CHAPTER IV *DEFECTS IN CRYSTALS*

4.1 Introduction

When Peierls wrote his seminal paper on the thermal transport properties of solids, he did include a short section on the role of "lattice perturbations." He proposed that defects hindered the flow of "lattice waves." However, his discussion remained qualitative. Peierls was curious about the impact of defects on heat transfer and conductivity. He even drafted a manuscript on this topic, but his efforts were firmly rebuffed by none other than the famous Pauli, a member of his Ph.D. committee. Pauli opposed the publication of Peierls's manuscript and wrote, "The residual resistivity is caused by dirt, and one should not dwell in the dirt." In his review commentary, Pauli added, "You should find more sensible questions to be answered; I find that you recently have concerned yourself too much with small issues." The content of the draft manuscript that Peierls shared with Pauli is unknown. Sadly, it was surprising to see one of the fathers of modern science argue that some subjects should not be studied, almost as a matter of principle, and that the study of defects was considered undignified at the time. However, two essential facts are clear: defects are naturally intrinsic to materials, and one can control and enhance materials' properties with defects and impurities.

We can classify different kinds of defects by their spatial dimension:

i) *Zero dimensional defects or point defects* This category includes vacancies, interstitial defects, and substitutional defects, as shown in Figure 4.1.

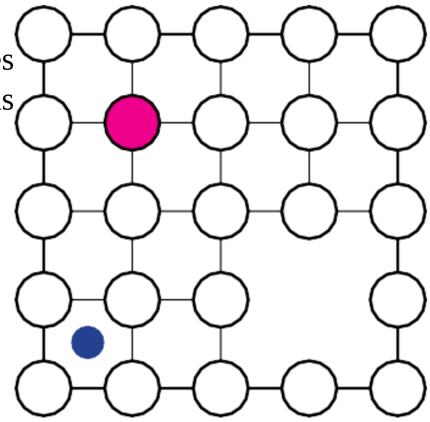


Figure 4-1: Point defects

ii) *One-dimensional defects such as disclinations and dislocations* (Figure 4-2). Disclinations derive from inserting or subtracting a block of atoms in the crystal lattice. Dislocations derive from the insertion or subtraction of an atomic plane.

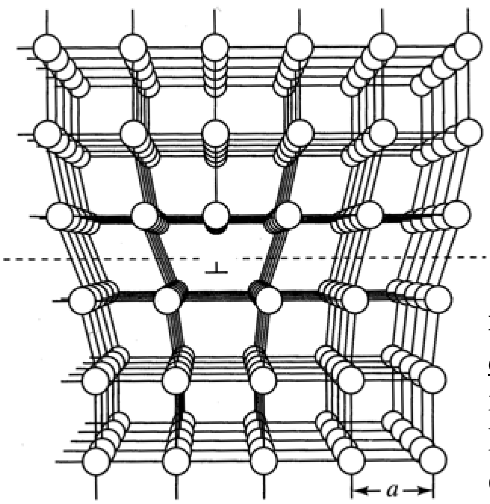


Figure 4-2: *Insertion of an extra half-plane creating an edge dislocation*

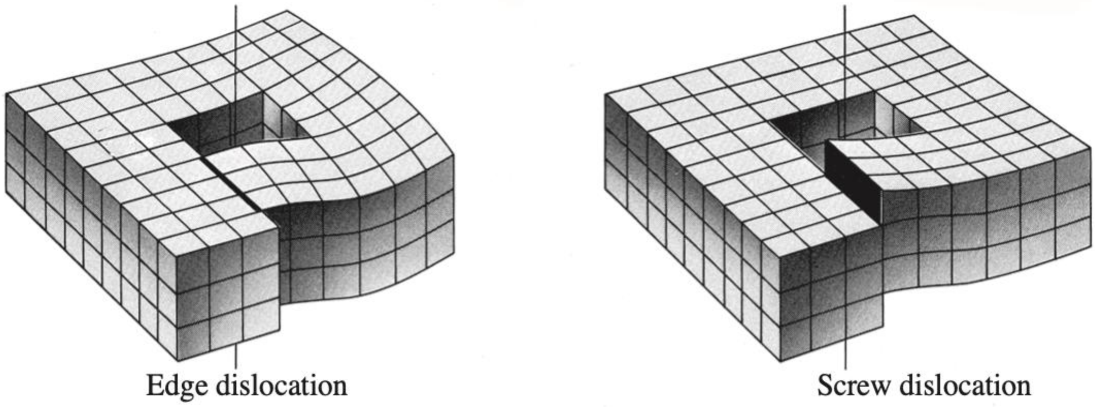


Figure 4-3: *DISLOCATIONS in periodic structures have to obey the translational symmetries of the lattice. Here, we create an edge dislocation (left) and a screw dislocation (right) in a cubic crystal by cutting through a crystal plane and moving one of the surfaces from one row to the other. The continuity of the lattice is conserved. After that, the two surfaces are joined together again. The dislocation core can be empty or full (the resulting structure is then disordered).*

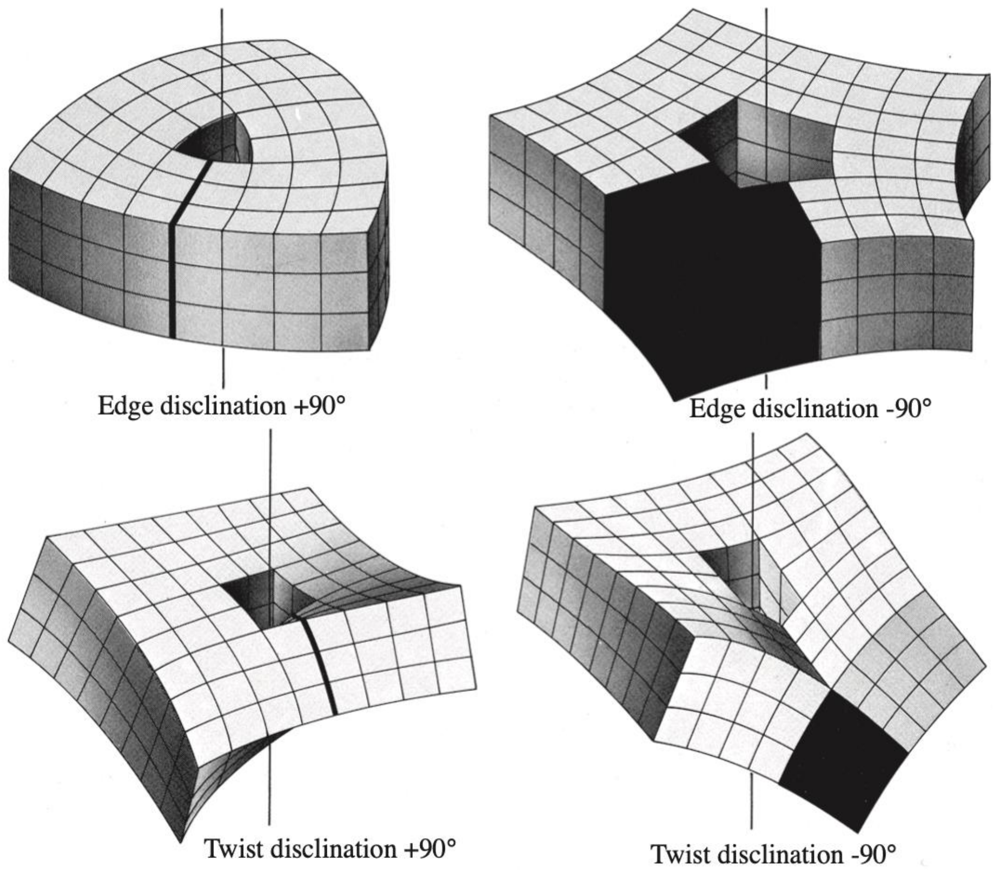
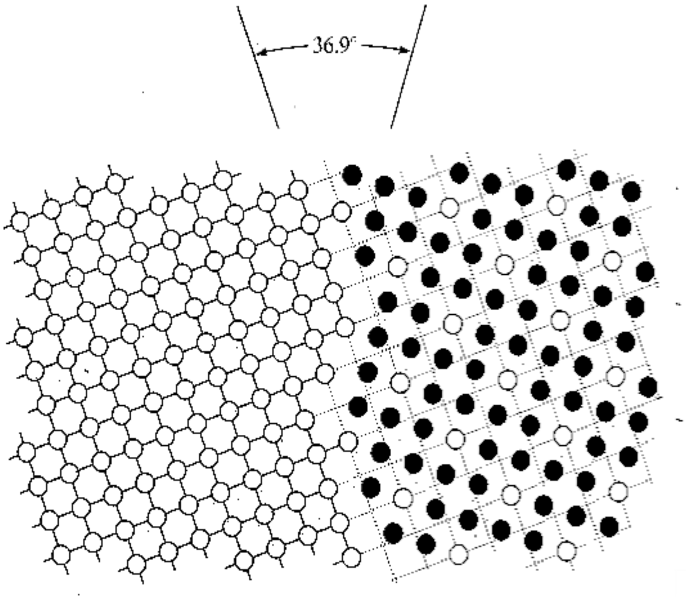


