2.1.2 Frenkel Defects

- Frenkel defects are, like Schottky defects, a speciality of **ionic crystals**. Consult this illustration modul for pictures and more details.
  - In fact, the discussion of this defect in **AgCl** in **1926** by **Frenkel** more or less introduced the concepts of point defects in crystals to science.
- In ionic crystals, **charge neutrality** requires (as we will see) that defects come in **pairs** with opposite charge, or at least the sum over the net charge of all charged point defects must be zero.
  - "**Designer defects**" (defects carrying name tags) are *special cases* of the general point defect situation in non-elemental crystals. Since any ionic crystal consists of at least two different kinds of atoms, at least two kinds of vacancies and interstitials are possible in principle.
  - Thermodynamic equilibrium always allows *all* possible kinds of point defects simultaneously (including charged defects) with arbitrary concentrations, but always requiring a minimal free enthalpy *including the electrostatic energy components* in this case.
  - However, if there is a charge inbalance, electrostatic energy will quickly override everything else, as we will see. As a consequence we need charge neutrality in total *and* in any small volume element of the crystal - we have a kind of independent boundary condition for equilibrium.
  - Charge neutrality calls for at least *two* kinds of differently charged point defects. We could have more than just two kinds, of course, but again as we will see, in real crystals usually two kinds will suffice.
- One of two simple ways of maintaining charge neutrality with two different point defects is to always have a vacancy - interstitial pair, a combination we will call a **Frenkel pair**.
  - The generation of a Frenkel defect is easy to visualize: A lattice ion moves to an interstitial site, leaving a vacancy behind. The ion will always be the positively charged one, i.e. a cation interstitial, because it is pretty much always smaller than the negatively charged one and thus fits better into the interstitial sites. In other words; its formation enthalpy will be smaller than that of a negatively charged interstitial ion. Look at the pictures to see this very clearly.
  - It may appear that electrostatic forces keep the interstitial and the vacancy in close proximity. While there is an attractive interaction, and close Frenkel pairs do exist (in analogy to excitons, i.e. close electron-hole pairs in semiconductors), they will not be stable at high temperatures. If the defects can diffuse, the interstitial and the vacancy of a Frenkel pair will go on independent random walks and thus can be anywhere, they do not have to be close to each other after their generation.
- Having vacancies and interstitials is called **Frenkel disorder**, it consists of Frenkel pairs or the **Frenkel defects**.
  - Frenkel disorder is an extreme case of general disorder; it is prevalent in e.g. **Ag - halogen** crystals like **AgCl**. We thus have

$$\boxed{n_i = n_V = n_{FP}}$$

- This implies, of course, that **vacancies carry a charge**; and that is a bit of a conceptual problems. For ions as interstitials, however, their charge is obvious. How can we understand a charge "nothing"?
  - Well, vacancies can be seen as charge carriers in analogy to **holes** in semiconductors. There a missing electron - a hole - is carrying the *opposite* charge of the electron.
  - For a vacancy, the same reasoning applies. If a **Na^+** lattice ion is missing, a *positive* charge is *missing* in the volume element that contains the corresponding vacancy. Since "missing" charges are non-entities, we have to assign a *negative* charge to the *vacancy* in the volume element to get the charge balance right.
  - Of course, any monoatomic crystal could (and will) have arbitrary numbers of vacancies *and* interstitials at the same time as intrinsic point defects; but only if charge consideration are important $n_i = n_V$ holds exactly; otherwise the two concentrations are uncorrelated and simply given by the formula for the equilibrium concentrations.
  - Indeed, since the equilibrium concentrations are never exactly zero, *all* crystals will have vacancies *and* interstitials present at the same time, but since the formation energy of interstitials is usually much larger than that of vacancies, they may be safely neglected for most considerations (with the big exception of Silicon!).
- Of course, in biatomic ionic crystals, there could (and will) be *two* kinds of Frenkel defects: cation vacancy and cation interstitial; anion vacancy and anion interstitial; but in any given crystal one kind will always be *prevalent*.
  - We will take up all these finer points in modules to come, but now let's just look at the simple limiting case of pure Frenkel disorder.

Calculation of the Equilibrium Concentration of Frenkel Defects

- Lets consider a simple ionic crystal, e.g. **AgCl** (being the paradigmatic crystal for Frenkel defects). With ***N*** = number of positive ions in the lattice and ***N'*** = number of interstitial sites, we obtain
  - ***N'* = 2*N*** for interstitials in the tetrahedral position
    N'* = 6*N for the dumbbell configuration
    ***N'* = ...** etc.
  - The change of the free enthalpy upon forming n_{FP} Frenkel pairs is

$$\Delta G \;=\; n_{FP}\cdot H_{FP} \;-\; n_{FP}\cdot TS_{FP} \;-\; kT\cdot\left(\ln\frac{N!}{(N-n_V)!\cdot n_V!} + \ln\frac{N'!}{(N'-n_i)!\cdot n_i!}\right)$$

  - With H_{FP} and S_{FP} being the formation energy and entropy, resp., of a Frenkel pair. The configuration entropy is simply the sum of the entropy for the vacancy and the interstitial; we wrote n_V and n_i to make that clear (even so we already know that $n_V = n_i = n_{FP}$).
- With the equilibrium condition $\partial G/\partial n = 0$ we obtain for the concentration c_{FP} of Frenkel pairs

$$c_{FP} \;=\; \frac{n_{FP}}{N} \;=\; \left(\frac{N'}{N}\right)^{1/2} \cdot\; \exp\frac{S_{FP}}{2k} \;\cdot \exp -\frac{H_{FP}}{2kT}$$

  - The factor **1/2** in the exponent comes from equating the formation energy H_{FP} or entropy, resp., with a *pair* of point defects and not with an individual defect.
- What is the reality, i.e. what kind of formation enthalpies are encountered? Surprisingly, it is not particularly easy to find measured values; the link, however, will give some numbers.
- That was rather straight forward, and we will not discuss Frenkel defects much more at this point. We will, however, show in the next subchapter from first principles that, indeed, charge neutrality has to be maintained.

Questionaire

Multiple Choice questions to 2.1.2

Exercise 2.1-8

Quick Questions to 2.1.2 - 2.1.4