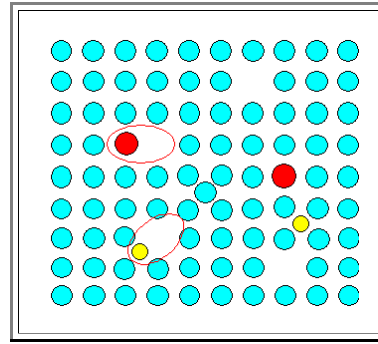


2.2.3 Essentials to Chapter 2.2: Extrinsic Point Defects and Point Defect Agglomerates

Besides intrinsic point defects, crystals always contain extrinsic point defects - impurity atoms on substitutional or interstitial sites.

- The concentration c_F of extrinsic point defects is pretty much constant - it cannot be in equilibrium. What is going on in a macroscopic way is given by the phase diagram of crystal plus impurity atoms
- If we discuss extrinsic point defects (in contrast to alloys), we discuss small c_F values. Nevertheless, c_F might be much larger than c_C , the equilibrium concentration of vacancies; especially at low temperatures.



The concentration c_C of impurity atom - vacancy complexes is easy to calculate, the decisive parameters are the concentrations of the partners and their binding energy H_C

- The situation is quite similar to the case of divacancies or multi-vacancies, except that c_F is constant. The concentration of extrinsic-intrinsic complexes *in equilibrium* decreases with temperature

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

With extrinsic point defects the crystal can no longer be in *global* equilibrium; what we are looking now is local equilibrium - the minimum of the free enthalpy obtainable under some fixed circumstances

Fixed circumstances may include that the concentration of the intrinsic point defects is not in (global) equilibrium. There are many reasons for that:

- Changing the equilibrium concentration of intrinsic point defects needs two ingredients:
 - sources and sinks for intrinsic point defects - external or internal surfaces (= grain boundaries), dislocations - other defects.
 - Sufficient mobility of the point defects to get away from or to the sources and sinks, respectively.

The latter condition always fails at low temperatures, as a result the formation of point defect clusters is favored.

- The decisive quantity is the total diffusion length L of a point defect during the thermal history of its crystal - how far can it "go" before it is frozen into immobility
- If $L >$ average distance to a sink, we will find mostly equilibrium conditions; if $L <$ average distance to a sink (**Si** case!), we will have to expect point defects complexes of n point defects at a concentration c_{nV} .
- The upper limit for n is the concentration of point defects contained in the volume L^3 .

$$c_{nV} = (c_{1V})^n \cdot \frac{z}{2} \cdot \exp \frac{\Delta S_{nV}}{k} \cdot \exp \frac{B_{nV}}{kT}$$

$c_{nV}(T)$ *increases* with $\exp\{B_{nV} / kT\}$ as soon as c_V stays constant.