Figure 4-4: *DISCLINATIONS in structured materials are possible because the rotations required to generate those defects are symmetry operations of the lattice. In a cubic lattice (order of symmetry 4), the minimal rotation is 90º. We can obtain edge disclinations by removing an edge of material (a) or adding one (b). We can have twist disclinations by a 90º rotation of the two cut surfaces around an axis perpendicular to them (c) or around an axis belonging to the initial cutting plane and intercepting the axis of the torus (d). Rotations by different values than 90º or multiples of it generate discontinuities in the lattice; the cut parts cannot be joined together without creating structural interruptions. As these heavy rotations create enormous stresses, ordinary crystals have no disclinations. The core of the disclination, encircling the disclination line, can be empty or full.*

iii) *Two-dimensional defects or grain boundaries.* These defects arise in the interface between two single crystals. Here, we consider grain boundary interfaces of two crystals having random orientations, with coincidence sites and those with a weak misorientation (small angle).



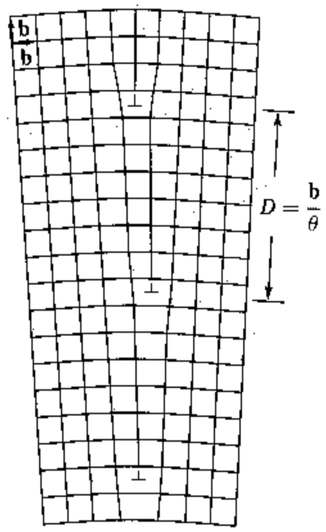


Figure 4-5: *A grain boundary, by general definition, is a disordered zone in a crystal. In coincidence site lattice (CLS) theory, a grain boundary is characterized by the periodic superposition of two lattices. In Σ=5 boundaries, there is a virtual coincidence for every five atoms of the lattices across the boundary (a). An equidistant stack of dislocations can model a small angle boundary (b).*

Symmetric crystalline boundaries are twins and stacking faults. A twin crystal has a unique orientation relation with its parent crystal formed by many processes, e.g., during crystal growth, if the crystal is subjected to stress or temperature/pressure conditions different from those during growth, two or more intergrown crystals are formed symmetrically, having a mirror plane. For example, compound twins in FCC crystals (Figure 4-6) are common growth faults. They are sometimes referred to as Σ3 CSL boundaries since three atoms are mirrored across the mirror plane twin boundary.

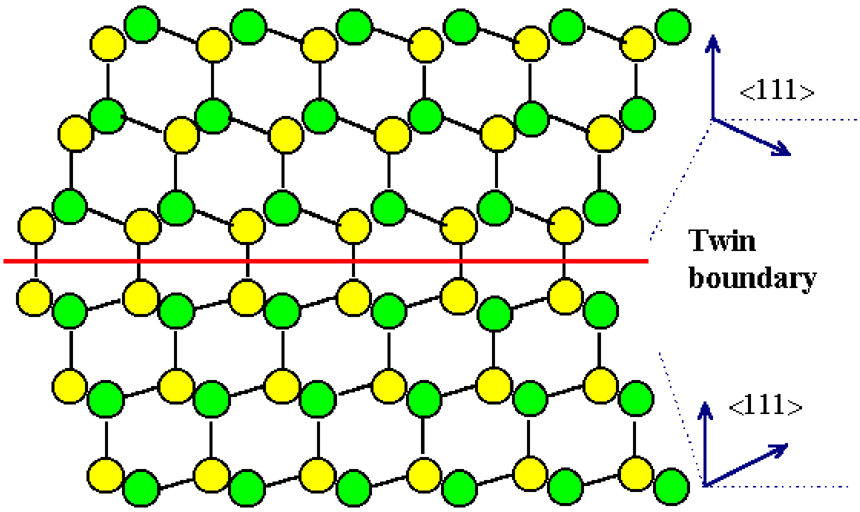


Figure 4-6: *A twin is characterized by a mirror symmetry between two crystals.*

iv) _Three-dimensional defects include amorphous phases, glassy materials, quasicrystals, and fractals._

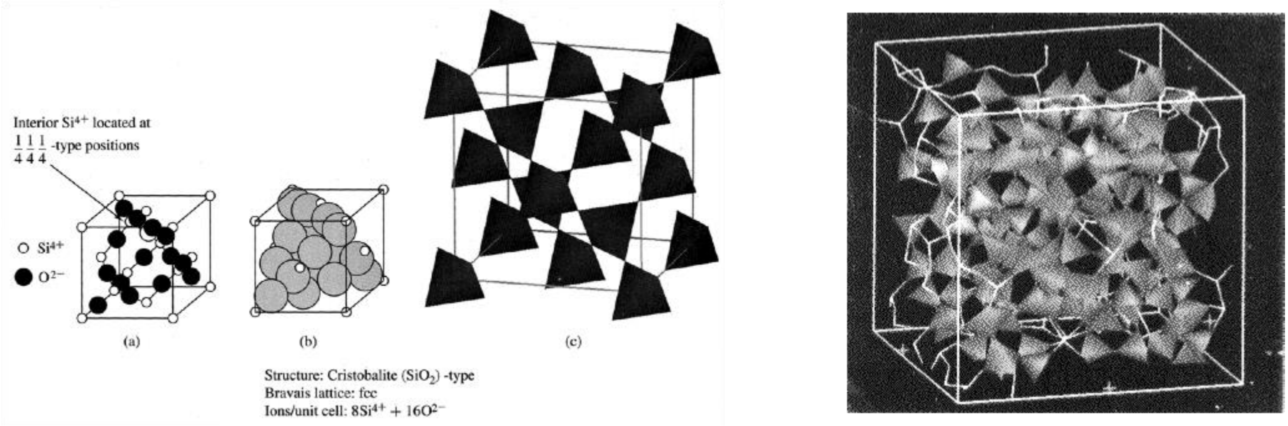


***Figure 4-7**: Crystal silica (a) is characterized by an arrangement on a crystal lattice similar to a diamond based on tetrahedrons of SiO_4^{4-} . If liquid silicate is cooled down fast enough, the ions cannot rearrange, and a glass forms.*

It is well known from crystallography that covering a two-dimensional surface with fivefold symmetry patterns is impossible. However, some materials show shapes and diffraction diagrams with a fivefold symmetry axis, others with symmetry 7, and higher order symmetries have been found.

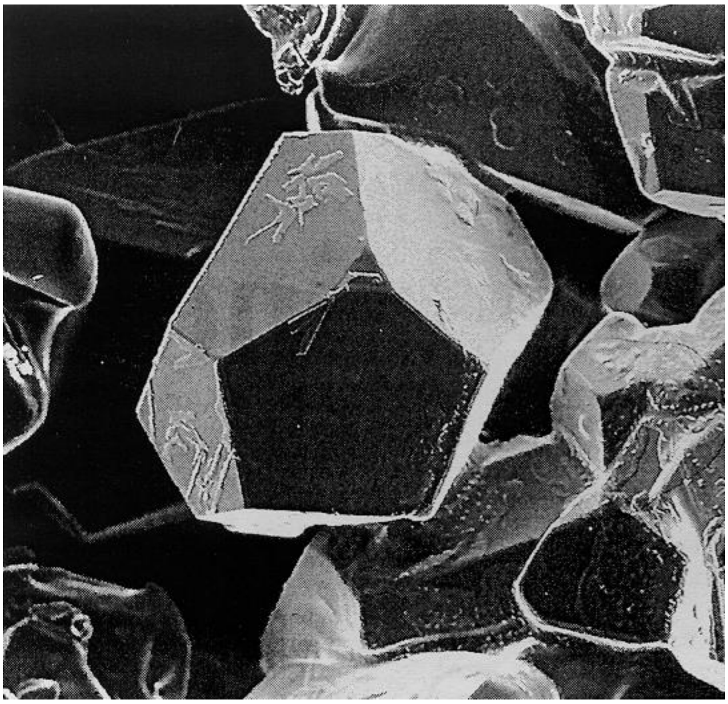


***Figure 4-8:** Image of a quasicrystal Al-Mn-Si, which shows a symmetry 5*

This unphysical symmetry derives from a periodic arrangement at a local scale, which cannot be reproduced in the long range. An example of such a structure in two dimensions is given by the Penrose tiling shown in Figure 4-9.

