Crystal Structure / Imperfections

Almost all materials crystallize when they solidify; i.e., the atoms are arranged in an ordered, repeating, 3-dimensional pattern. These structures are called crystals and are discernible during microstructural characterization [by optical microscopy, x-ray diffraction, transmission electron microscopy, etc.] of metals. Microstructure is of critical importance to the properties of metals.

Aspects of Microstructure:

• grain size and shape
• grain orientation
• phase(s) present
• size and distribution of second phases
• nature of grain boundaries and precipitates
• crystal imperfections

Each grain is a single crystal with a specific orientation.

Imperfections

"FORTUNATELY crystals are seldom, if ever, perfect."

These defects or imperfections include:

• thermal vibrations
  (0-D) point ------ {vacancies, interstitials, substitutional, ... }
  (1-D) line ------- {dislocations}
  (2-D) surface --- {grain/phase boundaries, surfaces,... }
  (3-D) volume --- {amorphous, liquid state, voids, ... }

Without the imperfections, materials would have little ductility [malleability] and thus cannot be formed into useful shapes.

• Increase strength by impurities / second phases
• Diffusion processes are possible because of vacancies / interstitials
• Grain boundaries affect mechanical properties [both at low and high temperatures]
Crystal Structure

• Lattice - of points is an arrangement of points in 3-D such that each point has identical surroundings

• Different Arrangements - 7 Systems (symmetry) & 14 Bravais Lattices

• Unit Cell - Building block describing the 3-D lattice by translation only

• Type of Arrangement / Atomic Bonding
  • Metallic  • Ionic  • Covalent

• Lattice Parameter / Lattice Constant - repeat distance along a, b, c (x, y, z) or (a₁, a₂, a₃)

• Relations between directions (a, b, c) and angles (α, β, γ) define the 7 systems

Important Parameters

- Number of atoms per unit cell
  - Primitive vs Conventional
    - SC: 1  BCC: 2  FCC: 4

- Coordination Number (CN):
  - number of equivalent nearest neighbors
    - SC: 6  BCC: 8  FCC: 12

- R (atomic radius) vs a (lattice constant):
  - a = 2R  \sqrt{3} a=4R  \sqrt{2} a=4R

- Packing Fraction (Atomic Packing Factor):
  - \( \text{APF} (%) = \frac{\text{no.atoms/u.c.} \times \text{vol.atom}}{\text{vol. u.c.}} \times 100 \)
    - SC: 52%  BCC: 68%  FCC: 74.1%

- CPDs:
  - <100>  <111>  <110>

- CPPs:
  - \{100\}  \{110\}  \{111\}

stacking of CPPs: fcc – ABCABCABC vs hcp – ABABAB (see figures)
Diamond structure (Fig. 3.4) – C, Si, Ge, etc:
FCC with 4 interior atoms (FCC with 2 atoms at each lattice point)
CN=4, 8 atoms/uc, cannot be reduced to a primitive unit cell

Polymorphism – more than one crystal structure
as T increases close packed structures transform to open structures

In general: hcp → fcc → bcc as Temp increases (reverse as P increases)

Notable exception – Fe: bcc at RT (α iron) → fcc (γ iron) → bcc (δ iron)
910°C 1400°C (see table on p.47 – note on the bottom of the table)

Zr: hcp (α) → bcc (β) @865°C

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NaCl Structure: (Na+ cation and Cl- anion) Fig. 3.10 KCl, MgO, UC
\[ a = 2(R_{Na} + R_{Cl}) \] CN=6 4 ion pairs/uc (like fcc) – 2 fcc lattices

CsCl Structure: (Cs+ cation and Cl- anion) Fig. 3.11 AgMg, RbCl, CuZn (β-Brass)
\[ a \text{ vs } R \] CN=8 1 ion pair/uc (like sc) – 2 sc lattices

Fluorite (CaF2) Structure: (Ca++ cation and F- anion) Fig. 3.12 UO2
\[ Ca \text{ (fcc with a) and F (sc with a/2) } a = \frac{4}{\sqrt{3}}(R^{+} + R^{-}) \] 4 CaF2/uc (like fcc)
\[ CN = 8 \text{ for Ca and 4 for F } \] advantage over UC for nuclear applications
Planes and Directions – Miller Indices – least integers with no common factors

Directions : [i j k] \(<i j k>\) - family

Planes : (h k l) \{h k l\} – family

reciprocals of intercepts on the x y z axes ↔ Directions are \(\perp\) to Planes

Examples : cubic ----- group work

hcp : hkil so that h+k+i=0 or hk•l ---- examples

(planes and then directions as normal to the planes)

Cubic :

Angle between 2 directions : \(\cos \theta = \frac{h_1h_2 + k_1k_2 + l_1l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2} \sqrt{h_2^2 + k_2^2 + l_2^2}}\)

Intersection of 2 planes (direction) :
cross product of normals to the planes \((h_1 k_1 l_1)\) and \((h_2 k_2 l_2)\) :

\([h k l] = [h_1 k_1 l_1] \times [h_2 k_2 l_2]\)

Implies that if \([h_1 k_1 l_1]\) falls in a plane \((h k l)\) \(\rightarrow [h_1 k_1 l_1] \cdot [h k l]=0\)

Bragg’s Law : \(n\lambda = 2d_{hkl} \sin \theta\)

where \(d_{hkl}\) is plane separation ----- Cubic : \(\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}\)

hcp : \(\frac{1}{d_{hkl}^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}\)
Kinetics of Vacancy Formation

Why vacancies occur or exist? ⇒ to disrupt the ordered structure or increase randomness ⇒ increases entropy although work (energy) is required to form or create a vacancy (i.e., to move a host atom from interior to surface).

