYSTALLOGRAPHY: Close-Packed Planes

FCC Metals: \((111)\)

HCP Metals: \((0001)\)

FCC Stacking: \(\ldots\text{ABCABCABC} \ldots\)

HCP Stacking: \(\ldots\text{ABABABABABAB} \ldots\)
CRYSTALLOGRAPHY: Close-Packed Planes

FCC Stacking (111)
...ABCABCABC...

HCP Stacking (0001)
...ABABABABABAB...
POLYCRYSTALLINE MATERIALS: EXAMPLE

Grain formation in solidification

Squares:
Represent unit cells

(a) Squares: Represent unit cells

(b) Squares: Represent unit cells

(c) Individual crystals or “grains”

(d) Grain boundaries
CRystals as Building Blocks

- Some engineering applications require single crystals:
  - Diamond single crystals for abrasives
  - Turbine blades

- Crystal properties reveal features of atomic structure.
  - Ex: Certain crystal planes in quartz fracture more easily than others.

(Courtesy Martin Deakins, GE Superabrasives, Worthington, OH. Used with permission.)

Fig. 8.30(c), Callister 6e. (Fig. 8.30(c) courtesy of Pratt and Whitney).

(Courtesy P.M. Anderson)
POLYCRYSTALS

- *Most* engineering materials are polycrystals.

- Nb-Hf-W plate with an electron beam weld.
- Each "grain" is a single crystal.
- If crystals are randomly oriented, overall component properties are not directional.
- Crystal sizes typ. range from 1 nm to 2 cm (i.e., from a few to millions of atomic layers).
SINGLE CRYSTAL vs. POLYCRYSTALS

- **Single Crystals**
  - Properties vary with direction: **anisotropic**.
  - Example: the modulus of elasticity (E) in BCC iron:
    - E (diagonal) = 273 GPa
    - E (edge) = 125 GPa
    - Data from Table 3.3, *Callister 6e.*

- **Polycrystals**
  - Properties **may/may not** vary with direction.
  - If grains are randomly oriented: **isotropic.**
    - (E_{poly} iron = 210 GPa)
  - If grains are **textured**, anisotropic.
    - Adapted from Fig. 4.12(b), *Callister 6e.*
      (Fig. 4.12(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC [now the National Institute of Standards and Technology, Gaithersburg, MD].)
DEM0: HEATING and COOLING of an IRON WIRE

- Fe demonstrates "polymorphism"—The same atoms can have more than one crystal structure.

![Diagram showing polymorphism in iron wire with temperature ranges and structural changes.](image)

- BCC Stable
- FCC Stable
- Liquid

Temperature, C

- T_c 768
- 914
- 1391
- 1536

Heat up:
- longer

Cool down:
- shorter!
- longer!
- magnet falls off
- shorter
SUMMARY

• Atoms may assemble into crystalline or amorphous structures.

• We can predict the density of a material, provided we know the atomic weight, atomic radius, and crystal geometry (e.g., FCC, BCC, HCP).

• Material properties generally vary with single crystal orientation (i.e., they are anisotropic), but properties are generally non-directional (i.e., they are isotropic) in polycrystals with randomly oriented grains.
CHAPTER 12: STRUCTURE AND PROPERTIES OF CERAMICS

ISSUES TO ADDRESS...

• Structures of ceramic materials:  
  How do they differ from that of metals?
• Point defects:  
  How are they different from those in metals?
• Impurities:  
  How are they accommodated in the lattice and how do they affect properties?
• Mechanical Properties:  
  What special provisions/tests are made for ceramic materials?
CERAMIC BONDING

• Bonding:
  -- Mostly ionic, some covalent.
  -- % ionic character increases with difference in electronegativity.

• Large vs small ionic bond character:

Table of Electronegativities

Adapted from Fig. 2.7, *Callister 6e*. (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.)
IONIC BONDING and STRUCTURE

• **Charge Neutrality:**
  --Net charge in the structure should be zero.

  \[ A_m^+ X_p^- \]
  \[ m, p \text{ determined by charge neutrality} \]

• **Stable structures:**
  --maximize the # of nearest oppositely charged neighbors.