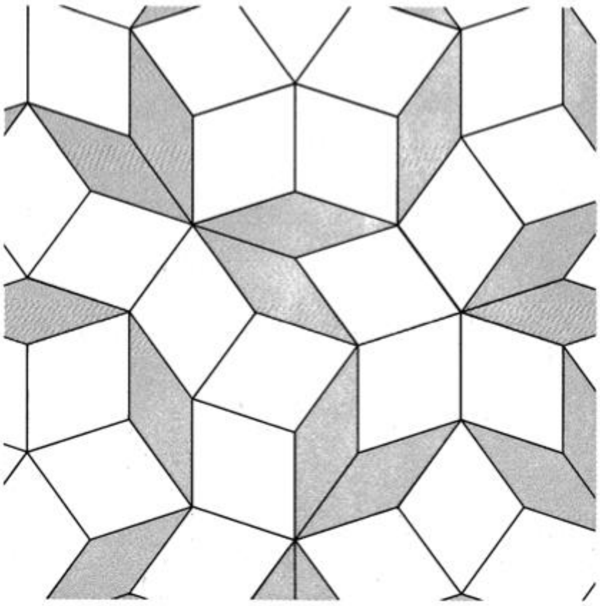


Figure 4-9: *Penrose tiling in two dimensions formed by two kinds of diamond shapes. This arrangement is not periodic but shows a five-fold rotational symmetry around a local axis.*

Fractal structures are persistent in nature, e.g., trees, snowflakes, and dendrites of solidified metal microstructures are all characterized by structures reproduced at different scale levels.

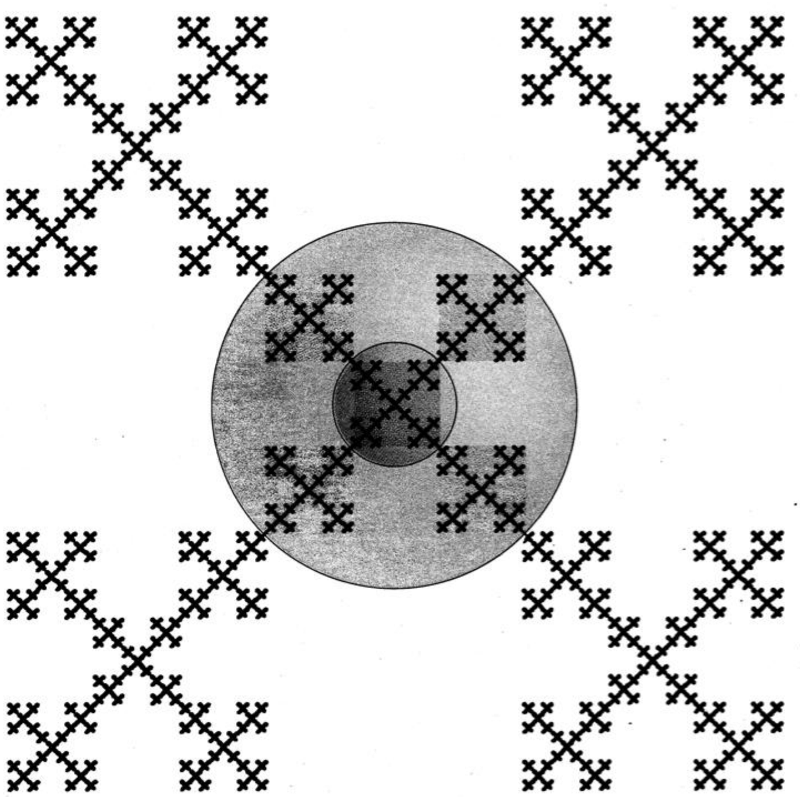


Figure 4-10: *Two-dimensional fractal structure. In a crystal structure, if we take three times the radius, the quantity of matter in the circle formed is* $r^2 = 9$ *times larger than in the initial circle. In this fractal, doing the same, the increase in the material is by a factor of 5. The fractal dimension is then 1.46.*

A particularity of fractals is that mass does not increase as r^3 but instead follows the law:

$$M(r) = Ar^d \quad \text{with d < 3}$$

Thus, the density of a fractal material decreases as the size of the repetitive fractal unit increases.

$$\rho(r) = \frac{M(r)}{V(r)} = Cr^{d-3}$$

4.2 Point defects - introduction

This section examines different types of point defects and the methods to create them. We can distinguish between intrinsic point defects (self-interstitials in a pure metal) and extrinsic point defects (impurity interstitials). In a model made of solid spheres, we can imagine these defects as it is illustrated below:

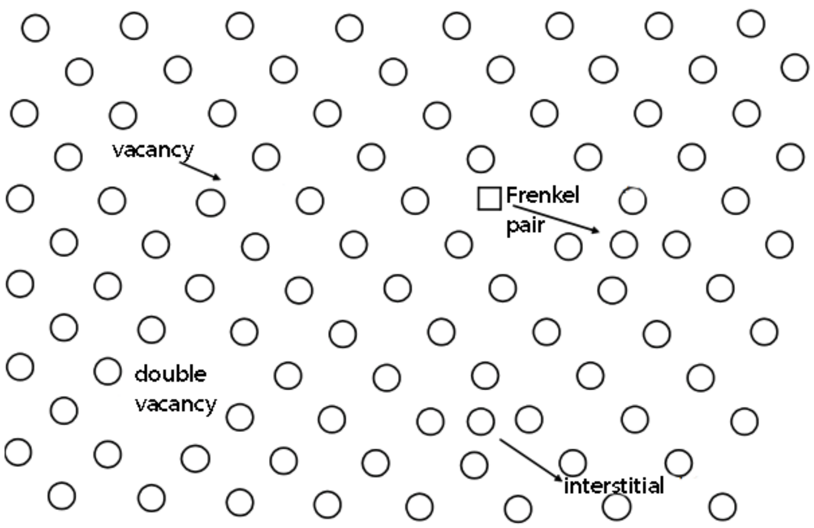


Figure 4-11: *Self-interstitial point defects: vacancy, double vacancy, self-interstitial, Frenkel pair*

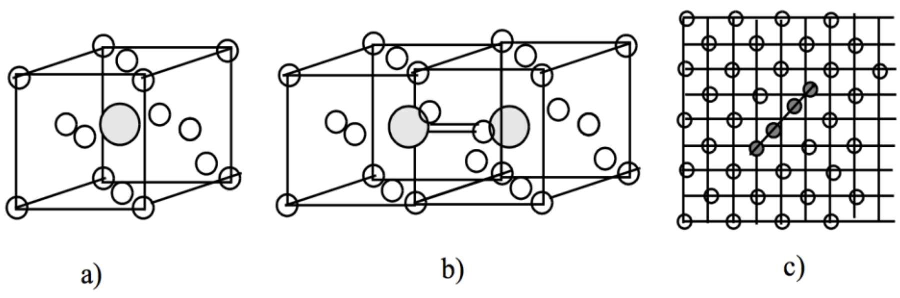


Figure 4-12: *Interstitials in FCC have three possible configurations: a) centered, b) split interstitials (sometimes called dumbbell interstitials), and c) crowdion interstitial (one additional atom along the close-packed direction, e.g., <110>. Its existence is controversial and never proven as it is hard to distinguish between intrinsic interstitials.*

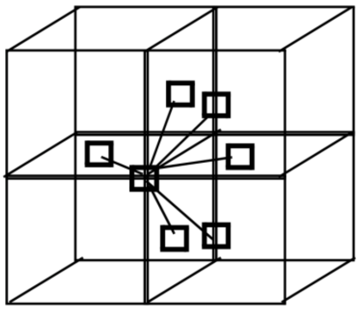


Figure 4-13: *A double vacancy defect in an FCC structure has six possible orientations*

