Point defects
Defects in crystalline materials

- all crystalline materials contain defects and deviations from the ideal crystalline structure
- defects have a strong impact on material properties, e.g.:
  - dislocations contribute to strengthening of materials
  - pure Fe is very soft and malleable, but addition of even a small amount of carbon (<2.1 wt.% results in much stronger steel
  - pure crystalline Al₂O₃ (corundum) is transparent, Cr³⁺ impurity → red colour (ruby); additions of Fe²⁺ and Ti⁴⁺ → blue colour (sapphire)
  - semiconductors (donor and acceptor impurities)
  - impurities increase electrical resistance → electrical wires made of very pure Cu
Defects in crystalline materials

- people made use of defects in materials already a long time ago, even though they did not know the precise mechanisms which make materials better
- brass (alloy of Cu and Zn) – ageing of Cu with ZnO $\rightarrow$ reaction of Zn vapours with Cu (Zn was originally not recognized as a metal)
- forging – defects in the metal/alloy make it stronger and tougher (dislocations not known until $\sim$1930)
Defects in crystalline materials

Types of defects in metallic and ceramic materials

▶ point – vacancies, interstitials, substitutional atoms
▶ line – dislocations
▶ planar – grain boundaries, stacking faults
▶ volume – voids, pores, gas bubbles, inclusions of other materials, precipitates

Point defects

- disruptions of “perfect” atomic/ionic arrangements in a crystal structure
- defects affecting small regions of several neighbouring atoms/ions – shifts of positions → local strain fields
- due to local strain fields, point defects can interact with other defects in the material
- usually, it can be assumed that point defects do not interact with each other – sufficiently low defect concentrations (e.g. when the concentration is $10^{-6}$, the mean distance between point defects is 100 atomic planes)
Types of point defects

- vacancies
- interstitials (self- or impurity)
- substitutional atoms
- Frenkel defect
- Schottky defect (especially in ionic crystals)

Schottky and Frenkel defects in an ionic solid [2]

Intrinsic and extrinsic point defects

- **intrinsic** – vacancies and self-interstitials
- **extrinsic** – substitutional and interstitial solute/impurity atoms
- all crystals in a thermodynamic (TD) equilibrium contain *intrinsic* point defects, whose concentration is determined by Arrhenius relation

\[
 c_{PD} = A \exp \left( -\frac{G_f}{k_B T} \right) = A \exp \left( \frac{S_f}{k_B} \right) \exp \left( -\frac{H_f}{k_B T} \right),
\]

where \( G_f \), \( S_f \) and \( H_f \) denote Gibbs free energy, entropy and enthalpy related to defect formation.

- all real materials also contain *extrinsic* point defects – impurities and/or solutes; e.g. even the purest Si crystal contains a few ppm of interstitial O and substitutional C
Vacancies

- a lattice point from which an atom or ion is missing
- all crystalline materials contain vacancies (for $T \neq 0$)
- vacancy sources and sinks – regions at which a dislodged atom can be placed, e.g. the free surface of the crystal, grain boundary, empty half-plane of an edge dislocation
- when an atom remains inside the crystal in an interstitial position $\rightarrow$ vacancy - interstitial pair (Frenkel defect)
- Schottky defect – a pair of vacancies with opposite charges in ionic crystals; the term also sometimes used for a vacancy in materials made from neutral atoms
- vacancy formation: during solidification, increasing temperature, radiation damage
- influence on diffusion rate in crystalline substances
Equilibrium vacancy concentration

- The total Gibbs free energy $G(T, p)$ of a material depends on vacancy concentration.
- Thermodynamic equilibrium at constant temperature and pressure $\Leftrightarrow G = H - TS$ reaches a minimum.
- Consider $n$ vacancies formed by removing $n$ atoms from the crystal lattice comprising $N$ lattice points to the crystal surface, then

$$\Delta G = G^n - G^0 = \Delta H_f^n - T \Delta S^n,$$

where $\Delta H_f^n = n \Delta h_f$ ($h_f$ is the enthalpy related to formation of a single vacancy), $T$ is the thermodynamic temperature and $\Delta S^n$ is the change in entropy related to formation of $n$ vacancies.

