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NEW APPROACH TO THE DETERMINATION OF PHASE EQUILIBRIUM IN THE Zn-Te SYSTEM

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Abstract: The polyassociative model of the liquid phase was applied to describe the phase equilibrium in the Zn-Te system. The thermodynamic functions describing the formation of liquid associates were obtained, taking into account the experimental data on the p-T-x equilibrium in the system. The model of polyassociative solutions with the parameters obtained in this work satisfactorily describes the p-T-x diagram of the system. The numerical results of the analysis of the phase equilibrium confirmed the possibility of applying the polyassociative model to the Zn-Te system in a wide temperature range.

Keywords: phase equilibria, solubility, liquid phase epitaxy, II-VI semiconductor compound

1. Introduction

Our previous papers on the modeling of phase equilibria in the Cd-Hg-Te system [1–3] have shown that a phase diagram can be successfully described by the model of polyassociative solutions. According to this model, an $A^{II}B^{VI}$ semiconductor solution can be represented as a set of complexes with differing compositions and along with atoms of initial components.

In this work, the model of polyassociative solutions was applied to the analysis of the p-T-x phase diagram of the Zn-Te system. ZnTe can serve as an active substance for registration of X-ray and nuclear radiation. The $\mathrm{Zn}_x\mathrm{Cd}_{1-x}\mathrm{Te}$ solid solution can serve as a buffer layer in highly effective heterostructures applied in IR devices.

2. Main theoretical assumptions

The phase equilibrium of the Zn-Te system has been investigated theoretically and experimentally in references [4–9]. The obtained experimental data on the p-T-x equilibrium in this system allowed to select the model of phase interactions and to describe the phase diagram in a theoretical way. The theoretical analysis was based on the model of associative solutions with one complex in the liquid phase [5, 6]. In this case, the complicated shape of the liquidus of the system is described by taking into account the interactions between the complexes and free atoms of Zn and Te according to the sub-regular solution theory [6]. This in turn allowed to determine the liquidus curves and vapor pressure of volatile components over the melt with high accuracy.

Taking into consideration the deficiency of the sub-regular solution model caused by the difficulties of the physical interpretation of the dependence of interaction parameters on the composition of the liquid phase, as well as the difficulty of the distribution of the obtained thermodynamic information in the multicomponent phases of the $\mathrm{A}^{\mathrm{II}}\mathrm{B}^{\mathrm{VI}}$ system, the analysis could not be completed. In the present work, the aforementioned difficulties can be eliminated by applying the model of polyassociative solutions in order to describe and analyze the phase equilibrium in the Zn-Te system, whose specific features can be seen in Figure 1, which presents its liquidus.

According to the the model of polyassociative solutions, the T-x phase equilibrium can be described as follows [1–3]:

$$\Delta S^F_{\mathrm{ZnTe}}(T^F_{\mathrm{ZnTe}} - T)/RT + \ln\left(\frac{x_{\mathrm{Zn}} \cdot x_{\mathrm{Te}}}{x^{Sl}_{\mathrm{Zn}} \cdot x^{Sl}_{\mathrm{Te}}}\right) = 0 \tag{1}$$

where $\Delta S^F_{\mathrm{ZnTe}}$, T^F_{ZnTe} are the entropy and the temperature of fusion, respectively; x_{Zn}, x_{Te} are the concentrations of the free (unassociated) atoms of zinc and tellurium, respectively, T is the absolute temperature, R is the gas constant and Sl refers to the liquid phase of stoichiometric composition.

The concentrations of the complexes in a solution are related to the total content of a component in the liquid phase according to the mass-balance equations:

$$\begin{aligned} &x_{\mathrm{Zn}}G - x_{\mathrm{ZnTe}} - 2\cdot(x_{\mathrm{Zn_2Te}} + x_{\mathrm{Zn_2Te_3}}) - x_{\mathrm{ZnTe_2}} - x_{\mathrm{Zn}} = 0;\\ &x_{\mathrm{Te}}G - x_{\mathrm{ZnTe}} - x_{\mathrm{Zn_2Te}} - 2\cdot x_{\mathrm{ZnTe_2}} - 3\cdot x_{\mathrm{Zn_2Te_3}} - x_{\mathrm{Te}} = 0 \end{aligned} \tag{2}$$

where $G = 1 + 2\cdot(x_{\mathrm{Zn_2Te}} + x_{\mathrm{ZnTe_2}}) + x_{\mathrm{ZnTe}} + 4\cdot x_{\mathrm{Zn_2Te_3}}$, x_{Zn}, x_{Te} are the atomic fractions of zinc and tellurium in the melt (total concentrations).