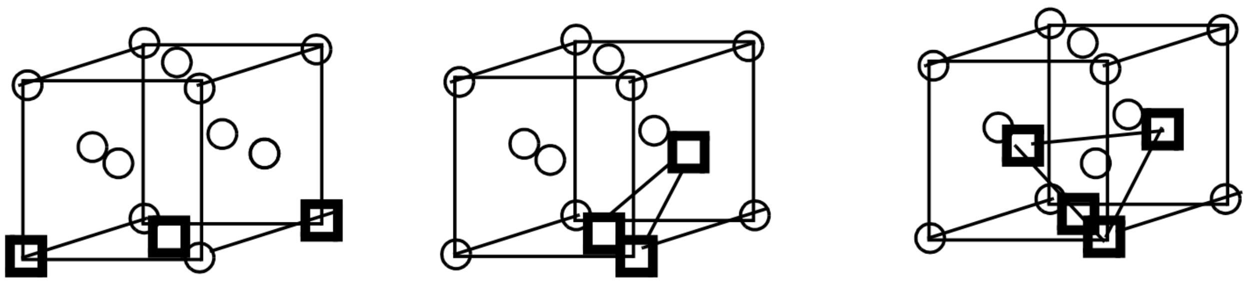


Figure 4-14: *A triple vacancy represented in three possible configurations are, from left to right, linear, planar, tetrahedral (the most stable)*

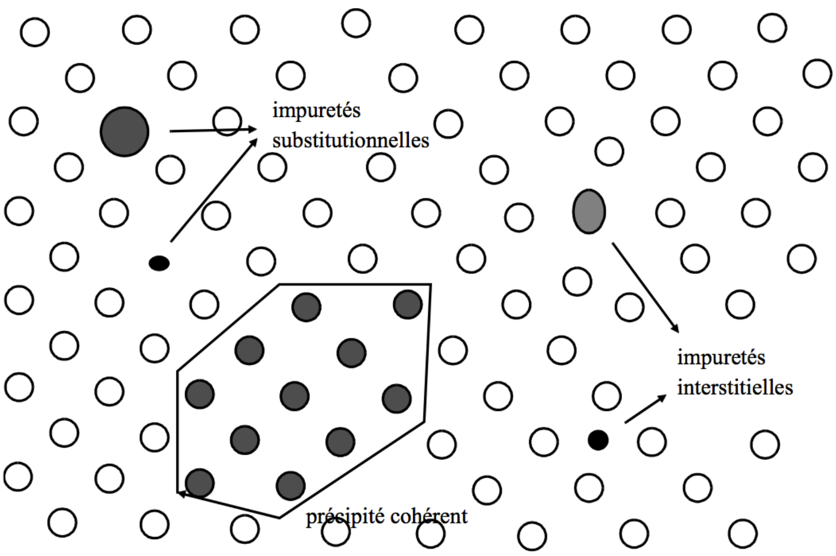


Figure 4-15: *Extrinsic point defects. Interstitial and substitutional impurities*

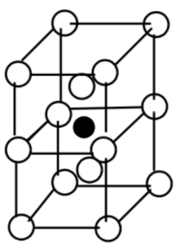


Figure 4-16 : *Interstitial impurities in cubic centered metals, for example C , N, O in Fe, Ta, Nb, Cr are usually located in octahedral sites.*

Point defects in ionic crystals

Ionic crystals must have charge neutrality to be at equilibrium.

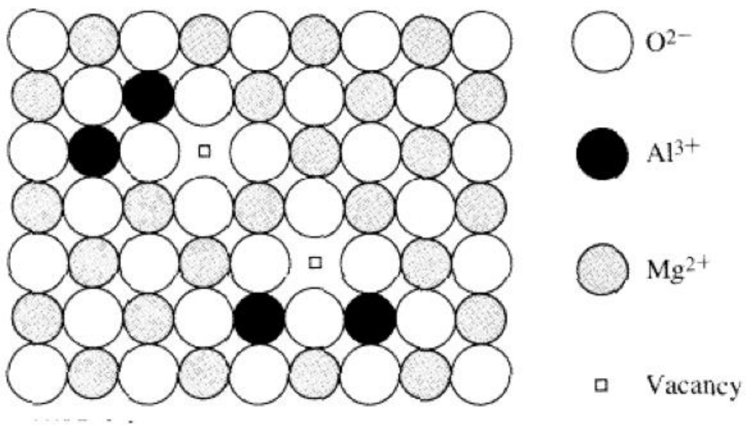


Figure 4-17: *Defects in ionic crystals. There must be two atoms of Al for each missing Mg to ensure neutrality in MgO. This is an example of defects generated by substitutional atoms.*

Vacancy defects in ionic crystals can be of two kinds (figure 4-18):

1) Schottky defects vacant cation+ and vacant anion-

2) Frenkel defects vacant cation+ and interstitial anion-
or vacant anion- and interstitial cation+

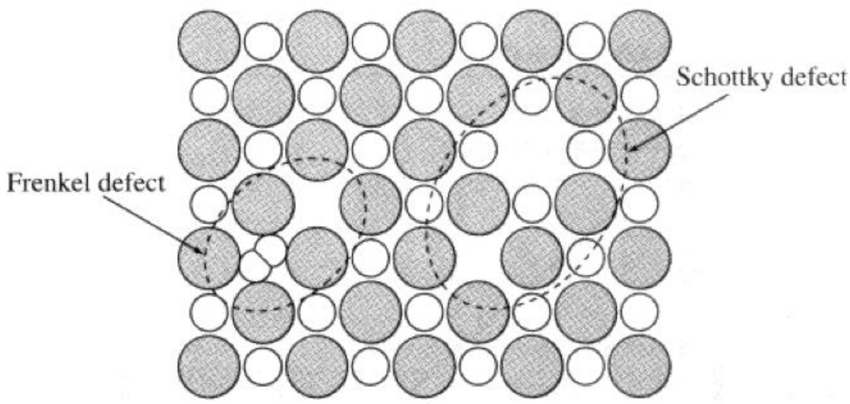


Figure 4-18: *Defects in ionic crystals: Frenkel and Schottky pairs.*

4.2.1 Formation energy for point defects

a) Vacancies

An estimated value for the formation energy of a vacancy can be calculated by considering that *p* bonds have to be cut inside the crystal to extract an atom, and *p/2* bonds have to be rebuilt when that atom is deposited on the external surface. The formation energy corresponds thus to the rupture of *p/2* atomic bonds. That is, an atom's sublimation energy corresponds to the rupture of *p/2* atoms. We can write that we have approximately:

$$U_{fv} \equiv E_{sub} \approx \frac{p}{2} B$$

where E_{sub} is the sublimation energy, and B is the energy of an atomic bond.

In covalent and ionic crystals, this relationship proves to be close to reality (it is the case of central forces). Nevertheless, central forces should be considered in the case of metals. From experimental results, we use:

$$U_{fv} \approx 0.25 E_{sub} \quad to \quad 0.5 E_{sub} \tag{4.1}$$

This decrease comes from rearranging the lattice around the vacancy, stabilizing it, and reducing its energy.

b) Interstitials

The formation of an interstitial in a lattice entails a heavy expansion in the local volume δV. An interstitial can be compared to a sphere of volume $\delta V \sim b^3$, which has to fit inside a hole of radius $R<<b$ ($R\sim 0$ in the face-centered cubic). The elastic energy due to distortion (U_{dist}) is very high, around 2 to 3 μb^3. We have:

$$U_{fi} \sim U_{dist}$$

The formation energy for an interstitial atom is a function of the structure and the volume of the interatomic spaces in the considered crystal. However, as a general rule, interstitial atoms need more energy than vacancies for their formation and are thus more challenging to create.

c) Substitutional defects

Substitutional defects can be formed when another atom of similar size replaces an atom of the lattice. Here, we calculate the elastic distortion from the presence of an atomic-sized inclusion in the framework of continuum mechanics.