- For most metals, $h_f \approx 1 \text{ eV}$.
Equilibrium vacancy concentration

\[ \Delta G = G^n - G^0 = \Delta H_f^n - T \Delta S^n \]

formation of vacancies is accompanied by an increase of entropy \( \Delta S^n \), which consists of two contributions (\( \Delta S^n = \Delta S_v^n + \Delta S_c^n \)):

1. **vibrational entropy** \( \Delta S_v^n \) – change of thermal vibrations of atoms in the vicinity of the vacancy, increases with increasing temperature and decreases with increasing cohesive forces, \( \Delta S_v^n = n \Delta s_v \)

2. **configurational** \( \Delta S_c^n \) – entropy of mixing, corresponds to the number of microstates realizing a given macrostate (i.e. microstates are different ways in which vacancies are located in the lattice)

Boltzmann relation for configurational entropy

\[ S_c^n = k_B \ln \Omega_n, \]

where \( \Omega_n \) is the number of ways to place \( n \) vacancies in \( N \) lattice points of a crystal (i.e. the number of microstates of a given TD system), i.e. \( \Omega_n = \frac{N!}{n!(N-n)!} \)
Equilibrium vacancy concentration

$$\Delta G = n(\Delta h_f - T\Delta s_v) - T\Delta S^n_c$$

$S^n_c = k_B \ln \frac{N!}{n!(N-n)!}$

- equilibrium vacancy concentration $\Leftrightarrow \frac{\partial \Delta G}{\partial n} \bigg|_{n=n_{eq}} = 0$

- first, we solve $\frac{\partial \Delta S^n_c}{\partial n}$ using Stirling formula (an approximation of factorial for large numbers) $lnN! = N \ln N - N$
Equilibrium vacancy concentration

\[ \Delta G = n(\Delta h_f - T\Delta s_v) - T\Delta S^n_c \]

\[ S^n_c = k_B \ln \frac{N!}{n!(N-n)!} \]

\[ \text{equilibrium vacancy concentration} \iff \frac{\partial \Delta G}{\partial n} \bigg|_{n=n_{eq}} = 0 \]

\[ \text{first, we solve } \frac{\partial \Delta S^n_c}{\partial n} \text{ using Stirling formula (an approximation of factorial for large numbers)} \]

\[ \frac{\partial \Delta S^n_c}{\partial n} = k_B \frac{\partial}{\partial n} \left[ \ln N! - \ln n! - \ln(N-n)! \right] \]

\[ = k_B \frac{\partial}{\partial n} \left[ N \ln N - N - n \ln n + n - (N-n) \ln(N-n) + (N-n) \right] \]

\[ = k_B \frac{\partial}{\partial n} \left[ N \ln N - n \ln n - (N-n) \ln(N-n) \right] \]

\[ = k_B \left[ - \ln n - 1 + \ln(N-n) + 1 \right] \]

\[ = k_B \ln \frac{N-n}{n} \approx -k_B \ln \frac{n}{N} \]
Equilibrium vacancy concentration

\[
\left. \frac{\partial \Delta G}{\partial n} \right|_{n=n_{eq}} = \left. \frac{\partial}{\partial n} \left[ n(\Delta h_f - T\Delta s_v) - T\Delta S_c^n \right] \right|_{n=n_{eq}}
\]

\[
= \Delta h_f - T\Delta s_v + k_B T \ln \frac{n_{eq}}{N} = 0
\]

\[
\frac{n_{eq}}{N} = \exp \left( \frac{\Delta s_v}{k_B} \right) \exp \left( -\frac{\Delta h_f}{k_B T} \right)
\]

- term \( \exp \left( -\frac{\Delta h_f}{k_B T} \right) \) rapidly increases with increasing temperature
- term \( \exp \left( \frac{\Delta s_v}{k_B} \right) \) does not depend on temperature, constant \( \sim 3 \), i.e.

\[
\frac{n_{eq}}{N} = C \exp \left( -\frac{\Delta h_f}{k_B T} \right)
\]
Equilibrium vacancy concentration

