Set 1

Theme: Defects and solid solubility.

Defects are classified according to their dimensionality, how they affect the composition and if they originate from impurities. In this respect, terms as point-, line- and plane defects, stoichiometric and non-stoichiometric defects, and intrinsic and extrinsic defects. It is difficult to produce materials that are so pure that the defect situation at all temperatures is dominated by intrinsic defects, controlled by the thermodynamics of that compound. The dominating defect-type is structure specific.

Consider a sample of NaBr (with NaCl type structure) that is very pure. By measuring the defect related properties (here with origin in intrinsic defects) one finds that the dominating defect type is Schottky defects.

1.1. Sketch the Schottky-defects in NaBr. What effective charges are ascribed to the defects?

1.2. The formation enthalpy for Schottky defects are determined to be 200 kJ/mol. Calculate relative ratio of the defect concentrations at room temperature and at 1300 K.

1.3. If the defect concentration is 10^{10} defects/mol NaBr, give an estimate over how many unit cells one on average must cross on going from one Schottky defect to another.

1.4. Is it reasonable to note the situation under 1.2. and 1.3. as point defects?

1.5. Consider then an impurity dominated/extrinsic defect situation. Imagine that an aliovalent substitution is taking place, viz. a solid solubility phase where Na^+ in this case is partly substituted with Mn^{2+}. Let 1% of Na^+ be exchanged with half as much Mn^{2+}. Write an illustrating formula for the phase (inclusive the number of vacancies or interstitials that are crated due to the substitution.)

1.6. Draw a sketch that shows how the defect concentration varies with the inverse of temperature for impure NaBr (viz. assume extrinsic situation at low temperatures and intrinsic at high temperatures).

1.7. Assume that the conduction in NaBr is solely ionic, viz. it is ions that transport the charge, not electrons. It is Na^+ that is the cause of ion transport. The conduction is therefore directly dependant on the concentrations on Na+ positions (viz. octahedra positions in a ccp of Br-anions). How will the conduction be affected by the presence of Mn^{2+} as described under 1.5?

1.8. For Mn^{2+} substituted NaBr a locally ordered structure will form. The ordering occurs within a layer of (100) plane. Consider three such layers, each of 5x5 atom positions. The top and bottom layer has got normal NaCl-type structure. In the middle layer an ordering occurs. Vacancies occur in the corners and in the center (of the 5x5 structural elements). Mn^{2+} impurity atoms lie in the middle on each of the four edges. The other positions are normally filled. Sketch the superstructure.

2.1. Imagine that Na^+ is completely changed with Ag^+, viz. we now consider the compound AgBr. Do you expect this to alter the defect situation?

2.2. Draw possible paths for moving the ions (assume that it is the cations that are most mobile) in respectively NaBr and AgBr. How many possible interstitial positions are there per. Na^+ (in the perfect structure)?

2.4. On basis of the considerations ahead, do you believe NaBr or AgBr will be best at transporting ions the solid state (viz. show ionic conduction)?

The following problems are taken from the book *Understanding Solids*...

3.7 The enthalpy of formation of vacancies in pure nickel is $\Delta H = 97.3$ kJ mol^{-1}. What is the fraction of sites vacant at 1100 °C?

3.10 The enthalpy of formation of vacancies in pure aluminium is $\Delta H = 72.4$ kJ mol^{-1}. The density of aluminium is 2698 kg m^{-3}. What number of atom positions is vacant at 600 °C?

3.11 Calculate how the fraction of Schottky defects in a crystal of KCl varies with temperature if the value of ΔH_s is 244 kJ mol^{-1}.

3.14 Silver bromide, AgBr, has cubic unit cell with an edge of 0.576 nm. There are four silver atoms in the unit cell; assume that there are four interstitial positions available for silver atoms. Calculate the absolute number of interstitial defects present per cubic metre at 300K.

3.20 The fraction of Schottky defects in nickel oxide, NiO, at 1000°C is 1.25 x 10^{-4}. The cubic unit cell contains four nickel atoms and has a cell edge of 0.417 nm. Calculate the number of nickel vacancies present.

3.23 A total of 9 mol% of Y_2O_3 is mixed with 91 mol% ZrO_2 and heated until a uniform product with high oxygen ion conductivity is obtained. The resulting crystal is stabilized zirconia with the formula $Y_xZr_yO_z$. Determine x, y and z, explaining your answer.

3.24 CaO forms a solid solution with Bi_2O_3 to give a material with a high anionic conductivity. If 10 mol% CaO is reacted with 90 mol% Bi_2O_3, what is the formula of the final solid and what are the numbers and types of vacancies created?

3.25 What defects will form in the crystals made by adding small amounts of compound A to compound B:

(a) A = LiBr, B = $CaBr_2$?

(b) A = $CaBr_2$, B = LiBr?

(c) A = MgO, B = Fe_2O_3?

(d) A = MgO, B = NiO?

3.26 What defects will form in the crystals made by adding small amounts of compound A to compound B:

(a) A = $CdCl_2$, B = NaCl?

(b) A = NaCl, B = $CdCl_2$?

(c) A = Sc_2O_3, B = ZrO_2?

(d) A = ZrO_2, B = HfO_2?

What type of defects will dominate in the following compounds?

4.1. UO_{2+x} with CaF_2 type structure as starting point.

4.2. W_nO_{3n-1} with ReO_3 type structure for WO_3

4.3. AgCl with NaCl type structure

4.4. RbBr with NaCl type structure

4.5. $ZrC_{0.1}$ with hcp type structure as starting point

4.6. $Ni_{1-x}O$ as analog to $Fe_{1-x}O$ but with less non-stoichiometry.

4.7. $Mn_{1.1}Sb$ with partially filled NiAs-type structure

4.8. α-Fe with some dissolved carbon

4.9. $LaCoO_{2.98}$ with perovskite type structure

4.10. Pure Cu

5.1. Give representative formulas for solid-solubility phases between (i) Al_2O_3 and Cr_2O_3, (ii) NaCl and NaBr, (iii) Fe and Co, (iv) $LaCrO_3$ and $LaCoO_3$.

5.2. Explain how the volume will vary in these solid solubility phases under assumption that Vegards law applies. Sketch how positive deviations will appear. What can a positive deviation indicate?

5.3. Consider the solid solubility phase between MnAs and FeAs. MnAs have unit cell dimensions a = 570 pm, b = 360 pm and c = 630 pm. FeAs have unit cell dimensions a = 540 pm, b = 338 pm and c = 610 pm. A two phase area exists for the interval 20-50 mol% MnAs. Draw how the unit cell dimensions vary according to Vegards law.

6.1. What is meant by defect creating solid solubility?

6.2. Make examples for systems where (i) the concentration of cation vacancies in KCl increases (ii) concentration of Ag^+ interstitial in AgCl increases (iii) concentration of oxygen vacancies increases in ZrO_2 (iv) concentration of F- interstitial increases in CaF_2.