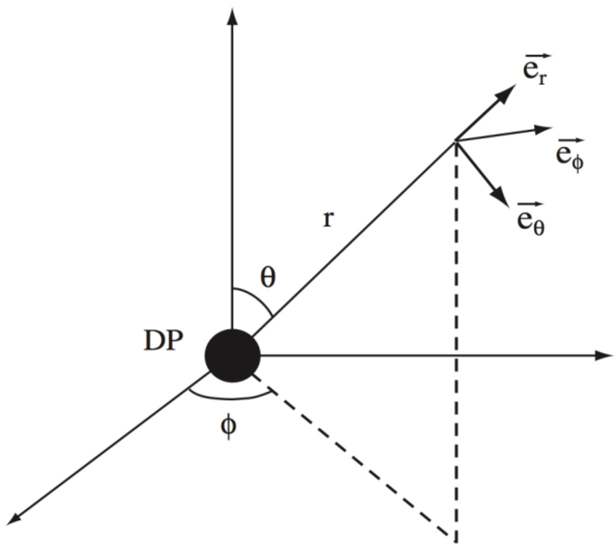


Figure 4-19: *Point defects generally show a spherical symmetry. The natural choice for the calculations is then a spherical system of coordinates.*

Strain tensor:

$$\varepsilon_{rr} = \frac{\partial u_r}{\partial r} \qquad \varepsilon_{\theta\theta} = \frac{1}{r}\frac{\partial u_\theta}{\partial \theta} + \frac{u_r}{r} \qquad \varepsilon_{\phi\phi} = \frac{1}{r\sin\theta}\frac{\partial u_\phi}{\partial \phi} + \frac{u_\theta}{r\tan\theta} + \frac{u_r}{r}$$

$$2\varepsilon_{r\theta} = \frac{\partial u_\theta}{\partial r} + \frac{1}{r}\frac{\partial u_r}{\partial \phi} - \frac{u_\theta}{r}$$

$$2\varepsilon_{r\phi} = \frac{\partial u_\phi}{\partial r} + \frac{1}{r\sin\theta}\frac{\partial u_r}{\partial \phi} - \frac{u_\phi}{r} \qquad (4.2)$$

$$2\varepsilon_{\theta\phi} = \frac{1}{r\sin\theta}\frac{\partial u_\theta}{\partial \phi} + \frac{1}{r}\frac{\partial u_\phi}{\partial \theta} - \frac{u_\phi}{r\tan\theta}$$

Hooke's law in an isotropic solid:

$$\sigma_{ij} = K u_{kk}\delta_{ij} + 2\mu(u_{ij} - \frac{1}{3}\delta_{ij}u_{kk})$$

with $K = \lambda + 2/(3\mu)$ (λ and μ being Lamé parameters)

Model

Consider the point defect as a sphere representing atom B inserted in a cavity corresponding to an atom of type A in the matrix. The difference in size between the inclusion of radius 'ρ and the cavity of radius ρ creates a distortion, which takes back both radiuses to an equilibrium radius ρ_E. As a result, internal stresses are produced within the matrix and the inclusion.

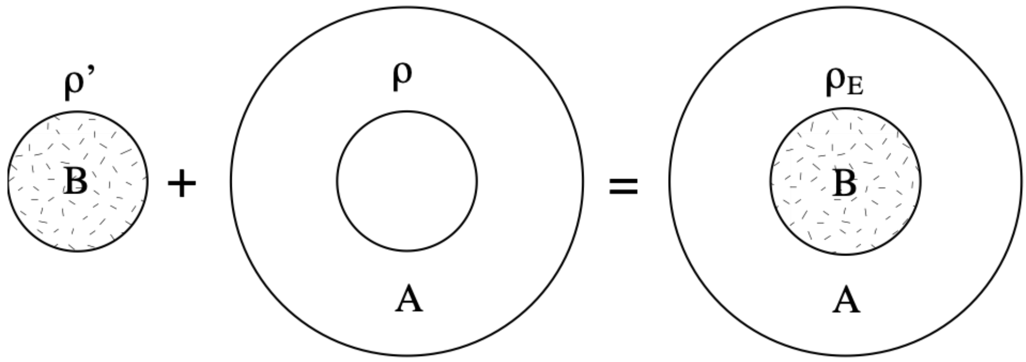


Figure 4-20: *Point defect B causes a distortion of the matrix from ρ_A to ρ_E.*

We want to calculate:

1) the equilibrium radius

2) the stresses and the strains in A and B

3) several physical and measurable quantities: ΔV/V, elastic energy, etc.

Procedure to follow:

1. The strain field $\vec{u} = \vec{u}(r)$ has to satisfy the equilibrium equation (3.78):

$$2(1-\nu)\overrightarrow{grad}(div\vec{u}) - (1-2\nu)\overrightarrow{rot}(\overrightarrow{rot}\vec{u}) = 0$$

But the point defect exhibits a central symmetry $\vec{u} = \vec{u}(r)$ which implies:

$\overrightarrow{rot}\vec{u} = 0$ so that $\overrightarrow{grad}(div\vec{u}) = 0$

or else $div\vec{u} = const$

Let $div\vec{u} = 3a$ (4.3)

In spherical coordinates:

$$div\vec{u} = \frac{1}{r^2 \sin\theta}\left[\partial_r(r^2 \sin\theta u_r) + \partial_\theta(r\sin\theta u_\theta) + \partial_\phi(ru_\phi)\right] \tag{4.4}$$

Since spherical symmetry has this condition $u_\theta = u_\phi = 0$ we obtain the following:

$$u_r = ar + \frac{b}{r^2} \tag{4.5}$$

2. We know then the displacement field; we can calculate the strain tensor

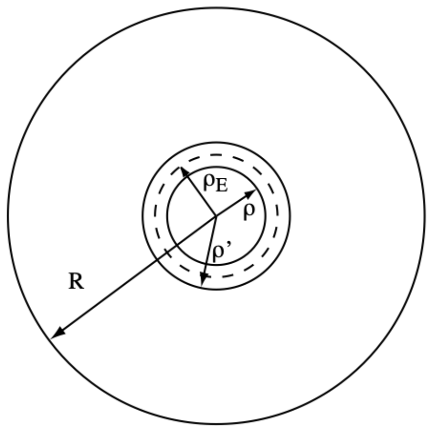
$u_{rr} = \frac{\partial u_r}{\partial r} = a - \frac{2b}{r^3}$ $u_{\theta\theta} = u_{\phi\phi} = \frac{u_r}{r} = a + \frac{b}{r^3}$ and $u_{r\theta} = u_{r\phi} = u_{\theta\phi} = 0$

$$\sigma_{rr} = K(u_{rr} + u_{\theta\theta} + u_{\phi\phi}) - \frac{2}{3}\mu(u_{rr} + u_{\theta\theta} + u_{\phi\phi}) = 3Ka - \frac{4\mu b}{r^3} \tag{4.6}$$

$$\sigma_{\theta\theta} = \sigma_{\phi\phi} = 3Ka + \frac{2\mu b}{r^3} \tag{4.7}$$

The stress tensor is derived by applying Hooke's law:

3. The solution to this problem considers the elastic constants of the two materials, the boundary conditions, and the difference in size between the matrix and the inclusion.



Elastic constants:
Matrix: μ, ν, K
Inclusion: μ’,ν’,K’

Initial radiuses:
Matrix: ρ, R
Inclusion: ρ'

Matrix:

$$u_r = ar + \frac{b}{r^2} \tag{4.8}$$

$$\sigma_{rr} = 3Ka - \frac{4\mu b}{r^3} \tag{4.9}$$

$$\sigma_{\theta\theta} = \sigma_{\phi\phi} = 3Ka + \frac{2\mu b}{r^3} \tag{4.10}$$

Inclusion:

$$u_r' = a'r \tag{4.11}$$

To avoid the function diverging, it must be $b' = 0$

$$\sigma_{rr}' = \sigma_{\phi\phi}' = \sigma_{\theta\theta}' = 3K'a' \tag{4.12}$$

Boundary conditions:

1) $\sigma_{rr}'(\rho_E) = \sigma_{rr}(\rho_E)$

$$\rightarrow 3K'a' = 3Ka - \frac{4\mu b}{\rho_E^3} \tag{4.13}$$

2) $\sigma_{rr} = 0$ for r = R

$$\rightarrow 3Ka - \frac{4\mu b}{R^3} = 0 \tag{4.14}$$

3) $\rho_E - \rho' = u'(\rho_E)$ (4.15)

4) $\rho_E - \rho = u(\rho_E)$ (4.16)

Conditions 3) and 4) imply $\rho' - \rho = a\rho_E + \frac{b}{\rho_E^2} - a'\rho_E$ (4.17)

We take: $\eta = \frac{\rho' - \rho}{\rho_E}$ (size factor) (4.18)

To obtain:

$$a' = -\frac{4\mu\eta}{3K' + 4\mu} \tag{4.19}$$

$$a = \frac{4\mu b}{3KR^3} \tag{4.20}$$

$$b = \eta \frac{\rho_E^3}{1 + \frac{4\mu}{3K'}} \tag{4.21}$$

$$\rho_E = \rho' + \frac{4\mu}{3K' + 4\mu}(\rho - \rho') \tag{4.22}$$

Measurable physical quantities.

