

Set 4

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 of 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 a 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 created 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 5×5 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 5×5 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.
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- 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)?
- 2.3. Give coordinates for the interstitial positions. What type of structure would you get if 100% of these was filled, while all normal cation position was unoccupied?
- 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)?

Non-stoichiometric iron oxide, wüstite, Fe_{1-x}O , exists in a considerable compositional interval. When x increases, Fe^{III} is produced instead of Fe^{II} (oxidation). In Fe_3O_4 (spinel type structure) Fe^{II} adopts octahedra positions and Fe^{III} tetrahedra positions within a fcc (ccp) pattern of oxygen anions.

- 3.1. What fraction of octahedra- and tetrahedra positions are filled in Fe_3O_4 ?
- 3.2. Is it reasonable to expect a similar type coordination relationship for the different Fe-species in wüstite as described for Fe_3O_4 ?
- 3.3. Draw 1/8 of the NaCl-type structure for wüstite, calculate interatomic distances ($a=430.7$ pm), and discuss whether it will be beneficial with Fe^{III} in tetrahedra holes.
- 3.4. Explain the terms ‘defect cluster’ and use this on wüstite.
- 3.5. Draw a 4 : 1 cluster and a 13 : 4 cluster (the numbers mean; number of empty places : number of interstitials).
- 3.6. Assume that $x = 0.08$ and $a = 430.7$ pm. Calculate the (x-ray) density for the compound according to all of the following defect models; (a) FeIII enters normal octahedra positions, no interstitials are formed. (b) FeIII enters tetrahedra positions and vacancies occur on normal octahedra positions. (c) oxygen interstitials are created on tetrahedra positions. No vacancies are formed on the cation “sub-lattice”.

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. $\text{W}_n\text{O}_{3n-1}$ with ReO_3 type structure for WO_3
- 4.3. AgCl with NaCl type structure
- 4.4. RbBr with NaCl type structure
- 4.5. $\text{ZrC}_{0.1}$ 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. $\text{Mn}_{1.1}\text{Sb}$ with partially filled NiAs-type structure
- 4.8. α -Fe with some dissolved carbon
- 4.9. $\text{LaCoO}_{2.98}$ 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 $a = 570 \text{ pm}$, $b = 360 \text{ pm}$ and $c = 630 \text{ pm}$. FeAs have unit cell dimensions $a = 540 \text{ pm}$, $b = 338 \text{ pm}$ and $c = 610 \text{ pm}$. A two phase area exists for the interval 20-50 mol% MnAs . Draw how the unit cell dimensions vary according to Vegards law.
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- 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 .