- equilibrium vacancy concentration for silver and aluminium at room temperature (RT), $\Delta h_f^{(Ag)} = 1.1 \text{ eV}$, $\Delta h_f^{(Al)} = 0.72 \text{ eV}^*$, $k_B = 8.6173 \cdot 10^{-5} \text{ eV/K}$, for RT $k_B T \sim 0.025 \text{ eV}$

$$c_v^{(Ag)} = \frac{n_{eq}}{N} \approx 3 \exp\left(-\frac{1.1}{0.025}\right) \approx 10^{-19}$$

$$c_v^{(Al)} = \frac{n_{eq}}{N} \approx 3 \exp\left(-\frac{0.72}{0.025}\right) \approx 10^{-12}$$

- equilibrium vacancy concentration for silver and aluminium near the melting point, $T_M^{(Ag)} = 1235 \text{ K}$, $T_M^{(Al)} = 933 \text{ K}$

$$c_v^{(Ag)} \approx 3 \exp\left(-\frac{1.1}{0.025} \frac{300}{1230}\right) \approx 10^{-5}$$

$$c_v^{(Al)} \approx 3 \exp\left(-\frac{0.72}{0.025} \frac{300}{930}\right) \approx 10^{-4}$$

*Shewmon, Diffusion in Solids. Springer, 2016*
**Equilibrium vacancy concentration**

- Equilibrium vacancy concentration is determined by components $n(\Delta h_f - T\Delta s_v)$ and $-T\Delta S^n_c$.
- Rapid changes of the entropy term for small vacancy concentrations.

Minimization of Gibbs free energy as a function of number of vacancies.
Vacancies – entropy and enthalpy of formation

\[
\frac{n_{eq}}{N} = \exp \left( \frac{\Delta s_v}{k_B} \right) \exp \left( - \frac{\Delta h_f}{k_B T} \right) = C \exp \left( - \frac{\Delta h_f}{k_B T} \right)
\]

▶ how to determine entropy and enthalpy of vacancy formation?
Vacancies – entropy and enthalpy of formation

\[
\frac{n_{eq}}{N} = \exp \left( \frac{\Delta s_v}{k_B} \right) \exp \left( -\frac{\Delta h_f}{k_B T} \right) = C \exp \left( -\frac{\Delta h_f}{k_B T} \right)
\]

- how to determine entropy and enthalpy of vacancy formation?
- Arrhenius equation: \( c = C \exp\left( -B \frac{1}{T} \right) \rightarrow \ln(c) = \ln(C) - B \frac{1}{T} \)

![Graphs showing exponential dependence and Arrhenius equation](image)
Vacancy motion

- equilibrium vacancy concentration does not tell us anything about how long it takes to reach the equilibrium
- vacancy motion realized by jumps of neighbouring atoms into the vacancy – an energy barrier (atom bonds) must be overcome
- energy for overcoming the barrier – thermal vibrations
- a jump is made only if energy of thermal vibrations is larger than the barrier ($\Delta g_m$, activation free energy for vacancy motion)

- probability of an atom having energy sufficient for a jump

$$p \propto \exp \left( - \frac{\Delta g_m}{k_B T} \right)$$

Schematics of diffusion of an atom to a neighbouring vacant lattice site [3]
Vacancy motion

- energy of thermal vibrations at RT \(3k_B T \approx 0.08 \text{ eV}\) is usually much lower than the activation free energy \(\Delta g_m \approx 1 \text{ eV}\) → a large thermal fluctuation is necessary
- probability of such fluctuation, i.e. frequency of jumps, is in a 1D case
  \[ R_v = \nu_0 \exp\left(-\frac{\Delta g_m}{k_B T}\right), \]
where \(\nu_0\) is the frequency with which the atom “attempts” a jump, i.e. the frequency of atom vibrations in a given diffusion direction
- because \(\Delta G = \Delta H - T \Delta S\)
  \[ R_v = \nu_0 \exp\left(\frac{\Delta s_m}{k_B}\right) \exp\left(-\frac{\Delta h_m}{k_B T}\right) \]
Vacancy motion – vacancy mechanism of diffusion

▶ in reality, we are usually more interested in motion of atoms – self-diffusion by vacancy mechanism

▶ in order to make a jump, the atom has to be next to a vacancy – the probability of a jump of an atom in a crystal structure is given by the product of:
  
