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CALCULATION OF FROZEN-IN DEFECT EQUILIBRIUM IN ZnS : Cu : Al : Bi : Cl

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ZnS:Cu:Al:Bi:Cl DEFEKTIDE KINNIKÜLMUTATUD TASAKAALU ARVUTAMINE. Kalju LOTT ja Leo TÜRN

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INTRODUCTION

Using Brower's approximation in the electroneutrality condition, numerical values of the slopes in the high temperature native defect concentration dependence upon the component partial vapour pressure can be found [1]. This method is used also for resolving the defect structure in ternary compounds [2]. A method for the calculation of the high temperature equilibrium is proposed in [3].

The description of frozen-in equilibrium of defects in compound semiconductors is the practical output for the investigation of the high temperature equilibrium of defects. In this paper a method for the calculation of the frozen-in equilibrium of defects in ZnS:Cu:Al:Bi:Cl is proposed.

DESCRIPTION OF THE FROZEN-IN EQUILIBRIUM OF DEFECTS

First a system of quasichemical equations for the description of the high temperature equilibrium will be solved. The defect model contains single point defects as well as double and triple associated defects. We take into account the low diffusion rate at high cooling rate of the crystal. The situation corresponding

to the frozen-in high temperature equilibrium is described by the following equations and conditions:

1. The equations of balance of the same type of defects.

2. The total concentration of the same type of defects does not change during the cooling process. Only interchanging of charges between defects according to the rules of ionization at frozen-in temperature occurs.

3. No defects of new type will be created or disappear during the cooling of the crystal.

CALCULATION OF FROZEN-IN DEFECT CONCENTRATIONS

For calculation purposes we selected defects in ZnS:Cu:Al:Bi:Cl falling in three groups:

Group A: Neutral double and triple associated defects having no charged analogue: $(Cu_iCu_{Zn})^\times$, $(Cu_{Zn}Cl_S)^\times$, $(Al_{Zn}Bi_S)^\times$, $(Cl_SBi_S)^\times$, $(Cu_{Zn}Al_{Zn})^\times$, $(Cu_iBi_S)^\times$, $(Al_{Zn}Al_{Zn}V_{Zn})^\times$, $(Bi_SBi_SZn_i)^\times$, $(Bi_SBi_SV_S)^\times$, $(Cl_SAl_{Zn}V_{Zn})^\times$, $(Cl_SCl_SV_{Zn})^\times$, $(Cu_{Zn}Bi_SZn_i)^\times$, $(Cu_{Zn}Bi_SV_S)^\times$, $(Cu_{Zn}Cu_{Zn}Zn_i)^\times$, $(Cu_{Zn}Cu_{Zn}V_S)^\times$, $(Cu_iAl_{Zn}V_{Zn})^\times$, $(Cu_iCl_SV_{Zn})^\times$, $(Cu_iCu_iV_{Zn})^\times$.

Altogether 18 defects.

Group B: Defects existing in three different states of ionisation: $V_S^\times$, $V_S^{\cdot}$, $V_S^{\cdot\cdot}$; $V_{Zn}^\times$, $V_{Zn}^{\prime}$, $V_{Zn}^{\prime\prime}$; $Zn_i^\times$, $Zn_i^{\cdot}$, $Zn_i^{\cdot\cdot}$; $(V_SV_{Zn})^{\prime}$, $(V_SV_{Zn})^\times$, $(V_SV_{Zn})^{\cdot}$; $(Zn_iV_{Zn})^{\prime}$, $(Zn_iV_{Zn})^\times$, $(Zn_iV_{Zn})^{\cdot}$.

Altogether 15 defects.