a) Volume variation

$$\frac{\Delta V}{V}=\frac{4\pi R^2 u_r(R)}{\frac{4}{3}\pi R^3}=3\frac{u_r(R)}{R}=3\left(a+\frac{b}{R^3}\right) \tag{4.23}$$

Replacing *a* and *b*:
$$\frac{\Delta V}{V}=3\eta\left(\frac{\rho_E}{R}\right)^3\frac{1+\frac{4\mu}{3K}}{1+\frac{4\mu}{3K'}}=3\eta c\frac{1+\frac{4\mu}{3K}}{1+\frac{4\mu}{3K'}} \tag{4.24}$$

$c=\left(\frac{\rho_E}{R}\right)^3$ corresponds to the concentration of point defects

b) Elastic energy

$$W=W_{inclusion}+W_{matrice}$$

$$W=\frac{1}{2}\sigma'_{rr}(\rho_E)(\rho'-\rho_E)4\pi\rho_E^{\ 2}+\frac{1}{2}\sigma_{rr}(\rho_E)(\rho_E-\rho)4\pi\rho_E^2\approx\frac{1}{2}\sigma'_{rr}(\rho_E)(\rho'-\rho)4\pi\rho_E^2 \tag{4.25}$$

with $\sigma'_{rr}=3K'a'$ we find:

$$W=\pi\mu\rho_E^3\eta^2\frac{8}{1+\frac{4\mu}{3K'}} \tag{4.26}$$

Order of magnitude of the elastic energy

$$\mu a^3=\mu\rho^3\sim 1eV \qquad \text{and} \qquad 1+\frac{4\mu}{3K'}\sim\frac{3}{2}$$
$$W\sim 16\eta^2[eV]$$

4.2.2 Concentration of vacancies at thermodynamic equilibrium

The equilibrium concentration of vacancies at constant *P* and *T* is found by minimizing Gibbs free energy: *G* = *H* - *TS*.

For example, if we introduce *n* vacancies on (*N*+*n*) sites of the lattice, the variation in free energy is:

$$\Delta G=n\Delta G_V^F-TS_m \tag{4.27}$$

where: $\Delta G_V^F=E_V^F+PV_V^F-TS_V^F$

is the free energy of formation for one vacancy

and $S_m=k\ln\frac{(N+n)!}{N!n!}$ is the entropy of mixing

The thermodynamic equilibrium implies: $\frac{\partial\Delta G}{\partial n}=0$

It follows then (cf. exercise) that the concentration of vacancies at equilibrium is:

$$C_V = \frac{n}{n+N} = e^{-\frac{\Delta G_V^F}{kT}} \tag{4.28}$$

or else

$$C_V = e^{\frac{S_V^F}{k}} e^{\frac{E_V^F + PV_V{}^F}{kT}} = C_0 e^{-\frac{E_V^F + PV_V{}^F}{kT}} = C_0 e^{-\frac{H_V^F}{kT}} \tag{4.29}$$

E_V^F is the formation energy for a vacancy ~ 1 eV /atom= 1. 10^{-5} Joules

$H_V{}^F$ is the formation enthalpy of a vacancy

V_V^F is the formation volume of the vacancy ~ atomic volume ~ 10^{-29} m^3

P is the atmospheric pressure $\sim 10^5$ Pa

PV_V^F $\sim 10^{-25}$ Joules $= 6.0\,10^{-2}\,eV\,/\,atom$

at normal pressure, this term is negligible compared to the formation energy. It intervenes only at high-pressure levels.

S_V^F is the formation entropy of the vacancy. This value is due to the change in the vibration entropy of the crystal S_V when we introduce a vacancy defect.

In the following, we calculate the formation entropy of a vacancy defect and then C_0 .

Here, we give the procedure to be followed, but this chapter is not subject to the final examination. We consider N atoms vibrating at the same frequency ν. A vacancy changes the vibration frequency (photons) of x nearby atoms, which see their frequency go from ν to 'ν= ν+Δν.

i)Einstein approximation

We must first show that the vibration entropy S_ν is given by:

$$S_\nu = 3Nk\left(1 + \ln\frac{kT}{h\nu}\right)$$

Each atom is modeled as three oscillators. Each of them receives quanta of energy hν. Thus, there are n_i oscillators of energy ε_i = (i+1/2) hν for N atoms. We then have 3N oscillators attributed to the energy levels ε_i.

The number of possible configurations is written as:

$$\Omega = \frac{3N!}{\Pi n_i!} \tag{4.30}$$

with $\sum_i n_i = 3N$

The free energy of the system is $F = E - TS$

$$
\begin{aligned}
F &= \sum_i n_i\varepsilon_i - kT\ln\Omega = \\
&= \sum_i n_i\varepsilon_i - kT\left[3N\ln 3N - 3N - \left(\sum_i n_i \ln n_i - n_i\right)\right] = \\
&= \sum_i n_i\varepsilon_i - kT\left[3N\ln 3N - \sum_i n_i \ln n_i\right] = \\
&= \sum_i n_i\varepsilon_i + kT\sum_i n_i \ln\frac{n_i}{3N}
\end{aligned}
\qquad (4.31)
$$

The probability that *the minimum of F gives n_i oscillators of energy* ε_i under the condition that $\sum_i n_i = 3N$

We use, in this case, the Lagrange function:

$$\Phi = F - \lambda\left(\sum_i n_i - 3N\right) \qquad (4.32)$$

$$\Phi = \sum_i n_i\varepsilon_i - kT\left[3N\ln 3N - \sum_i n_i \ln n_i\right] - \lambda\left(\sum_i n_i - 3N\right)$$

$$\frac{\partial\Phi}{\partial n_i} = 0 = \varepsilon_i + kT(\ln n_i + 1) - \lambda$$

from which $n_i = e^{\frac{\lambda}{kT}-1}\cdot e^{-\frac{\varepsilon_i}{kT}}$ and $3N = \sum_i n_i = e^{\left(\frac{\lambda}{kT}-1\right)}\cdot\sum_i e^{-\frac{\varepsilon_i}{kT}}$

Therefore :

$$\frac{n_i}{3N} = \frac{e^{-\frac{\varepsilon_i}{kT}}}{\sum_i e^{-\frac{\varepsilon_i}{kT}}} = \frac{e^{-\frac{\varepsilon_i}{kT}}}{L} \qquad (4.33)$$

$L = \sum_i e^{-\frac{\varepsilon_i}{kT}}$ is the partition function

Combining (4.32) and (4.33)

$$
\begin{aligned}
F &= \sum_i 3N\frac{e^{-\frac{\varepsilon_i}{kT}}}{L}\varepsilon_i + kT\sum_i 3N\frac{e^{-\frac{\varepsilon_i}{kT}}}{L}\left(-\frac{\varepsilon_i}{kT} - \ln L\right) = \\
&= -3NkT\ln L
\end{aligned}
\qquad (4.34)
$$

Now: $S = -\left.\frac{\partial F}{\partial T}\right|_V = 3N\left(k\ln L + \frac{kT}{L}\left.\frac{\partial L}{\partial T}\right|_V\right)$

$$L = \sum_i e^{-\frac{\varepsilon_i}{kT}} = \sum_i e^{-\frac{(i+\frac{1}{2})h\nu}{kT}} = e^{-\frac{h\nu}{2kT}} \cdot \sum_{i=0}^{\infty} e^{-\frac{ih\nu}{kT}} =$$

$$= e^{-\frac{h\nu}{kT}}(1 + e^{-\frac{h\nu}{kT}} + e^{-\frac{2h\nu}{kT}} + e^{-\frac{3h\nu}{kT}} + \dots$$

$$= e^{-\frac{h\nu}{2kT}} \cdot \frac{1}{1 - e^{-\frac{h\nu}{kT}}}$$

If T>>0, then $\frac{h\nu}{kT}$ is small, and then $e^{-\frac{h\nu}{kT}} = 1 - \frac{h\nu}{kT}$

and $L \cong \frac{1 - \frac{h\nu}{2kT}}{\frac{h\nu}{kT}} \cong \frac{kT}{h\nu}$ from where

$$S_v = 3Nk\left(\ln\frac{kT}{h\nu} + 1\right) \tag{4.35}$$

ii) Evaluation of the Grüneisen constant

We want to show that $\gamma = \frac{d(\ln\nu)}{d(\ln V)}$ is a constant.