  ▶ the probability of finding a vacancy in one of the neighbouring sites

\[
\frac{n_{eq}}{N} z = z \exp \left( - \frac{\Delta g_f}{k_B T} \right),
\]

where \( z \) is the coordination number of the crystal structure

▶ the jump rate, i.e. the probability of thermal fluctuation necessary for realizing a jump

\[
R_v = \nu_0 \exp \left( - \frac{\Delta g_m}{k_B T} \right)
\]

▶ the frequency of jumps of an atom in a crystal is then

\[
R_a = \frac{1}{\tau} = \nu_0 z \exp \left( - \frac{\Delta g_f + \Delta g_m}{k_B T} \right),
\]

where \( \tau \) is the average time between individual jumps
Vacancy motion – vacancy mechanism of diffusion

- because $\Delta G = \Delta H - T\Delta S$ and $\exp \left( \frac{\Delta s_v + \Delta s_m}{k_B} \right) \sim 1$, we can write

$$R_a = \frac{1}{\tau} = \nu_0 z \exp \left( - \frac{\Delta g_f + \Delta g_m}{k_B T} \right)$$

$$= \nu_0 z \exp \left( \frac{\Delta s_v + \Delta s_m}{k_B} \right) \exp \left( - \frac{\Delta h_f + \Delta h_m}{k_B T} \right)$$

$$\approx \nu_0 z \exp \left( - \frac{\Delta h_f + \Delta h_m}{k_B T} \right)$$

- the frequency with which atoms jump into vacancies depends on two energies – energy for vacancy formation and energy needed for the jump
Vacancy motion – vacancy mechanism of diffusion

\[ \tau \approx \frac{1}{\nu_0 z} \exp \left( \frac{\Delta h_f + \Delta h_m}{k_B T} \right) \]

- for silver and aluminium at RT, \( \Delta h_f^{(Ag)} = 1.1 \text{ eV}, \Delta h_m^{(Ag)} = 0.6 \text{ eV}, \Delta h_f^{(Al)} = 0.72 \text{ eV}, \Delta h_m^{(Al)} = 0.68 \text{ eV} \), \( \nu_0 = 10^{13} \text{ s}^{-1} \), \( z = 12 \) (both Ag and Al are FCC)
  \[ \tau^{(Ag)} \approx 3 \cdot 10^{14} \text{ s} \]  
  (one jump in \( 10^7 \) years)  
  \[ \tau^{(Al)} \approx 3 \cdot 10^{9} \text{ s} \]  
  (one jump in 100 years)

- for silver and aluminium near the melting point, \( T_M^{(Ag)} = 1235 \text{ K}, T_M^{(Al)} = 933 \text{ K} \)
  \[ \tau^{(Ag)} \approx 7 \cdot 10^{-8} \text{ s} \]  
  (approx. 14 million jumps per s)  
  \[ \tau^{(Al)} \approx 3 \cdot 10^{-7} \text{ s} \]  
  (approx. 3 million jumps per s)

Vacancy motion – vacancy mechanism of diffusion

- random walk in 3D – Einstein relation $\langle r^2(t) \rangle = 6Dt$, $D$ is the diffusion coefficient and $\langle r^2(t) \rangle$ is the mean square displacement after an elapsed time $t$

- if $a$ is the mean distance between atoms in a crystal lattice, we can estimate $D$ from the average time between jumps $\tau$

$$D = \frac{a^2}{6\tau} = \frac{a^2 \nu_0 z}{6} \exp \left( -\frac{\Delta g_f + \Delta g_m}{k_B T} \right)$$

$$D = \frac{a^2 \nu_0 z}{6} \exp \left( \frac{\Delta s_f + \Delta s_m}{k_B} \right) \exp \left( -\frac{\Delta h_f + \Delta h_m}{k_B T} \right)$$

$D = D_0 \exp \left( -\frac{E_d}{k_B T} \right)$

- $D_0$ is a temperature independent coefficient and $E_d = \Delta h_f + \Delta h_m$ is activation energy for diffusion
Vacancy motion – diffusion of vacancies

- in some cases, diffusion of vacancies themselves (i.e. not diffusion of atoms by vacancy mechanism) might be of interest
- how does the equation for the diffusion coefficient for vacancies $D^v$ look like?
- what is the relationship between the diffusion coefficient for vacancies $D^v$ and for self-diffusion by vacancy mechanism $D$?
Vacancy motion – diffusion of vacancies