According to the method of quasi-chemical approximation, the constant for the formation of a complex can be written as:

$$\frac{x_{\mathrm{Zn}}^{p}x_{\mathrm{Te}}^{q}}{x_{\mathrm{Zn_pTe_q}}}=K_{pq}(T) \tag{3}$$

where K_{pq} is the dissociation constant for the $\mathrm{Zn_pTe_q}$ complex.

In Equations (2)–(3), we took into account the fact that the Zn-Te liquid phase can be represented as a set of complexes (ZnTe, $\mathrm{Zn_2Te}$, $\mathrm{Zn_2Te_3}$, $\mathrm{ZnTe_2}$) as well as of free atoms of Zn and Te. Such an associative composition of the $\mathrm{A^{II}B^{VI}}$ melt of semiconductors and its applicability to the analysis of phase equilibrium in related systems, such as Cd-Te, Hg-Te has already been presented by us in [1–3].

It should be noted that in Equation (1), we neglected the difference between the mole thermal capacities of ZnTe and of liquid zinc and tellurium. This was acceptable due to the small value of this number in Equation (1). The same was observed in the case of similar calculations of the phase equilibrium in Cd-Te and Hg-Te systems [1–3].

To estimate the partial pressure of the components above the saturated solution, we assumed that only the free atoms of zinc and tellurium influence the value of the pressure in the system. In this case, the partial pressures of the components in accordance with the Raoult's law are as follows:

$$p_{\mathrm{Zn}}=x_{\mathrm{Zn}}p_{\mathrm{Zn}}^{0}(T); \quad p_{\mathrm{Te_2}}=x_{\mathrm{Te}}^{2}p_{\mathrm{Te_2}}^{0}(T) \tag{4}$$

where $p_{\mathrm{Zn}}^{0}(T)$, $p_{\mathrm{Te_2}}^{0}(T)$ are the saturated pressures of zinc and diatomic tellurium, respectively, at a given temperature.

In the last expression, we took into account the existence of diatomic molecules of Te. The data on the saturated vapor pressure of tellurium at high temperatures were taken from [5]:

$$\lg p_{\mathrm{Te_2}}^{0}(\mathrm{atm.})=-\frac{5960.2}{T}+4.7191; \quad T>723\ \mathrm{K} \tag{5}$$

This temperature dependence is fully applicable and has already been used in order to describe the gas phase in Cd-Te and Hg-Te systems [1–3, 5].

The saturated vapor pressure of zinc at relatively low temperatures was investigated experimentally in great detail, however, in the temperature range for which we investigated the Zn-Te system equilibrium the data on the pressure is scarce [10].

We opted for a dependence described by the following function [10]:

$$\lg p_{\mathrm{Zn}}^{0}(\mathrm{atm.})=12.301-\frac{6967}{T}-2.162\lg T+2.298\cdot 10^{-4}T \tag{6}$$

In fact, the calculated values of the saturated vapor pressure of zinc obtained using the above data in the low temperature range ($T<1000\,\mathrm{K}$) were in agreement with experimental data, even at high temperatures, which was of crucial importance.

The data on temperature and entropy of fusion were taken from [5, 6] and their values were as follows: $T^F_{\mathrm{ZnTe}} = 1563\,\mathrm{K}$, $\Delta S^F_{\mathrm{ZnTe}} = 44.3\,\mathrm{J/mol \cdot K}$.

Equations (1)–(6) fully describe the p-T-x equilibrium in the investigated binary system. The temperature dependence of dissociation constants, which is a fundamental issue for this model, was determined according to the following criteria. The first obstacle to applying the model was the lack of experimental data on the vapor pressure at the temperature of the congruent melting of ZnTe. These data are necessary to estimate the concentration of free atoms of zinc and tellurium (x^{Sl}_{Zn}, x^{Sl}_{Te} in Equation (1)) at the melting point. In the case of the phase diagram of Cd-Te and Hg-Te systems [1–3], the vapor pressure under these conditions was determined without difficulty.

