Defects in Crystal

case of vacancies – reason to occur and equilibrium concentration

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- Instead if an atom is taken away from its site and transferred inside the crystal this is called Frenknel defect.
- At thermal equilibrium, $T \neq 0$, a certain number of vacancies are always present. A surprising consequence is that a certain concentration of vacancy at equilibrium lowers the free energy (G) of a crystal at constant temperature and pressure, giving a more stable crystal.

Estimation of number of vacancies at equilibrium

* Is possible to estimate the density of vacancy at the equilibrium. To do that we first need to define the free energy for a crystal.
* According to thermodynamics the change in the free energy of a chemical reaction in a close system is:

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

which ΔH is the enthalpy variation and ΔS the entropy variation.
* From a thermodynamic point of view, a solid containing vacancies constitutes a solid solution where the vacancies are dissolved in. In analogy with equilibrium problems with liquid solvent and solution, we can treat the solid like a solvent and the vacancies as a solute, and the problem may be treated in terms of the thermodynamics of chemical reactions and solutions.

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- Let's consider a reaction that starts from a perfect crystal with N sites and 0 vacancies (G_0), and ends up in a crystal with N sites and n vacancies (G_n). Hence the change in free energy is:

$$\Delta G = G_n - G_0 \tag{2}$$

- To evaluate properly the free energy we have to evaluate the entropy S and the entalpy H.
- In,addition vacancy increases the enthalpy of the crystal due to energy required to break bonds

Entropy evaluation

- in thermodynamics the entropy of a system is:
$$S = k_b ln(\Omega) \tag{3}$$
Where Ω represents all the possible microstates of the system, which describe all of the possible ways that a system could be found.
- Hence, in this case the problem reduces to figure out how many ways we can distribute n vacancies in N site:
$$\Omega = \frac{N!}{(N-n)!(n!)} \tag{4}$$
If $n = 0$ we obtain $\Omega = 1$ and as a consequence the entropy of a perfect crystal S_0 is null.
- Using stirling approximation for $N \to \infty$:
$$S = k_b \left(N \ln(N) - (N-n)\ln(N-n) - n \ln(n) \right) \tag{5}$$

Entalpy evaluation

- The enthalpy is defined as follow:
  $$H = U + \sigma V$$
  where the stress σ is a generalisation of the pressure p.
- In our case, the H_0 is a constant independent on the number of vacancies, nonetheless, H_n has a linear dependence on the number of vacancies n.
- This is because the enthalpy shows how much energy and work are required to create a vacancy. If we assume that the enthalpy required to create a vacancy is $H_{vac} = U_{vac} + \sigma V_{vac}$, hence the entalpy to create n vacancies the H_n term is proportional to n:
  $$H_n = n(U_{vac} + \sigma V_{vac}) \tag{6}$$
  .

Minimum of the free energy

* Now we have all the ingredients to estimate the number of vacancies for which we have the minimum in $\Delta G = \Delta H - T\Delta S$.
* Hence imposing $0 = \frac{d}{dn}\Delta G$ we yield with:
$$\frac{n}{N-n} = e^{-\frac{H_{vac}}{k_B T}}$$
considering also the approximation $N >> n$
$$c_{n_{Vac}} = \frac{n}{N} = e^{-\frac{U_{vac}+\sigma V_{vac}}{k_B T}} \tag{7}$$
* Here we have found that only for a certain density of vacancies the minimum is reached.

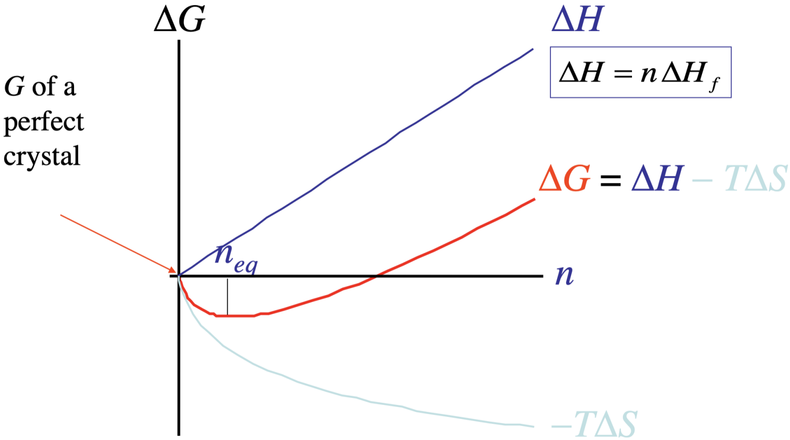

Figure 1: Caption

Temperature dependence

- We can see that for $T \to 0$, theoretically we don't have any vacancies in the crystal. But when the temperature increases the vacancies also increase.

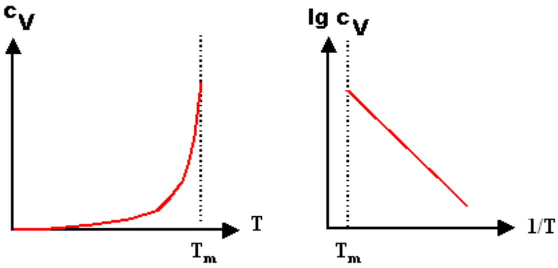

Figure 2: Caption

Pressure dependence

- Neighboring atoms tend to move into the vacancy, which creates a tensile stress field The stress/strain field is nearly spherical and short-range.
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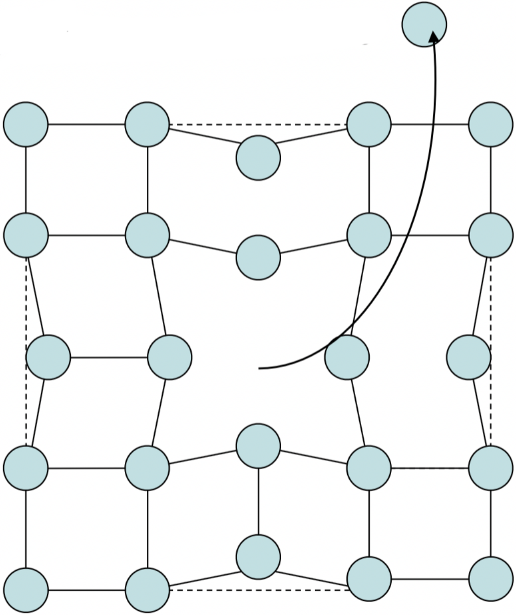
Pressure dependence



How to find vacancies experimentally

- Vacancies are areas with low electron densities. Moreover, they are kind of attractive to a positron because they form a potential well for a positron - once it falls in there, it will be trapped for some time
- some positrons will be trapped inside vacancies and their percentage will depend on the vacancy concentration.The trapped positrons will enjoy a somewhat longer life span. The average life time of all positrons will thus go up with an increasing number of vacancies, i.e. with increasing temperature.

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