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$$D^v = \frac{a^2 \nu_0 z}{6} \exp \left( -\frac{\Delta g_m}{k_B T} \right) = \frac{a^2 \nu_0 z}{6} \exp \left( \frac{\Delta s_m}{k_B} \right) \exp \left( -\frac{\Delta h_m}{k_B T} \right)$$

$$= D^v_0 \exp \left( -\frac{E_d}{k_B T} \right), \quad E_d = \Delta h_m$$
Vacancy motion – diffusion of vacancies

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- what is the relationship between the diffusion coefficient for vacancies $D^v$ and for self-diffusion by vacancy mechanism $D$?

\[
D^v = \frac{a^2 \nu_0 z}{6} \exp \left(- \frac{\Delta g_m}{k_B T} \right) = \frac{a^2 \nu_0 z}{6} \exp \left( \frac{\Delta s_m}{k_B} \right) \exp \left( - \frac{\Delta h_m}{k_B T} \right) = D_0^v \exp \left( - \frac{E_d}{k_B T} \right), \quad E_d = \Delta h_m
\]

\[
D^v = D / c_v, \quad c_v = \frac{n_{eq}}{N}
\]
Energy of vacancy formation and motion

Energy of vacancy formation $E_f$ and motion $E_m$ for selected metals together with energy of self-diffusion $E_{SD}$:

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Cu</th>
<th>Al</th>
<th>Ni</th>
<th>Mg</th>
<th>Fe</th>
<th>W</th>
<th>NiAl</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_f$</td>
<td>1.0–1.1</td>
<td>0.76</td>
<td>1.4</td>
<td>0.9</td>
<td>2.13</td>
<td>3.3</td>
<td>1.05</td>
</tr>
<tr>
<td>$E_m$</td>
<td>1.0–1.1</td>
<td>0.62</td>
<td>1.5</td>
<td>0.5</td>
<td>0.76</td>
<td>1.9</td>
<td>2.4</td>
</tr>
<tr>
<td>$E_{SD}$</td>
<td>2.0–2.2</td>
<td>1.38</td>
<td>2.9</td>
<td>1.4</td>
<td>2.89</td>
<td>5.2</td>
<td>3.45</td>
</tr>
</tbody>
</table>

Divacancies

- combination of a pair of vacancies $\rightarrow$ lower number of broken bonds between atoms $\rightarrow$ divacancy has a lower energy than two separate vacancies – decrease by binding enthalpy $h_{b}^{2v}$

$$\Delta h_{f}^{2v} = 2\Delta h_{f} - h_{b}^{2v}$$

- $h_{b}^{2v} \sim 0.1 - 0.3$ eV

- activation energy for divacancy movement is lower than for single vacancies $\rightarrow$ divacancy migration is easier

$$n_{eq}^{2v} \approx \exp \left( - \frac{\Delta h_{f}^{2v}}{k_{B}T} \right) = \exp \left( - \frac{2\Delta h_{f} - h_{b}^{2v}}{k_{B}T} \right)$$

$$n_{eq}^{1v} \approx \exp \left( - \frac{\Delta h_{f}}{k_{B}T} \right)$$

$$\frac{n_{eq}^{1v}}{n_{eq}^{2v}} \approx \exp \left( \frac{\Delta h_{f} - h_{b}^{2v}}{k_{B}T} \right)$$

- the fraction of single vacancies decreases with increasing $T$, but even close to the melting point, single vacancies prevail
Vacancy clusters

- can be formed during vacancy supersaturation – e.g. after quenching, deformation or irradiation
- lack of nearby vacancy sinks (diffusion length $r = \sqrt{6D\tau}$) – vacancies can combine into divacancies, trivacancies and larger clusters/aggregates $\rightarrow$ decrease of the total enthalpy of the material
- vacancy clusters can grow into voids/cavities or contribute to formation of stacking fault tetrahedra in FCC metals (defects constituting of stacking faults at four $\{111\}$ planes, which are connected by six stair-rod dislocations at the edges

Stacking faults tetrahedra in quenched Au (Cottrell, Philos. Mag. 6 (1961), 1351)
Formation and annihilation of vacancies

- vacancy concentration depends on temperature – formation and annihilation of vacancies at suitable sites (vacancy sources and sinks)

