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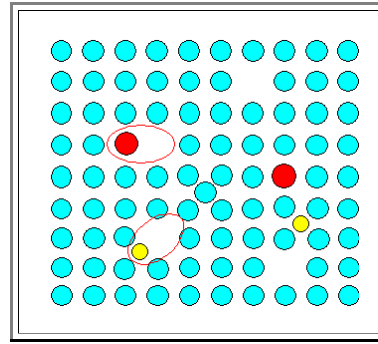
- The concentration c_C of impurity atom - vacancy complexes is easy to calculate, the decisive parameters are the concentrations of the partners and their binding energy H_C

  - 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:

    1. sources and sinks for intrinsic point defects - external or internal surfaces (= grain boundaries), dislocations - other defects.
    2. 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.