Thus, Energy ↑ & Entropy ↓ / minimize Gibbs Free Energy (G) / \[ dG = 0 \]
(F = Free Energy, H = Enthalpy) \[ G = F + PV = H - TS = E + PV - TS \]
\[ [E] = eV, J\text{ per atom} (1\ eV = 1.6\times10^{-19}\ J);\ Q = \text{Cal per mole} & 1\text{eV=23kCal/mole} \]

Equilibrium Vacancy Concentration:
G(o) = GFE of perfect lattice and G(n) = GFE of lattice with n vacancies
If \( N = \) Number of Atoms, the introduction of the vacancies increases the entropy
⇒ \[ S_{\text{conf}} = k \ln W \text{ configurational entropy with } W \text{ being the number of} \]
different ways of arranging the N atoms and \( n_v \) vacancies on \( N+n \) lattice cites : \( W = (N+n)!C_n = (N+n)C_N = (N+n)!N!n! \), where \( N! = N(N-1)(N-2)\ldots1 \)

Thus \[ G(n) - G(o) = \Delta G = n g_v - kT \ln W \], where \( g_v \) is the GFE to form a vacancy. For thermal equilibrium,

\[ \frac{\partial \Delta G}{\partial n} = 0 = g_v - kT \frac{\partial \ln W}{\partial n} \]
To show \[ \frac{\partial \ln W}{\partial n} = \ln \frac{N+n}{n} \], use Stirling’s approximation
⇒ \[ \ln N! = N \ln N - N \] for large \( N \) ⇒ True for \( n \) also since in general \( n \) is also very large (millions)

Thus, \[ \ln \left( \frac{n}{N+n} \right) = - \frac{g_v}{kT} \] ⇒
\[ \frac{n}{N} \approx \frac{n}{N+n} = C_v = \exp\left(-\frac{g_v}{kT}\right) \], since

\( N\gg n \). \( C_v \) is the vacancy concentration and \[ g_v = E_v + PV_v - TS_v \approx E_v(\text{or} E_f) \]

Arrhenius Equation

\[ \text{slope} = E/k \text{ or } Q/R \]
Divacancies

At very high temperatures, many vacant lattice sites find neighboring site vacant too (Fig. 6.1 text) ⇒ divacancies/$E_v^{(2)} = 2E_v - B$, $B$ is the binding energy of a divancy (this is the energy required to separate a divancy into two isolated monovacancies).

\[
C_v^{(2)} = \frac{\beta}{2} \exp \left( -\frac{2E_v - B}{kT} \right), \beta \text{ is the cordination number} \Rightarrow \text{see text Eq. 6.15-6.22}
\]

or

\[
\frac{C_v^{(2)}}{C_v^2} = \frac{\beta}{2} \exp \left( \frac{B}{kT} \right)
\]

Interstitials

(self) Similarly, $n_i = C_i = \exp\left( -\frac{E_i}{kT} \right)$, $n_i = \text{interstitial atoms}$ and $N_i = \text{No. of interstitial sites} (\neq N, \text{no. of atoms})$.

$E_i >> E_v$ ⇒ thus the no. of interstitials (self) produced by thermal energy is relatively small.

Example Calculation:

For Copper (fcc) $Q_v = 20 \text{ kCal/mole}$ $B = 7 \text{ kCal/mole}$ $Q_i = 90 \text{ kCal/mole}$

<table>
<thead>
<tr>
<th>$T$ °C (K)</th>
<th>$C_v$</th>
<th>$C_v^{(2)}$</th>
<th>$C_v^i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT (293)</td>
<td>1.20x10^{-15}</td>
<td>1.45x10^{-24}</td>
<td>7.3x10^{-68}</td>
</tr>
<tr>
<td>500 (773)</td>
<td>2.21x10^{-6}</td>
<td>2.80x10^{-9}</td>
<td>3.57x10^{-26}</td>
</tr>
<tr>
<td>1073 (1346) (TM = 1083)</td>
<td>5.65x10^{-4}</td>
<td>2.63x10^{-5}</td>
<td>2.43x10^{-15}</td>
</tr>
</tbody>
</table>

***Self interstitials are produced more easily by radiation
Ionics (MX and MX$_2$ types)

Schottky \( \Rightarrow \) \( C_{vX} = C_{vM} = \exp\left(-\frac{g_s}{2kT}\right) \)  
Frenkel \( \Rightarrow \)  

\[
\begin{align*}
C_{vM} &= C_{iM} = \exp\left(-\frac{gf}{2kT}\right) \\
C_{vX} &= C_{iX} = \exp\left(-\frac{gf}{2kT}\right)
\end{align*}
\]

Divalent Impurity \( \Rightarrow \) Extrinsic vs Intrinsic

e.g. Cation (+ive) vacancies created
due to addition of Ca$^{++}$ in NaCl
\( \Rightarrow \) charge neutrality.

n ppm of Ca$^{++}$ means nx10$^{-6}$ Cation vacancies created
(these are athermal and not
dependent on temperature but equal
to the divalent impurity concentration)

\( \Rightarrow \) Can get the relationship \( (C_{vM} \text{ vs } T) \) as before

1. \( qD_{NDM} + q_{MNM} = q_{XN_X} \) \( \Rightarrow \) charge neutrality, where \( q_M = q_X (\text{MX type}) \)

2. \( N_{DM} + N_M + N_{VM} = N_X + N_{vx} \) \( \Rightarrow \) no. sites for \( M^{++}+M^+ = \) no. \( X^- \) sites

- Can do the same calculation for \( C_v^+ \) for MX$_2$ type (such as CaF$_2$ and/or UO$_2$)
  - see Text

Experimental Determination of \( C_v \):
- Simmons-Balluffi Experiment
- Quenched-in Resistivity
- FIM - imaging of atoms (for low \( C_v \))