Starting from the free energy of the crystal formed by N atoms:

$$\begin{aligned} G &= N\varepsilon - 3NkT(\ln\frac{kT}{h\nu} + 1) + PV \\ &= N\left(\varepsilon + 3kT\left(\ln\frac{h\nu}{kT} - 1\right)\right) + PV \end{aligned} \tag{4.36}$$

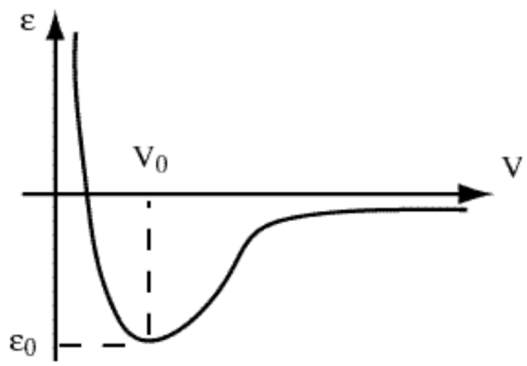
ε is the energy of each atom.

At constant pressure and temperature values, thermodynamic equilibrium holds for $dG = 0$. However, as dV is not necessarily zero:

$$\left.\frac{\partial G}{\partial V}\right|_{T,P} = 0$$

$$\left.\frac{\partial G}{\partial V}\right|_{T,P} = N\left[\left.\frac{\partial \varepsilon}{\partial V}\right|_{T,P} + 3kT\left.\frac{\partial ln\nu}{\partial V}\right|_{T,P}\right] + P = 0 \tag{4.37}$$

It is now necessary to calculate $\left.\frac{\partial \varepsilon}{\partial V}\right|_{T,P}$



Assuming small variations in V around V_0 :

$$\varepsilon = \varepsilon_0 + \frac{1}{2}(V - V_0)^2 \left.\frac{\partial^2 \varepsilon}{\partial V^2}\right|_{\varepsilon=\varepsilon_0} \tag{4.38}$$

We note that $\frac{\partial \varepsilon}{\partial V} = 0$ in $\varepsilon = \varepsilon_0$.

The total energy variation ΔE as a function of ΔV = V - V_0 can be written as:

$$\Delta E = N(\varepsilon - \varepsilon_0) = \frac{1}{2}N(V - V_0)^2 \left.\frac{\partial^2 \varepsilon}{\partial V^2}\right|_{\varepsilon=\varepsilon_0} = -\int_{V_0}^{V} P\,dV$$

which corresponds to the work done by the external pressure P.

Thus, if we define: $\beta = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T = 0$ we have: $P = \frac{-(V - V_0)}{V_0 \beta}$

From this: $-\int_{V_0}^{V} P\,dV = \frac{(V - V_0)^2}{2\beta V_0} = \frac{1}{2}N(V - V_0)^2 \left.\frac{\partial^2 \varepsilon}{\partial V^2}\right|_{\varepsilon=\varepsilon_0}$

Therefore: $\left.\frac{\partial^2 \varepsilon}{\partial V^2}\right|_{\varepsilon=\varepsilon_0} = \frac{1}{N\beta V_0}$

and $\varepsilon - \varepsilon_0 = \frac{1}{2}(V - V_0)^2 \frac{1}{N\beta V_0}$

and

$$\left.\frac{\partial \varepsilon}{\partial V}\right|_{T,P} = \frac{V - V_0}{N\beta V_0} \tag{4.39}$$

Combining (4.39) and (4.37)

$$\frac{V - V_0}{N\beta V_0} + 3NkT \left.\frac{\partial \ln \nu}{\partial V}\right|_{T,P} + P = 0 \tag{4.40}$$

Differentiating (4.40) to T:

$$\frac{1}{\beta V_0}\left.\frac{\partial V}{\partial T}\right|_P + 3Nk \left.\frac{\partial \ln \nu}{\partial \nu}\right|_{T,P} = 0$$

$3Nk = C_v$ for high temperatures (Dulong-Petit law), so that:

$$\frac{d\ln \nu}{dV} = -\underbrace{\frac{1}{V_0}\left.\frac{\partial v}{\partial T}\right|_P}_{=\alpha} \cdot \frac{1}{\beta C_v} = \frac{\alpha}{\beta C_v}$$

and

$$\frac{d\ln \nu}{d\ln V} = -\frac{\alpha V_0}{\beta C_v} = -\gamma \tag{4.41}$$

where γ is called the Grüneisen parameter.

In metals, this constant takes values between 2 and 3.

Some typical examples are: $\gamma_{Al} = 2.06$
$\gamma_{Ni} = 1.7$
$\gamma_{Ag} = 2.6$
$\gamma_{Au} = 2.93$

iii) Vacancy formation energy

We suppose that a vacancy is surrounded by x atoms, which changes their frequency from ν to 'ν (when the vacancy is formed), whereas the other atoms are not perturbed. The variation in the vibrational entropy of the lattice gives the formation entropy of the vacancy.

$$\begin{aligned} S_V^F &= S_V(3(N-x),\nu) + S_V(3x,\nu') - S_V(3N,\nu) = \\ &= 3(N-x)k\left(\ln\frac{kT}{h\nu}+1\right) + 3xk\left(\ln\frac{kT}{h\nu'}+1\right) - 3Nk\left(\ln\frac{kT}{h\nu}+1\right) = \\ &= 3xk\ln\frac{\nu}{\nu'} = -3xk\ln\frac{\nu}{\nu'} = -3xk\ln\left(1+\frac{\Delta\nu}{\nu}\right) \end{aligned}$$

Since Δν is small, then $S_V^F = -3xk\dfrac{\Delta\nu}{\nu}$

We show before (4.41) that:

$$\frac{d(\ln\nu)}{d(\ln V)} = \frac{V}{\nu}\cdot\frac{d\nu}{dV} = -\gamma$$

$$\frac{\Delta\nu}{\nu} \cong -\gamma\frac{\Delta V}{V}$$

$\dfrac{\Delta V}{V} = \dfrac{V_V^F}{xV_{at}}$ from which $S_V^F = 3k\gamma\dfrac{V_V^F}{V_{at}}$

$V_V^F \sim \dfrac{1}{2}V_{at}$ and $\gamma \sim 2$ yield:

$$S_V^F \sim 3k \tag{4.43}$$

From this:

$$C_0 = e^{\frac{S_V^F}{k}} \sim 20$$

Thus, the equilibrium concentration of vacancies can be estimated for ambient temperature at $C_V \approx 3\cdot 10^{-16}$.

4.2.3 Creation of Vacancies

There are three possible ways to create vacancy defects:

a) Quenching
b) Strain hardening
c) Irradiation

a) *Quenching*

Quenching can produce an oversaturation of vacancies.

Consider the formula (4.28): $C_V(T) = e^{-\frac{\Delta G_V^F}{kT}}$

During rapid cooling, vacancies are "frozen" in the crystal. However, at temperature T_0, the concentration remains $C_V(T) > C_V(T_0)$, corresponding to a metastable state.
The cooling speed needed to produce vacancies, dT/dt_{max}, is in the order of magnitude of $10^6\ K/s$.

The quenching speeds are a function of the following:

1 - the thermal conductivity
2 - the heat capacity
3 - the shape of the sample
4 - the soaking fluid (water, nitrogen, liquid helium)

Measurement of the density of vacancy defects

We proceed with a series of isochronous annealings followed by quenching at the temperature of liquid helium (figure 4-21).