- with respect to the vacancy diffusion length, grain boundaries or surface of the crystal are usually too far → the best sites for vacancy formation and annihilation are dislocations with an edge component

- vacancy annihilation/formation at an edge dislocation → dislocation climb

Dislocation climb with (a)-(b) annihilation and (c)-(d) formation of a vacancy
Methods of measuring vacancy concentration

- approaches to study vacancy concentration‡:
  - at TD equilibrium (high temperatures)
  - after quenching (quenching experiments)
  - observation of vacancy equilibration

- in principle, each physical property influenced by vacancies can be employed to investigate their concentration

- the most important experimental methods are e.g.:
  - thermal expansion
  - electrical resistance
  - positron annihilation spectroscopy
  - thermal conductivity
  - heat capacity

Measuring vacancy concentration – thermal expansion

- vacancy formation → creating of an extra lattice site → volume increase
- principle: measurement of temperature dependence of lattice parameter change $\Delta a$ (X-ray diffraction) and change in sample length $\Delta l$ (dilatometry)
- $\Delta l$ contains both the thermal expansion of the material and the length change due to formation of point defects (mainly vacancies)
- if the thermal expansion (i.e. lattice parameter change) is subtracted from the total change of the sample length, concentration of point defects can be obtained (holds for cubic crystals)

$$\frac{n_v}{N} = 3 \left( \frac{\Delta l}{l} - \frac{\Delta a}{a} \right)$$
Measuring vacancy concentration – thermal expansion

Thermal expansion ($\frac{\Delta L}{L}$) and lattice parameter change ($\frac{\Delta a}{a}$) for Al [4] (adapted from: Simmons, Balluffi, *Physical Review* 119 (1960), 600–605)
Measuring vacancy concentration – positron annihilation spectroscopy (PAS)

- Measurement of positron ($e^+$) lifetime in a material (time between entering the sample and annihilation)
- $\beta^+$ source emits $e^+$ and $\gamma$-ray simultaneously (a few ps difference), e.g. $^{22}$Na
- Sample-source-sample “sandwich”
- $e^+$ thermalization and diffusion in the material, trapping in defects, where the electron density is locally lower $\rightarrow e^+$ lifetime increases
- $e^+$ lifetime is characteristic for each type of defect (vacancy, divacancy, vacancy clusters, dislocations, ...)
- Sensitivity of the method – from approx. $c_v \approx 10^{-7}$
Measuring vacancy concentration – electric resistance

- electrons scatter at point defects $\rightarrow$ increase of electrical resistance
- quenching experiment – after quenching, the increase of resistance related to vacancies is

$$\Delta \rho = C \exp \left( - \frac{H_f}{k_B T_Q} \right),$$

where $C$ is a constant containing entropy of vacancy formation and $T_Q$ is the quenching temperature

- quenching from different temperatures $T_Q \rightarrow H_f$ can be determined from Arrhenius plot ($\ln \Delta \rho$ vs. $1/T_Q$)

- activation enthalpy $H_m$ for vacancy motion can be determined from the rate of annealing out of vacancies at different temperatures

- the rate of annealing out is inversely proportional to annealing time $t$ needed to reach a certain “annealed-out” resistance:

$$\frac{1}{t_1} = C \exp \left( - \frac{H_m}{k_B T_1} \right), \quad \frac{1}{t_2} = C \exp \left( - \frac{H_m}{k_B T_2} \right),$$

$$\Rightarrow \ln \frac{t_2}{t_1} = \frac{H_m}{k_B} \left( \frac{1}{T_2} - \frac{1}{T_1} \right),$$

where $H_m$ is the only unknown
Measuring vacancy concentration – electric resistance

Two stages in the evolution of el. resistance:

I. temperature sufficient for vacancy migration → formation of vacancy clusters which increase resistance less than single vacancies; activation energy $\sim 0.58$ eV

II. annihilation of vacancy clusters; activation energy $\sim 1.3$ eV (cf. the value of self-diffusion)
Measuring vacancy concentration – electric resistance

If the material contains both vacancies and interstitials, the process of annealing out defects is more complex:

I. approx. 20 K – interstitial migration (activation energy \( \sim 0.1 \text{ eV} \)) → annihilation of Frenkel pairs (vacancy–interstitial)

II. release of interstitials from impurity traps

III. around RT – probably annihilation of interstitials with vacancies not associated with Frenkel pairs and divacancy migration

IV. vacancy migration and clustering

V. annihilation of vacancy clusters

Evolution of electrical resistance with temperature of isochronal ageing of Cu irradiated by neutrons [5]
Measuring vacancy concentration – electric resistance

Relative change of electrical resistance after quenching $\Delta \rho / \rho_q$ for pure Al – isochronal ageing (600 s) at different temperatures $T_a$. $T_q$ are quenching temperatures.