Group C: Defects existing in two different states of ionisation: $Cu_i^\times$, $Cu_i^{\cdot}$; $Cu_{Zn}^\times$, $Cu_{Zn}^{\cdot}$; $Cl_S^\times$, $Cl_S^{\cdot}$; $Al_{Zn}^\times$, $Al_{Zn}^{\cdot}$; $Bi_S^\times$, $Bi_S^{\prime}$; $(Cu_{Zn}V_S)^\times$, $(Cu_{Zn}V_S)^{\cdot}$; $(Cu_iV_{Zn})^\times$, $(Cu_iV_{Zn})^{\prime}$; $(Cl_SV_{Zn})^\times$, $(Cl_SV_{Zn})^{\prime}$; $(Cu_{Zn}Zn_i)^\times$, $(Cu_{Zn}Zn_i)^{\cdot}$; $(Zn_iBi_S)^\times$, $(Zn_iBi_S)^{\cdot}$; $(Al_{Zn}V_{Zn})^\times$, $(Al_{Zn}V_{Zn})^{\prime}$; $(Bi_SV_S)^\times$, $(Bi_SV_S)^{\cdot}$; $(Al_{Zn}Zn_iV_{Zn})^\times$, $(Al_{Zn}Zn_iV_{Zn})^{\cdot}$; $(Al_{Zn}V_SV_{Zn})^\times$, $(Al_{Zn}V_SV_{Zn})^{\cdot}$; $(Bi_SZn_iV_{Zn})^\times$, $(Bi_SZn_iV_{Zn})^{\prime}$; $(Bi_SV_SV_{Zn})^\times$, $(Bi_SV_SV_{Zn})^{\prime}$; $(Cl_SZn_iV_{Zn})^\times$, $(Cl_SZn_iV_{Zn})^{\prime}$; $(Cl_SV_SV_{Zn})^\times$, $(Cl_SV_SV_{Zn})^{\cdot}$; $(Zn_iZn_iV_{Zn})^\times$, $(Zn_iZn_iV_{Zn})^{\cdot}$; $(Zn_iV_SV_{Zn})^\times$, $(Zn_iV_SV_{Zn})^{\cdot}$; $(Zn_iV_{Zn}V_{Zn})^\times$, $(Zn_iV_{Zn}V_{Zn})^{\prime}$; $(V_SV_SV_{Zn})^\times$, $(V_SV_SV_{Zn})^{\cdot}$; $(V_SV_{Zn}V_{Zn})^\times$, $(V_SV_{Zn}V_{Zn})^{\prime}$; $(Cu_{Zn}Zn_iV_{Zn})^\times$, $(Cu_{Zn}Zn_iV_{Zn})^{\prime}$; $(Cu_{Zn}V_SV_{Zn})^\times$, $(Cu_{Zn}V_SV_{Zn})^{\prime}$; $(Cu_iZn_iV_{Zn})^\times$, $(Cu_iZn_iV_{Zn})^{\cdot}$; $(Cu_iV_SV_{Zn})^\times$, $(Cu_iV_SV_{Zn})^{\cdot}$.

Altogether 54 defects.

The calculation of frozen-in defect equilibrium is different from the calculation of the defect equilibrium at high temperatures, where we got an eighth order system of equations and solved this by the triple iteration method.

First the sum of the defects of the same type in groups B and C can be found. Then equations will be created for all double and triple associated defects. We present the concentrations of all defects of the same type through one of them.

For example, the equilibrium between defects

$$V_S^\times \rightleftarrows V_S^{\cdot} \rightleftarrows V_S^{\cdot\cdot}$$

can be expressed as follows:

$$V_S^{\times} = V_S^{\cdot} + e', \qquad K_{B1} = \frac{[V_S^{\cdot}]n}{[V_S^{\times}]};$$

$$V_S^{\cdot} = V_S^{\cdot\cdot} + e', \qquad K_{B2} = \frac{[V_S^{\cdot\cdot}]n}{[V_S^{\cdot}]}.$$

From these equations we find:

$$[V_S^{\cdot}] = \frac{K_{B1}}{n}[V_S^{\times}],$$

$$[V_S^{\cdot\cdot}] = \frac{K_{B2}}{n}[V_S^{\cdot}] = \frac{K_{B1}K_{B2}}{n^2}[V_S^{\times}].$$

The sum $[V_S]_{TOT}$ of these defects can be expressed as follows:

$$[V_S]_{TOT} = [V_S^{\times}] + [V_S^{\cdot}] + [V_S^{\cdot\cdot}],$$

$$[V_S]_{TOT} = [V_S^{\times}]\left(1 + \frac{K_{B1}}{n} + \frac{K_{B1}K_{B2}}{n^2}\right),$$

$$\left(1 + \frac{K_{B1}}{n} + \frac{K_{B1}K_{B2}}{n^2}\right) = a_{V_S},$$

$$[V_S^{\times}] = \frac{[V_S]_{TOT}}{a_{V_S}}; \quad [V_S^{\cdot}] = \frac{K_{B1}[V_S]_{TOT}}{na_{V_S}}; \quad [V_S^{\cdot\cdot}] = \frac{K_{B1}K_{B2}[V_S]_{TOT}}{n^2 a_{V_S}}.$$

In this way we can find the concentrations of all defects via the total concentration of the same type of defects. To complete the calculation we solve the electroneutrality equation by the iteration method and check the validity of the equations of material balance.

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