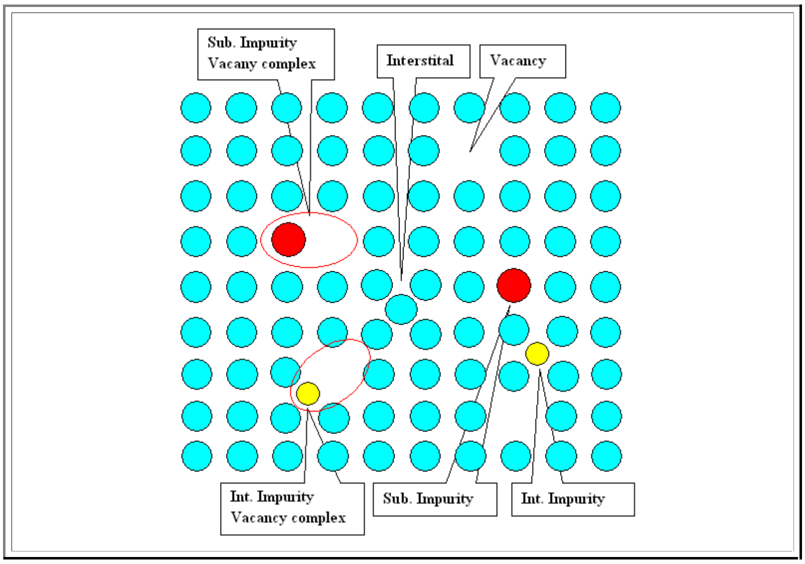
2.2 Extrinsic Point Defects and Point Defect Agglomerates

2.2.1 Impurity Atoms and Point Defects

- Consider a *real* crystal - take even a hyperpure single crystalline **Si** crystal if you like. It's not perfect! It just is not. It will always contain some impurities. If the impurity concentration is below the **ppm** level, then you will have **ppb**, or **ppt** or **ppqt** (figure that out!), or... - it's just never going to be zero.
  - The highest vacancy concentration your are going to have in simple metals close to the melting point is around **10^{-4} = 100 ppm**; in **Si** it will be far lower. On the other hand, even in the best **Si** you will have some **ppm** of **O_i** (oxygen interstitials) and **C_i**(Carbon substitutionals).
  - In other words - it is quite likely that besides your **intrinsic** equilibrium point defects (usually vacancies) squirming around in equilibrium concentration, you also have comparable concentrations of various **extrinsic** non-equilibrium point defects. So the question obviously is: what is going to happen between the vacancies and the "dirt"? How do intrinsic and extrinsic point defects interact?
- Let's look at the impurities first. Essentially, we are talking **phase diagrams** here. If you know the phase diagram, you know what happens if you put increasing amounts of an **impurity atom** in your crystal. Turned around: If you know what your impurity "does", you actually can construct a phase diagram.
  - However, using the word "*impurity*" instead of "*alloy*" implies that we are talking about *small* amounts of **B** in crystal **A**.
- The decisive parameter is the **solubility** of the impurity atom as a function of temperature.
  - In a first approximation, the equilibrium concentration of impurity atoms is given by the usual **Arrhenius representation**, akin to the case of vacancies or self-interstitials. This is often only a good approximation below the eutectic temperature (if there is one). Instead of the formation energies and entropies, you resort to **solubility energies** and **entropies** .
  - There is a *big difference with intrinsic point defects*, however. The concentration of impurity atoms in a given crystal is pretty much constant and not a quantity that can find its equilibrium value. After all, you can neither easily form nor destroy impurity atoms contained in a crystal.
  - That means that thermal equilibrium is only obtained at *one* specific temperature, if at all. For all other temperatures, impurity atoms are either **undersaturated** or **oversaturated**.
- Now the obvious: Vacancies, divacancies, interstitials etc. may interact with impurity atoms to form **complexes** - provided that there is some attractive interaction. Interactions may be elastic (e.g. the lattice deformation of a big impurity interstitial will attract vacancies) or electrostatic if the point defects are charged. Schematically it may look like this:



  - An impurity - vacancy complex (also known as **Johnson** complex) is similar to a divacancy, just one of the partners is now an impurity atom. The calculation of the **equilibrium concentration** of impurity - vacancy complexes thus proceeds in analogy to the calculations for double vacancies, but it is somewhat more involved. We obtain (for details use the link).

$$
\begin{aligned}
c_C &= \frac{z \cdot c_F \cdot c_V(T)}{1 - z \cdot c_F} \cdot \exp\frac{\Delta S_C}{k} \cdot \exp\frac{H_C}{kT} \\
&\approx z \cdot c_F \cdot c_V(T) \cdot \exp\frac{\Delta S_C}{k} \cdot \exp\frac{H_C}{kT}
\end{aligned}
$$

- With c_C = concentration of vacancy-impurity atom complexes, c_F = concentration of impurity atoms, c_V = equilibrium concentration of (single) vacancies, and ΔS_C or H_C = binding entropy or enthalpy, resp., of the pair. z , again, is the coordination number.
- That the coordination number z appears in the equation above is not surprising - after all there are always z possibilities to form one complex. Note that the term $1 - z \cdot c_F$ must be some correction factor, obviously accounting for the possible case of rather large impurity concentrations c_F. Why? - Well, for small c_F, this term is just about **1** and we get the approximation from above.
- Note also that as far as equilibrium goes, we have a kind of mixed case here. The impurity atoms have some concentration c_F that is *not* an equilibrium concentration. But if we redefine equilibrium as the state of crystal plus impurities (essentially we simply change the G_0 = Gibbs energy of the "perfect" crystal in one of our first equations), than the concentration c_C of vacancy-impurity atom complexes is an *equilibrium* concentration.

- The equation above for c_C is quite similar to what we had for the divacancy concentration.
  - If you forget the "correction factor" for a moment, we have identical exponential terms describing the binding enthalpy, and pre-exponential factors of $z \cdot c_V \cdot c_F$ for divacancies and $z \cdot c_V \cdot c_V$ for the vacancy - impurity complexes.
  - In both cases the concentrations decreases exponentially with temperature. However, assuming identical binding enthalpies for the sake of the argument, in an Arrhenius plot the slope for divacancies would be twice that of vacancy-impurity complexes - I sincerely hope that you can see why!
- The *total* vacancy concentration c_{1V}**(total)** (= concentration of isolated vacancies + concentration of vacancies in the complexes) as opposed to *the equilibrium concentration without impurities* c_{1V}**(eq)** is given by

$$
c_V(\text{total}) = c_V(\text{eq}) + c_C
$$

  - That's what equilbrium means! If impurity atoms snatch away some vacancies that the crystal "made" in order to be in equilibrium, it just will make some more until equilibrium is restored.
  - c_C thus can be seen as a correction term to the case of the perfect (impurity free) crystal which describes the perturbation by impurities. This implies that $c_V >> c_C$ under normal circumstances.
- We will find out if this is true and more about vacancy - impurity complexes in an exercise.
  - You don't have to do it all yourself; but at least look at it - it's worth it.

Exercise 2.2-1

Properties of Johnson complexes

Questionaire

Multiple Choice questions to 2.2.1

Exercise 2.2-2

Quick Questions to 2.2