(Khellaf et al., *Materials Transactions* 43(2), 2002, 186–198)
Interstitials

- atoms placed outside regular lattice sites
- two types of interstitial positions (interstices) in FCC, BCC a HCP structures:
  - octahedral – 6 nearest neighbours, number of interstitial positions per unit cell: 4 in FCC, 2 in HCP and 6 in BCC
  - tetrahedral – 4 nearest neighbours, number of interstitial positions per unit cell: 8 in FCC, 4 in HCP and 12 in BCC

Octahedral and tetrahedral interstitial positions in FCC, HCP and BCC structures [6]
Interstitials

- **self-interstitials**
  - both tetrahedral and octahedral positions in metals are too small for self-interstitials → energetically unfavourable (large repulsive forces between atoms which are too close); activation energy for self-interstitial formation is approx. $2 - 5 \times$ larger than for vacancy
  - energy can be reduced by so-called dumbbell configuration, in which two atoms share one lattice point; the lattice point is usually at their common centre of mass
  - in metals usually $n_i \ll n_v$
  - in more open structures (compared to metals) – e.g. Si – activation energy of self-interstitial formation is lower → higher concentration of self-interstitials

- **impurity/solute interstitials**
  - interstitial solid solution
  - only very small atoms (H, O, N, C, B)
  - even small atoms are usually larger than interstices → lattice deformation → low solubility ($<10\%$)
  - e.g. solubility of C in $\alpha$-Fe (ferrite) is less than 0.1 at.% (0.02 wt %)
Interstitials

FCC
100 dumbbell
(Al, Cu, Ni)

BCC
110 dumbbell
Fe

HCP
001 dumbbell
= 0001 dumbbell
(Zn)

Self-interstitial configurations in FCC, BCC and HCP [Wikimedia Commons]
Interstitial motion

- {100} plane in FCC structure containing a self-interstitial (shaded)
- interstitial motion – neighbouring atom is pushed into another interstitial position
- each atom moves only a short distance ⇒ low activation energy for interstitial motion (∼0.1 eV) → diffusion of self-interstitials is faster than diffusion of vacancies

Movement of a self-interstitial through a lattice [7]
Interstitial motion

- diffusion of impurity interstitials – overcoming of an energy barrier similar to diffusion by vacancy mechanism
- in contrast to diffusion by vacancy mechanism, an interstitial has always available sites to which it can jump

\[ D^i = \frac{a^2 \nu_0 p}{6} \exp \left( -\frac{\Delta g^i_m}{k_B T} \right) = D_0^i \exp \left( -\frac{E_d^i}{k_B T} \right), \]

where \( p \) is the number of neighbouring interstices and \( E_d^i = \Delta h_m^i \)

- smaller interstitials deform the surrounding lattice less \( \Rightarrow \) easier diffusion
- diffusion of impurity interstitials is faster in more open structures

Interstitial diffusion [Wikimedia Commons]
Non-equilibrium interstitial and vacancy concentration

- a higher (non-equilibrium) concentration of vacancies and interstitials can be formed under certain conditions

- **quenching**
  - higher concentration of point defects at a high temperature is retained after fast quenching due to slow diffusion at low temperatures
  - defects (mainly vacancies) cannot migrate to suitable sinks
  - vacancy clusters and pores can form

- **plastic deformation**
  - formation of dislocations
  - dislocation climb or movement of dislocations with jogs accompanied by formation/annihilation of vacancies

- **irradiation**
  - high-energy particles (e.g. neutrons, protons) kick out an atom from its equilibrium position → collision cascade during which $\sim 100 - 200$ interstitials and vacancies can be formed; radiation swelling
  - high-energy electrons ($>1$ MeV)
Substitutional atoms

