

DEVIATION OF A^2B^6 COMPOUNDS FROM STOICHIOMETRY: ELECTRONEUTRAL DEFECTS OR THE ADSORPTION OF ONE COMPONENT EXCESS?

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Abstract. In the A^2B^6 compounds the analytically determined concentration of the excess component appears to be significantly bigger than the concentration of electrically active defects. In several papers electroneutral defects were considered as a dominating contribution to solubility. In this paper arguments are brought to show that the observed effect is related to the adsorption of the excess component on crystal surfaces and interblock boundaries.

Key words: A^2B^6 compounds, deviation from stoichiometry, solubility.

INTRODUCTION

Recent direct studies of the nonstoichiometry of the A^2B^6 compounds have shown that the analytically determined concentration of the excess component appears to be significantly bigger than the concentration of electrically active defects. Therefore, electroneutral defects have often been considered as a dominating contribution to solubility. In this paper the validity of the conclusion about the localization of the excess component atoms in the crystal frame is disputed. Arguments are presented to show that the observed effect is related to the adsorption of the excess component on crystal surfaces and interblock boundaries.

EXPERIMENTAL

This paper presents the results of investigations of Zn-ZnS and Zn-ZnSe systems. The partial pressure of Zn vapour over the crystals was determined by atomic absorption photometry [1]. The ZnS monocrystals were additively coloured. The ZnSe polycrystal samples were obtained by precipitation from the gaseous phase using the reactions of Zn vapour with hydrogen selenide or Se.

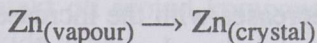
It was observed that the vapour-crystal equilibrium was established in 20–30 min, which is a significantly shorter time than that expected using the data about Zn diffusion. The concentration of the excess metal at a fixed Zn vapour pressure significantly decreased with the increase of temperature in the growth zone.

Processing of the experimental results led to the following formula for ZnSe:

$$x_{\text{Zn}} = \tilde{p}_{\text{Zn}} \exp \left[\frac{14000 \pm 300}{T} - (15.8 \pm 0.3) \right],$$

where x_{Zn} is the solubility of the excess Zn in the crystal within the temperature range of $T = 945\text{--}1092$ K, and \tilde{p} is the reduced pressure.

The enthalpy and entropy for the process



were found to be $\Delta H^0 = -116$ kJ/mol, $\Delta S^0 = -131$ kJ/(mol K). The former agrees with the enthalpy of Zn condensation.

The total excess of zinc in ZnS was calculated using the partial vapour pressure of zinc:

$$x_{\text{Zn}} = 5.5 \times 10^{-5} \text{ g-at} \cdot \text{mol}^{-1} = 1.4 \times 10^{18} \text{ cm}^{-3}.$$

DISCUSSION

The known methods of studying nonstoichiometry are based on the determination of quantities that correlate with the constituents (concentration of charge carriers, low-temperature thermal conductivity), or on direct determination of the amount of the excess component in the crystals of the compound.

In direct methods [2–8] the excess component is either extracted from the crystals by thermal extraction or its amount is determined by using the data from vapour-crystal equilibrium at a known temperature, the volume of the gaseous phase, and the partial pressure of the excess component. Using the direct measurements the analytically determined concentration of the excess component significantly exceeds the concentration of electrically active defects determined by high-temperature Hall effect

measurements [9] and EPR measurements [8]. This ratio is close to 100 for ZnSe and ZnS.

In the most favourable case (for CdSe [2]) the concentration of the excess component is in reasonable agreement with the concentration of the charge carriers. In reality the ratio of these quantities is close to three. For other cadmium chalcogenides the corresponding ratio is about 10. Based on this, electroneutral defects were considered as a dominating contribution to solubility in [5–7]. However, the validity of this assumption is disputed by the lack of data on the change of density of crystals. This proves directly the distribution of the excess component in the crystal.

Calculations show that in case of monomolecular covers the concentration of atoms located on ideal surfaces of cube-shaped monocrystals with 1 mm sides transformed to an equivalent volume concentration would be about $10^{17} \cdot \text{cm}^{-3}$. It is more than 10 times less than the analytically determined concentration of the excess component, which leads to the conclusion about the secondary role of adsorption processes. However, this conclusion can be disputed by analysing the primary information, in particular, the following experimental evidence:

- random deviations of the concentration values obtained for the same sample during repeated measurements appear to be of an order of magnitude larger than the errors of the analytical procedure;

- the solubility of the excess component at a fixed partial pressure of the vapour, as a rule, decreases with the increase in temperature, which is considerably easier to explain by adsorption than solubility;

- the observed value of the excess metal concentration depends only slightly on the nature of particular objects, for a fixed temperature it is approximately the same for ZnS [8], ZnSe [7], and CdS [6];

- tensiometric data obtained by Rau [2] for ZnSe–Se and CdSe–Se systems show directly the predominant role of the adsorption process.

CONCLUSIONS

The presented experimental evidence can be interpreted in terms of the formation of electroneutral defects; however, it can be explained considerably better by using the adsorption of Zn on crystal surfaces.

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A²B⁶ ÜHENDITE KÕRVALEKALLE STÖNNIOMEETRIAST: ELEKTRONEUTRAALSED DEFEKTID VÕI ÜHE KOMPONENDI LIIA ADSORPTSIOON?

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A²B⁶ ühendites analüütiliselt määratud komponendi liia kontsentratsioon ületab märkimisväärselt elektriliselt aktiivsete defektide kontsentratsiooni. Mitmetes töedes on tehtud järeldus elektroneutraalsete defektide domineerivast osast lahustuvuses. Käesolevas artiklis on väidetud, et täheldatud efekt oli seotud komponendi liia adsorptsiooniga kristalli pindadel ja plokkide vahel.

НЕСТЕХИОМЕТРИЯ СОЕДИНЕНИЙ А²В⁶: ЭЛЕКТРОНЕЙТРАЛЬНЫЕ ДЕФЕКТЫ ИЛИ АДСОРБЦИЯ ИЗБЫТОЧНОГО КОМПОНЕНТА?

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В соединениях А²В⁶ аналитически определяемая концентрация избыточного компонента значительно превосходит концентрацию электрически активных дефектов. В ряде работ был сделан вывод о доминирующем вкладе в величину растворимости электронейтральных дефектов. В представленной работе приводятся аргументы в пользу того, что наблюдаемый эффект связан с адсорбцией избыточного компонента на поверхности кристаллов и межблочных границах.