The experimental data on the pressure of zinc over the Zn-Te solution are usually limited by the low temperature region and do not provide accurate information on the dependence of the value of the pressure on temperature near the melting point. Therefore we considered these as free parameters. We applied the following procedure in order to estimate the pressure of tellurium at the fusion temperature. There are certain experimental data [9] on the dependence of pressure on temperature over a saturated melt that correlate well with reliable data from [4–7]. In order to find the pressure of tellurium at the fusion temperature of the compound basing on experimental data [9], the fourth-order polynomial extrapolation was done using the least-squares method. The extrapolations of the third and fourth order are shown in Figure 2. From the calculations, it follows that the pressure of tellurium at the fusion temperature of the compound does not depend appreciably on the order of the approximation and assumes the value of $p^{St}_{\mathrm{Te}_2} \approx 0.29\,\mathrm{atm}$. The analysis of the pressure values in similar systems, *i.e.* Cd-Te and Hg-Te, showed that the changes of these values in the given temperature range are very steep. Therefore, in this work, we assumed the calculated value of the pressure to be the maximum value.

The situation becomes more complicated when considering the pressure of zinc at the melting point. The liquidus course of Zn-Te in the region enriched by the metal makes it difficult to measure the pressure experimentally, which is the reason for the lack of experimental data above 1200 K. Therefore, the pressure of zinc at the melting point was found by means of extrapolation of experimental data [9] to the melting point. We also took into account the fact that the extrapolation of the pressure in the range of 0.8–1.5 atm. should yield the value of the sought parameter at the melting point This allowed us to limit the range of the values of thermodynamic parameters.

The experience gained from the investigation of the temperature dependence of the Cd-Te, Hg-Te liquid phase dissociation constants [1–3] and the theoretical analysis of the dependence of the shape of the liquidus on the dissociation of the solution allowed us to predict the shapes of certain functions before undertaking the numerical procedures. First, the basic liquid-phase complex should be ZnTe at temperatures close to the melting point. Crucially, the appearance of a simpler complex in the solution cannot lead to an asymmetry of the phase diagram. This means that at high temperatures, multiatomic complexes should have significantly higher concentrations. In [1–3], it was assumed that in order to lower the temperatures, the quantity of multiatomic complexes must increase and the concentration of ZnTe associates must decrease.

Thus, in this work the application of physical interpretation allowed us to determine the temperature dependence of the dissociation constant without using the typical and complicated procedures of the mathematical model for the determination of the parameters. Moreover, the proposed approach predicts thermodynamic functions which do not contradict the physical assumptions of the model of polyassociative solutions. This is crucial, because in the future the dissociation functions could be applied to model the p-T-x equilibrium in ternary and other solutions.

3. Results

The analysis of the experimental data allowed us to obtain the temperature dependence of the dissociation constants (Table 1).

Table 1. Temperature dependence of the dissociation constants of Zn-Te complexes in solution ($K = \exp(A - B/T + C/T^2)$)

Complex	A	B (K)	C (K^2)
ZnTe	1551.2	$4.759 \cdot 10^6$	$3.641 \cdot 10^9$
$\mathrm{Zn_2Te}$	1169.506	$3.712 \cdot 10^6$	$2.929 \cdot 10^9$
$\mathrm{Zn_2Te_3}$	106.034	$3.30 \cdot 10^5$	$2.337 \cdot 10^8$
$\mathrm{ZnTe_2}$	32.446	$8.753 \cdot 10^4$	$5.09 \cdot 10^7$

The concentrations of tellurium and zinc corresponding to dissociation constants in the stoichiometric solution at the melting temperature are $x^{Sl}_{\mathrm{Zn}} = 0.05641$ at. fr., $x^{Sl}_{\mathrm{Te}} = 0.17153$ at. fr., respectively. These concentrations of the free components yield the following values of the pressure of the components at the melting temperature of ZnTe: $p^{Sl}_{\mathrm{Zn}}(T^F_{ZnTe}) = 1.12$ atm., $p^{Sl}_{\mathrm{Te_2}}(T^F_{\mathrm{ZnTe}}) = 0.237$ atm. The calculated values of the vapor pressures of zinc and tellurium over the Zn-Te system were in good agreement with our estimations for the presented parameters.

The results of the calculations of the liquidus and the vapor pressure are presented in Figures 1–3.

The good agreement between our results and the experimental data allows to increase the accuracy of the description of the liquidus line and eliminates the oscillating character of the pressure of tellurium in the melt at high temperatures (Figure 2).