Adapted from Fig. 12.1, *Callister 6e.*
Coordination # and Ionic Radii

- Coordination # increases with

  Issue: How many anions can you arrange around a cation?

<table>
<thead>
<tr>
<th>$\frac{r_{\text{cation}}}{r_{\text{anion}}}$</th>
<th>Coord #</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; .155</td>
<td>2</td>
</tr>
<tr>
<td>.155-.225</td>
<td>3</td>
</tr>
<tr>
<td>.225-.414</td>
<td>4</td>
</tr>
<tr>
<td>.414-.732</td>
<td>6</td>
</tr>
<tr>
<td>.732-1.0</td>
<td>8</td>
</tr>
</tbody>
</table>

Adapted from Table 12.2, Callister 6e.

Adapted from Fig. 12.2, Callister 6e.

Adapted from Fig. 12.3, Callister 6e.

Adapted from Fig. 12.4, Callister 6e.
EX: PREDICTING STRUCTURE OF FeO

- On the basis of ionic radii, what crystal structure would you predict for FeO?

<table>
<thead>
<tr>
<th>Cation</th>
<th>Ionic radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$^{3+}$</td>
<td>0.053</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>0.077</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>0.069</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.100</td>
</tr>
<tr>
<td>Anion</td>
<td></td>
</tr>
<tr>
<td>O$^{2-}$</td>
<td>0.140</td>
</tr>
<tr>
<td>Cl$^{-}$</td>
<td>0.181</td>
</tr>
<tr>
<td>F$^{-}$</td>
<td>0.133</td>
</tr>
</tbody>
</table>

- Answer:

\[
\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{0.077}{0.140} = 0.550
\]

data from Table 12.3, Callister 6e.

- Based on this ratio,
  - Coord # = 6
  - Structure = NaCl

Data from Table 12.3, Callister 6e.
AmXp STRUCTURES

- Consider CaF$_2$: \[
\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{0.100}{0.133} \approx 0.8
\]

- Based on this ratio, coord # = 8 and structure = CsCl.
- Result: CsCl structure w/only half the cation sites occupied.

- Only half the cation sites are occupied since #Ca$^{2+}$ ions = 1/2 # F$^{-}$ ions.

Adapted from Fig. 12.5, Callister 6e.
DEFECTS IN CERAMIC STRUCTURES

• **Frenkel Defect**
  --a cation is out of place.

• **Shottky Defect**
  --a paired set of cation and anion vacancies.

\[ \text{Equilibrium concentration of defects } \sim e^{-Q_D/kT} \]

Adapted from Fig. 13.20, *Callister 5e*. (Fig. 13.20 is from W.G. Moffatt, G.W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, John Wiley and Sons, Inc., p. 78.) See Fig. 12.21, *Callister 6e*. 

![Diagram of Frenkel and Shottky Defects](image-url)
IMPURITIES

• Impurities must also satisfy charge balance

• Ex: NaCl \( \text{Na}^+ \bullet \text{Cl}^- \)

• Substitutional cation impurity
  
<table>
<thead>
<tr>
<th>initial geometry</th>
<th>( \text{Ca}^{2+} ) impurity</th>
<th>resulting geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \bullet \text{Na}^+ )</td>
<td>( \bullet \text{Na}^+ )</td>
<td>( \bullet \text{Ca}^{2+} )</td>
</tr>
</tbody>
</table>

• Substitutional anion impurity
  
<table>
<thead>
<tr>
<th>initial geometry</th>
<th>( \text{O}^{2-} ) impurity</th>
<th>resulting geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \bullet \text{Cl}^- )</td>
<td>( \bullet \text{Cl}^- )</td>
<td>( \bullet \text{O}^{2-} )</td>
</tr>
</tbody>
</table>
SUMMARY

• Ceramic materials have mostly covalent & some ionic bonding.
• Structures are based on:
  --charge neutrality
  --maximizing # of nearest oppositely charged neighbors.
• Structures may be predicted based on:
  --ratio of the cation and anion radii.
• Defects
  --must preserve charge neutrality
  --have a concentration that varies exponentially w/T.