

## 2.4 Point Defects in Ionic Crystals

### 2.4.1 Motivation and Basics

- Point defects in ionic crystals (e.g. **NaCl** or **AgCl<sub>2</sub>**) and oxides (e.g. **SnO<sub>2</sub>** or **ZrO<sub>2</sub>**) are quite important and put to technical uses.
- Unfortunately (from the metal oriented persons point of view) the scientific community working with those materials has its own way for dealing with point defects, which differs in some respects from the viewpoint of the metal and semiconductor community.
  - There are historical and "cultural" reasons for this, but there are also good reasons. Essentially, in dealing with more complicated crystals - and ionic materials or oxides are always more complicated than metals or simple semiconductors - a more chemical point of view is traditional and useful. Let us look at some important points that have to be considered in this context.
- First, we look at the **stoichiometry** of these crystals.
- Ionic crystals** must consist of at least two different kinds of ions. They may then contain point defects in concentrations far above thermal equilibrium (as defined relative to a perfect crystal), if the real material is non-stoichiometric. If you imagine a single crystal of, let's say, **NaCl** with the composition **Na<sub>1-δ</sub>Cl** and  $\delta \ll 1$ , i.e. close to, but not exactly at stoichiometry (which is what you always would expect in reality), your only way of forming a crystal seems to be to use some point defects as integral part of the crystal.
  - You *might* consider, e.g., to introduce a concentration of  $\delta$  vacancies on the Na lattice sites, or to put a concentration of  $\delta$  **Cl<sup>-</sup>** ions in interstitial positions, or to mix both defect types in a ratio where the sum of the concentrations somehow equals  $\delta$ .
  - But now *lets think again*. If you consider a crystal of **Na<sub>1-δ</sub>Cl**, you are really talking about a crystal with **N** atoms of negatively charged **Cl<sup>-</sup>** ions and **N · (1 - δ)** positively charged **Na<sup>+</sup>** ions, which means that the crystal would carry a net negative charge of  $e \cdot \delta \cdot N$  and thus a dramatically high energy. No such crystal can exist - there must always be equal numbers of **Na<sup>+</sup>** and **Cl<sup>-</sup>** ions - *as long as there are no impurity atoms*.
- This leads us to the second point, the necessity for **charge equilibrium** or "**zero net charge condition**" considered before.
- If we stay with the above example of **NaCl**, we are forced to conclude that a **NaCl** crystal would be necessarily perfectly stoichiometric - it cannot grow in any other way. However, no crystal exists without some impurities. If, for example, some **Ca** atoms are to be included into an otherwise perfectly stoichiometric **NaCl** crystal, they will always be doubly charged **Ca<sup>++</sup>** ions, and we now must remove twice the number of **Na<sup>+</sup>** ions to preserve charge neutrality (or introduce twice the number of additional **Cl<sup>-</sup>** ions). Obviously we now *must* introduce a **Na** vacancy for every **Ca<sup>++</sup>** ion included in the crystal (or **Cl<sup>-</sup>** interstitials and so on).
  - The concentration of vacancies now could be much higher than the *thermal equilibrium* concentration. But we still may have equilibrium; namely **chemical equilibrium**, or, if the defects are charged, **electrochemical equilibrium**!
- We see with this simple example, that there is a linkage between stoichiometry, charge neutrality, impurities and defects, with the added complication that it is not necessarily clear which kinds of point defects must be present in what concentration.
- We also see that point defects in concentrations that have nothing to do with the thermal equilibrium concentration in *perfect* crystals may be an integral part of a real ionic crystal.
- The simple example, however, makes also clear that stoichiometry, impurity, and charge neutrality considerations still do not tell us exactly what kinds of point defects are needed in which concentration, but at best will give some integral numbers.
- Let us look at a third point. It concerns the surface and its interaction with the surroundings - this is where many applications come in.
- Consider a **ZrO<sub>2</sub>** crystal in thermal equilibrium with a gas containing a certain **O<sub>2</sub>** concentration, at a temperature where the oxygen in the crystal is mobile to some extent (maybe because there are **O**-vacancies?). We must expect some "chemical" reaction to take place. Some additional oxygen may be incorporated into the crystal, or some oxygen may diffuse out of the crystal into the gas. The tendency of whatever is going to happen in this case will be determined by the conditions for *chemical* equilibrium, or, in other words, by the chemical potentials of the participating species.
  - But we must expect that point defects are involved in whatever happens across the interface. For the particular example given (which happens to describe the principle of an **oxygen sensor**) we must expect that some *electrical* effects take place as well because introducing excess oxygen (always negatively charged) into the crystal or taking some out, will influence the charge distributions and thus *electrical potentials* in the crystal.
  - Some *electrochemical* equilibrium will be reached that contains electrical potential differences - a voltage develops across the interface.

▶ The common denominator in all considerations made so far was: We always had some kind of linkage between "*chemistry*" as expressed in reactions between atoms or in stoichiometric considerations, and (usually charged) *point defects*..

▶ We now get the idea of what needs to be done for a general treatment of point defects and ionic crystals:

**We want to define point defects in a way  
where they can be included  
into the familiar concept of chemical reaction equations  
We then treat them the same way we treat chemical reactions**

▶ In other words, we want to write equations analogous to



$$\frac{[A]^n \cdot [B]^m}{[A_n B_m]} = \text{const.}$$

● With the option that "A" and "B" may refer not only to atoms, *but also to point defects*.

▶ We want to do this in a way where we can use the full box of tools developed for chemical reactions, e.g. the mass action law (shown above), chemical potentials and activities instead of concentrations, the concept of **kinetics**, of **chemical equilibrium**, etc.

▶ As it turns out, this is possible, but it is not *obvious* how to do this right. There are several approaches and compromises to achieve the best description. We will look at this in the next subchapter.