The appearance of a local maximum in the pressure *vs.* temperature dependence diagram of tellurium was caused by a decrease in the liquidus temperature near the melting point in the tellurium-rich region of diagram (Figure 1). This maximum appears at $x_{\mathrm{Te}} = 0.6 - 0.7$ at. fr. along with a noticeable

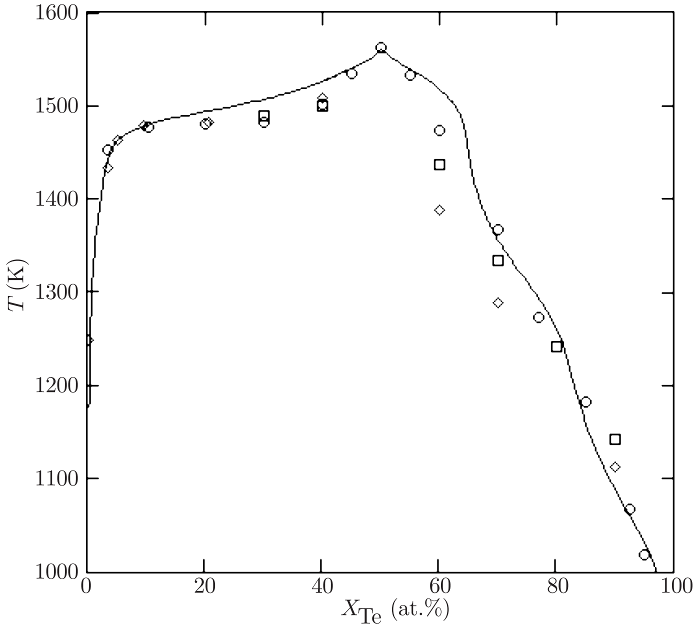

Figure 1. Liquidus temperature of the Zn-Te system *vs.* concentration of tellurium in the melt, where rhombs, squares, circles are the experimental data from [6], [8] and [11], respectively

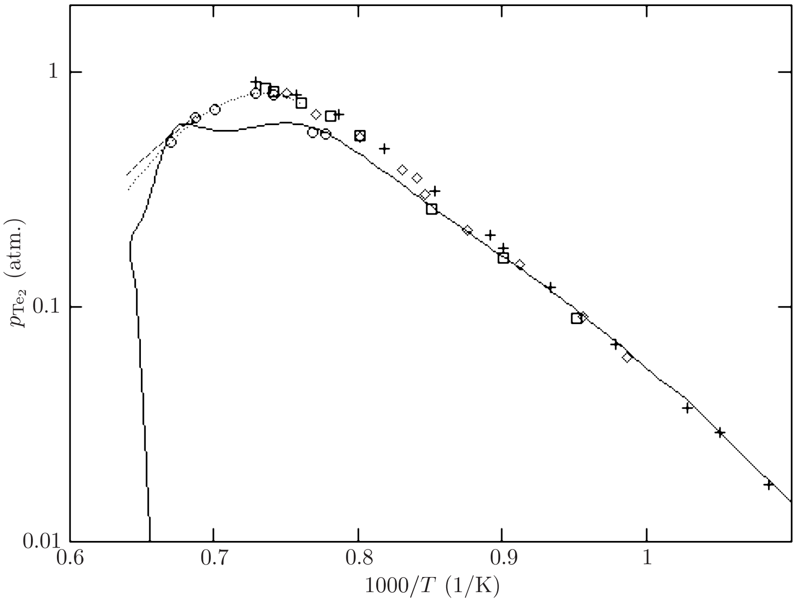

Figure 2. Temperature dependence of the partial pressure of tellurium along the liquidus of the Zn-Te system. Squares, rhombs are the experimental data from [5]; crosses and circles correspond to data from [7] and [9], respectively; the dashed line denotes a third-order polynomial extrapolation of the dependence of pressure on temperature; the dotted line corresponds to a fourth-order polynomial extrapolation