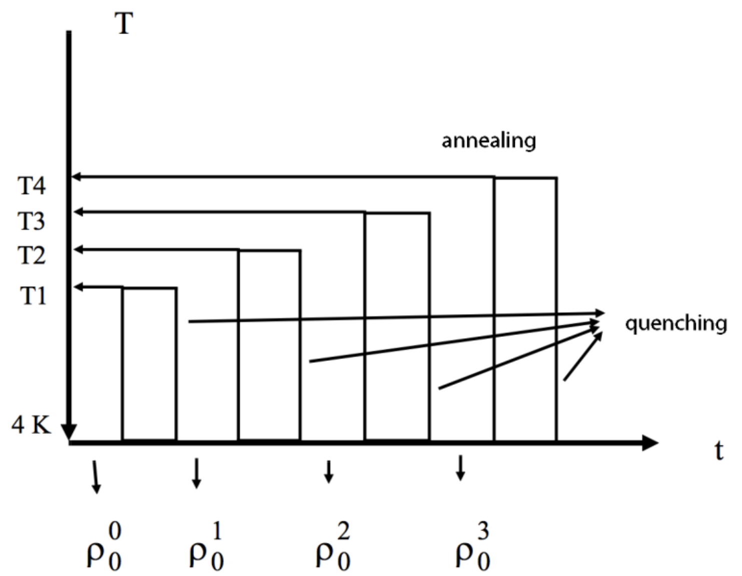
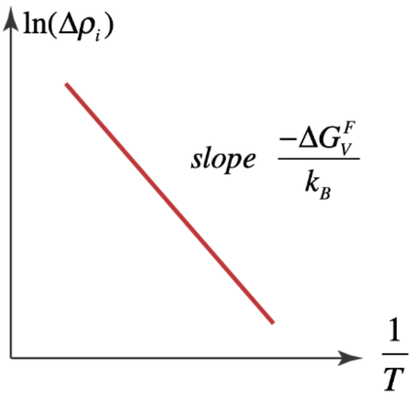


Figure 4-21: *Diagram of the isochronous anneals with consecutive quenching*

We have:
$$T = T_0 \rightarrow C_V = C_V^0 \rightarrow \rho = \rho_0 + \rho_T(T_0) \qquad \text{with } \rho_T = \alpha C_0 e^{-\frac{E_V^F}{kT_0}}$$
$$T = T_1 \rightarrow C_V = C_V^1 \rightarrow \rho = \rho_0^1 = \rho_0 + \rho_T(T_1) \qquad \Delta\rho_0^1 = \rho_0^1 - \rho_0$$
$$T = T_2 \rightarrow C_V = C_V^2 \rightarrow \rho = \rho_0^2 = \rho_0 + \rho_T(T_2) \qquad \Delta\rho_0^2 = \rho_0^2 - \rho_0$$

Then: $$\Delta\rho_0^1 = \alpha(C_V^1 - C_V^0) = \alpha C_0\left(e^{-\frac{E_V^F}{kT_1}} - e^{-\frac{E_V^F}{kT_0}}\right) \approx \alpha C_0 e^{-\frac{E_V^F}{kT_1}} \quad \text{since } e^{-\frac{E_V^F}{kT_0}} \approx 0$$

Plotting: $\ln\Delta\rho_0^i = \ln(\alpha C_0) - \frac{E_V^F}{k}\frac{1}{T_i}$ we get the formation energy of vacancies.



Example: $E_V^F(Al) = 0.76\, eV$ $\qquad$ $E_V^F(Cu) = 1.1\, eV$

b) Strain hardening

The interactions between dislocations (see Chapter VI) lead to the formation of vacancies and interstitials.

c) Irradiation

Irradiation of incident particles (electrons, neutrons, ions, photons) on matter produces the displacement of atoms. This is possible when the energy transmitted during the collisions is much larger than the energy of the bonds between atoms.

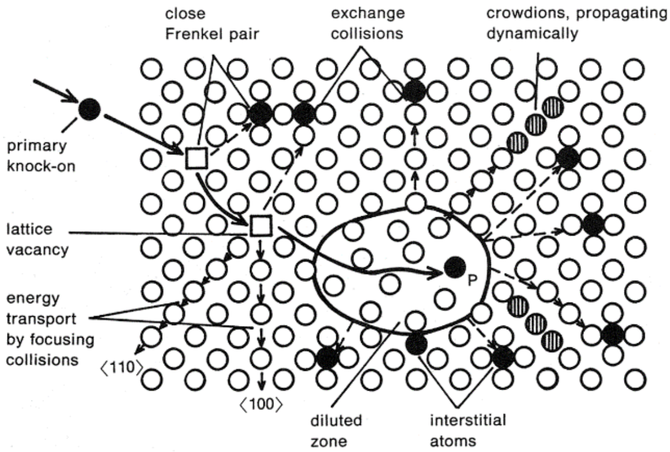


Figure 4-2: *Collision cascade producing lattice defects*

Figure 4-23: *Collision particle-atom, before and after (from left to right)*

In the case of a frontal elastic collision, we can calculate the maximum kinetic T_{max} energy transmitted to the atom of mass M:

$$T_{max} = \frac{4mM}{(m+M)^2}E \tag{4.46}$$

(mc^2 = 511 KeV for the electron).

We can also write for electrons: $T_{max} = \dfrac{2148(E+1.02)}{mc^2}$

where T_{max} is expressed in eV, E in MeV, and M is the atomic mass of the irradiated element.

Example
A = 100, E = 1 MeV $\rightarrow T_{max} = 43\ eV$

$T_{max} >> E_b$ (bond energy), e.g., 3-4 eV in copper.

We call threshold energy the limit beyond which there are irreversible atom displacements. If $T_{max} < E_d$ the energy is transformed into heat. In many cases, $E_d \sim 4E_b \sim 25\ eV$

The factor of 4 comes from the fact that the atom is not on the surface, and part of the bonds of the closest neighbors need to be broken as well.

The *cross-section* for the atomic displacement is given by (in barns):

$$\sigma_d = \frac{dc}{d(\phi \cdot t)} \tag{4.47}$$

with c = concentration of the vacancies created
ϕ = irradiation flux
$\phi \cdot t$ = amount of irradiation
It is possible to have a cascade phenomenon: an atom ejected from its site collides with other atoms and throws them out of their respective sites. The average number of atoms displaced (per unit volume) is:

$$N_d = n_0 \bar{n} \sigma_d \phi t \tag{4.48}$$

where n_0 is the number of atoms per unit volume, and $\bar{n}$ is the average number of displacements per primary atom.

$\bar{n} = 0.5\dfrac{\bar{T}}{E_d}$ with $\bar{T} =$ average energy transmitted by the incident particle.

Example: irradiation with neutrons at 1 MeV

In iron $\bar{n} = 390$
In copper $\bar{n} = 380$

Other effects of irradiation

i) Low-temperature transformations

- formation of new phases (generally non-stable)
- accelerated diffusion

ii) Mechanical properties alteration

- pinning of the dislocations by point defects
- weakening of materials

iii) Production of He gas bubbles

Nuclear reactions give the products of fission, one part of which is gaseous. For example:

$$Ni^{59} + n_{th}^{1} \rightarrow Fe^{56} + He^{4}$$

These gases can form bubbles interacting with dislocations or other defects, causing swelling. During irradiation, we observe an increase in the volume due to the displacement of atoms and, consequently, to the production of vacancies and gas.

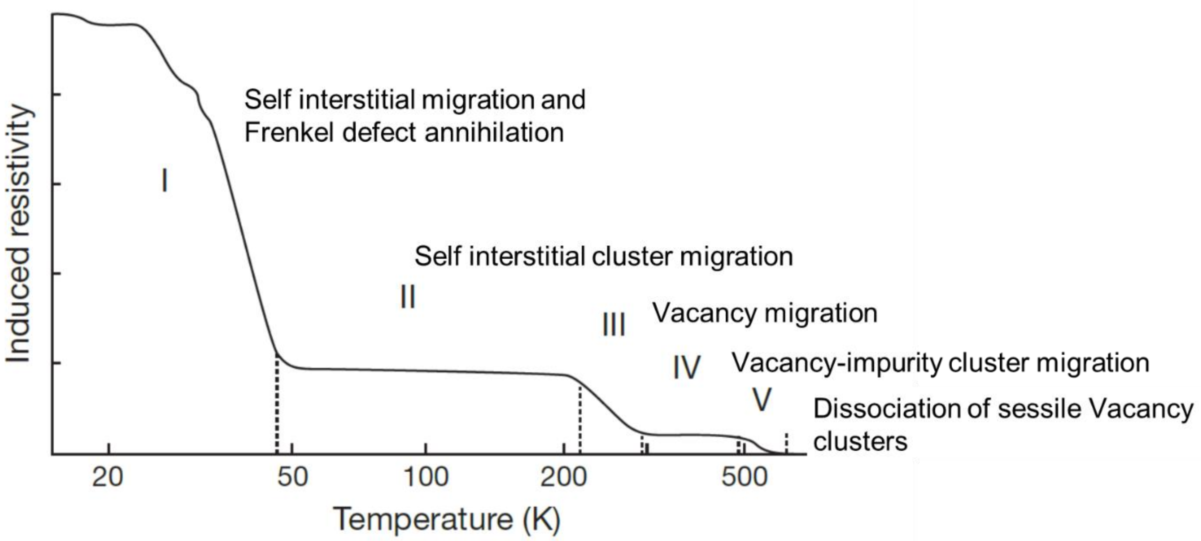


Figure 4-24: *Electrical Resistivity measurements in Copper schematically showing the five stages of recovery (defect annealing) from point defects produced irradiation 1*