Point Defects in Ionic Crystals

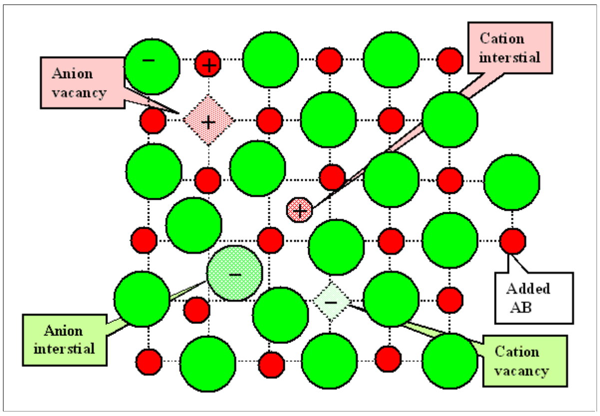
Most General (and Unrealistic) Case

It is important to be clear about the possibilities of producing defects in ionic crystals. It is also important to be clear about names:

- **Anions** move to a *positively* charged electrode also called *anode*, they are therefore *negatively* charged particles. Examples: The **Cl^-** ions in NaCl.
- **Cations** move to a negatively charged electrode also called *cathode*. Example: The **Na^+** ions in NaCl,

Illustration

- Now there is some room for confusion: If we take out the negatively charged cation **Na^+**, we have produced a *cation vacancy* that has a positive effective charge and thus behaves like an *anion*!
- Here is all that can happen in a simple **NaCl** crystal:



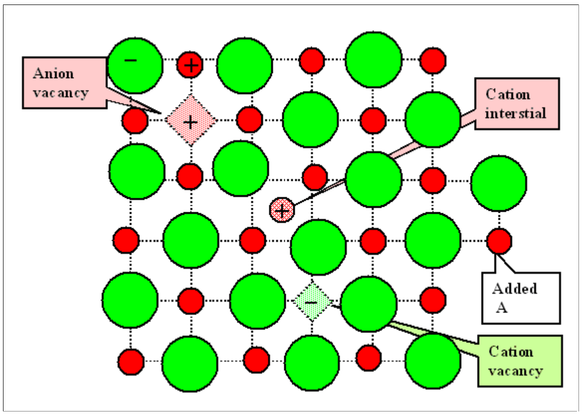
"General" Disorder

- Even for the most simple ionic crystals of the type **A^+B^-** like **LiCl** or **NaCl**, we can, *in principle*, produce arbitrary concentrations of two kinds of vacancies and two kinds of interstitials as shown on the left.
  However, as we already learned in dealing with Schottky defects, global **charge neutrality** must be maintained. *Arbitrary* concentrations are thus not really allowed, we *must* demand that the the sum of the positively charged defects equals the sum of the negatively charged defects. In other words: we have to obey the *charge conservation law*.
- If we also keep the number of atoms constant, we must add an **A** or **B** atom to the surface of the crystal for every pure vacancy we produce. In other (fancy) words, we have to obey the *mass conservation law.*
- The picture on the left would not have needed the **AB** molecule, because we have two interstitials, too. But since it is supposed to illustrate the *general* case, with arbitrary numbers of defects, it needs to include **A** and **B** atoms on the surface.

- As always, you must bear in mind that pictures as shown here are *schematic* **-** in more realistic pictures the ions would touch! However, in more realistic pictures it also would be harder to show what is intended.
- This will always be true if the anion is larger as the cation which is the case for many, but not all ionic crystals. We thus can safely assume that the concentration of *one* kind of interstitial, here the **anion interstitial**, is always far smaller than that of the other three defect kinds and we will simply neglect it from now on.
- However, for crystals with a big and heavy cation (e.g. **Ca^+**) and a light anion (e.g. **F^-**), the cation might just be as big as the anion, and occur as interstitial (e.g. in the so-called "Anti-Frenkel defects").

Most General (and Realistic) Case

- If we forget about the *anion interstitial*, we are left with three possible point defects.



Realistic Disorder

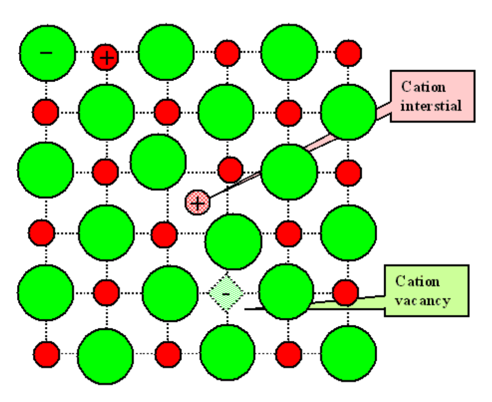
  - The three now possible defect types are shown on the left. This is the general case of the **mixed defects** treated in the backbone
  - Note that charge equilibrium demands that you *always* have more cation vacancies than anion vacancies or cation interstitials:

$$c_V(C) = c_V(A) + c_i(C)$$

  - This necessitates that some **AB** molecules must be added to the surface of the crystal if we keep the atom count in order, too (same concentration as the anion vacancy, to be precise).
- The realistic mixed case thus contains Schottky and Frenkel defects in parallel.
  - Note that the picture above does *not* show the equilibrium case, because we do not have charge neutrality - for that it would need another cation vacancy.
  - Every cation vacancy finds an anion vacancy as a fictive partner, forming a formal Schottky defect, and every cation interstitial finds a cation vacancy, too, for a formal Frenkel pair, and the concentration of the anion vacancies is just so that it meets both demands for partners.
  - We thus can identify $c_V(A)$ with the concentration of Schottky defects and $c_i(C)$ with the concentration of Frenkel defects.

Special Cases: Schottky and Frenkel Disorder

- Schottky and Frenkel disorder may now simply be seen as *extreme* cases of the mixed disorder.

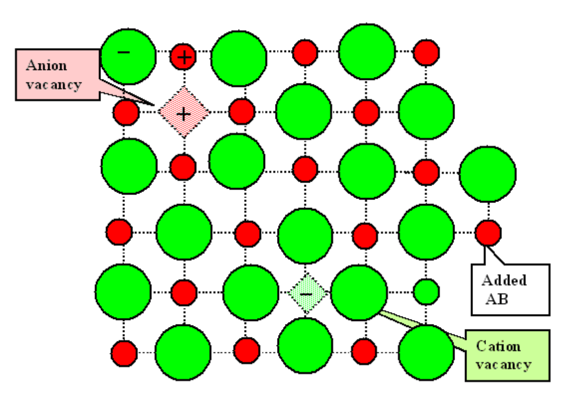


Frenkel disorder

  - **Frenkel disorder** is predominant if the formation enthalpy of Frenkel pairs is smaller than that of Schottky pairs, i.e.

    $H_{FP} < H_S$

    We then only - or at least predominantly - have Frenkel pairs, i.e. equal numbers of cation vacancies and cation interstitials. We do not have an **AB** molecule for Frenkel disorder.



Schottky disorder

Schottky disorder is predominant if the formation enthalpy of Schottky pairs is smaller than that of Frenkel pairs, i.e.

$H_S < H_{FP}$.

We only - or at least predominantly - have vacancy pairs, i.e. equal numbers of cation vacancies and anion vacancies. And - in contrast to Frenkel disorder - we always need to form a lattice molecule, our **AB** molecule, to preserve atom numbers.

Just how much smaller the relevant formation enthalpy has to be for factual predominance of one defect type remains to be seen - in an exercise.