- solute or impurity atoms which replace original atoms at regular lattice points
- the level of solubility given by several factors → **Hume-Rothery rules for substitutional solid solutions**:  
  - atomic radius – solute and solvent atoms must not differ by more than ±15%
  - crystal structure – good solubility for similar structures
  - electronegativity – if the electronegativity difference is large, an intermetallic compound is more likely to form instead of a solid solution
  - valency – a metal with higher valency is more likely do dissolve in a metal with lower valency; complete solubility can occur for the same valency
- if some of the Hume-Rothery rules is violated, only partial solubility is possible
- complete solubility observed for e.g. Cu and Ni
Point defects in non-metallic materials

- point defects in non-metallic, especially in ionic, structures – electric neutrality must be preserved, i.e. both anion and cation defects are formed
- Schottky defect – a pair of vacancies with opposite charges
- Frenkel defect – a pair vacancy-interstitial (interstitial is almost always a cation – smaller size → lower enthalpy of formation)

Schottky and Frenkel defects in an ionic solid [2]
Point defects in non-metallic materials

▶ example of a substitutional solid solution in MgO (NaCl type structure)

Substitutional solid solution of NiO in MgO. Ni$^{2+}$ ions substitute Mg$^{2+}$ indiscriminately, the requirement of preservation of electric neutrality is not violated [4].

Substitutional solid solution of Al$_2$O$_3$ in MgO. Due to electric neutrality, only two Al$^{3+}$ ions fill every three Mg$^{2+}$ sites leaving one Mg$^{2+}$ vacancy [4].
iron oxide (FeO) is never naturally found in perfect stoichiometric composition – Fe has more common oxidation numbers (Fe\(^{2+}\) and Fe\(^{3+}\)) \(\Rightarrow\) non-stoichiometric compound Fe\(_{0.95}\)O

Non-stoichiometric iron oxide (Fe\(_{1-x}\)O); one Fe\(^{2+}\) vacancy is formed for each two Fe\(^{3+}\) ions due to electric charge compensation [4]
Point defects in Si

- vacancies are well-localized in most crystalline materials – only small surrounding volume is affected (shifts in atoms positions)
- exception – Si at high temperatures (probably – still a theory) – so-called extended vacancy

![Extended vacancy diagram]
Point defects in Si

- Similarly there are theories of extended interstitials (at high temperatures in Si), crowdions (metastable state of an interstitial at low temperatures)

![Diagram showing extended interstitial and crowdion](Extended interstitial and crowdion)
Importance of defects – mechanical properties

- influence on dislocation movement – local disruptions of crystal periodicity
- dislocation motion in an undisturbed material – resolved shear stress is equal to critical resolved shear stress
- region containing a defect — larger stress is needed for dislocations to move → dislocation motion is more difficult → stronger material
- in more detail – later in the course

Mechanisms of material strengthening

- strain/work hardening
  - deformation → higher dislocation density → lower mobility
- solid solution hardening
  - stress fields around substitutional atoms or interstitials impede dislocation motion
- precipitation/age hardening
  - particles of other phases impede dislocation motion (types of interfaces – coherent, semicoherent, incoherent)
- dispersion strengthening
  - small, uniformly dispersed particles impede dislocation motion
- grain boundary strengthening
Importance of defects - electric, optic and magnetic properties

- function of semiconductor components significantly depends on presence and concentration of point defects – donor (e.g. P, As in Si) and acceptor (e.g. B, Al in Si) solutes
- solute elements increase electrical resistance – scattering of conduction electrons due to deviations from ideal periodicity of the lattice

Electric resistance of Cu alloys as a function of solute concentration [4]

Electric resistance of AuCu system [4]
Importance of defects - electric, optic and magnetic properties

- addition of silver salts in glass → photochromatic and photosensitive glass
- magnetic properties – ionic additions at different atomic sites of a given structure
- defects in ceramics – sensors (e.g. gas, humidity, temperature), catalytic converters of exhaust gases
Questions

- Explain why a complete solubility can occur in substitutional solid solutions but not in interstitial solid solutions.
- What point defects will form by adding MgO in Al$_2$O$_3$?
Further reading

- Y. Kraftmakher, Equilibrium vacancies and thermophysical properties of metals, Physics Reports 299 (1998), 79–188
References