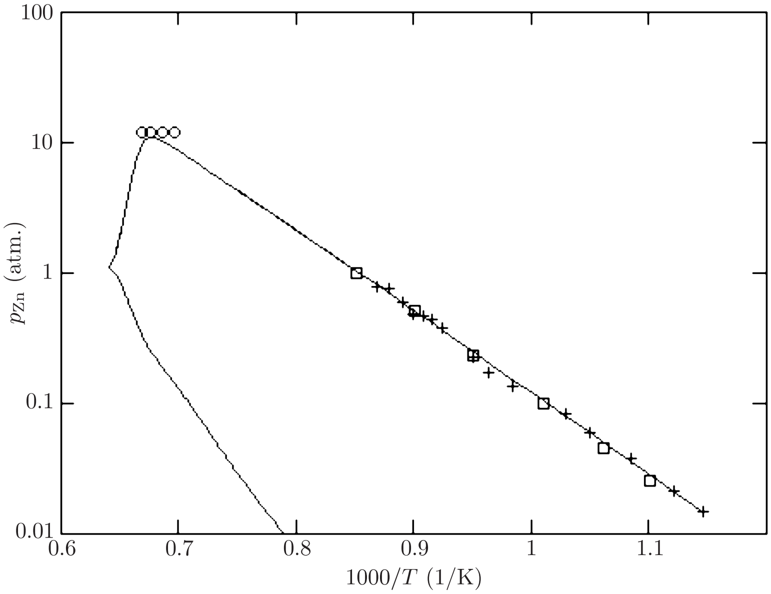

Figure 3. Temperature dependence of the partial pressure of zinc along the liquidus line of the Zn-Te system, where crosses, squares, circles are the experimental data from [5], [7] and [9], respectively

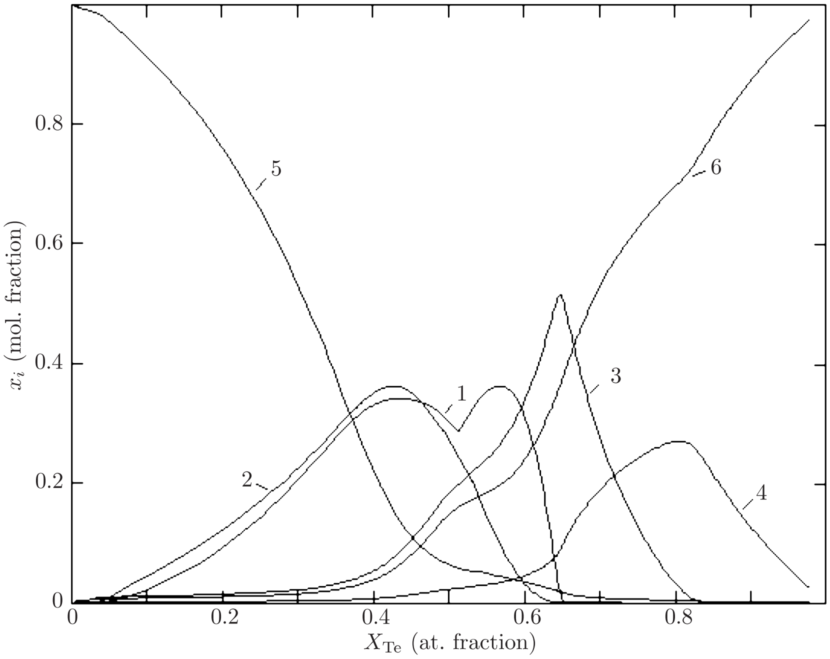

Figure 4. Dependence of the concentrations of associates on the total concentration of tellurium in the melt along the liquidus of the Zn-Te system; 1 – ZnTe; 2 – Zn_2Te; 3 – Zn_2Te_3; 4 – $ZnTe_2$; 5, 6 – free atoms of zinc and tellurium, respectively

decrease in the solubility of tellurium in the zinc solution for the metal-enriched region of the phase diagram. It is difficult to describe the phase diagram for the entire concentration range, since the dissociation parameter of the ZnTe complex strongly influences the shape of the liquidus curve in both parts of the diagram.

Figure 4 shows the dependence of the concentrations of associates on the composition of the melt along the p-T-x equilibrium of the Zn-Te system.

Figure 4 shows the complicated plots of the interactions of associates in the solution, resulting in the agreement between the calculated values of the phase equilibrium and the experimental results. It is difficult to analyse this situation because of the complicated shape of the experimental liquidus line and its sharp asymmetry compared to the equiatomic solution composition.

Our investigation showed that in order to obtain a liquidus curve that is steep enough near the melting temperature in the Te-rich region of the phase diagram [12], the concentration of associates must increase with a decrease in temperature below the melting point. This agrees with the general trends in the shape of the liquidus in binary systems. A further decrease in temperature leads to a decrease in concentration at which point the liquidus line represents more complex ternary compounds in the liquid phase. Therefore, we believe that the influence of the concentration of each associate on the temperature dependence allows to describe the complicated character of the phase equilibrium in the system.

4. Summary

We obtained a satisfactory description of the asymmetric T-x diagram and p-T equilibria in the Zn-Te system. We showed that the model of polyassociative solutions can be applied to the analysis of the phase equilibrium in $A^{II}B^{VI}$ semiconductor systems. The thermodynamic functions determined in this work can be used in order to analyze the phase equilibrium of multicomponent solid solutions formed on the basis of ZnTe.

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