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POLYASSOCIATIVE MODEL OF A^2B^6 SEMICONDUCTOR MELT AND p-T-x PHASE EQUILIBRIA IN Zn-Cd-Te SYSTEM

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Abstract: This work presents a numerical analysis of p-T-x phase equilibrium in the Zn-Cd-Te ternary system in the framework of the polyassociative solution model. On the basis of the experimental data on p-T-x phase equilibrium in the ternary system, thermodynamic functions describing the formation of liquid associates were found. It was shown that the results of the mixing of components in the Zn-Cd-Te ternary melt are related to the occurrence of ZnCdTe and $ZnCdTe_3$ associates. Dissociation parameters of these complexes were calculated and subsequently used in order to efficiently describe p-T-x phase equilibrium of the system in a wide temperature range.

Keywords: phase equilibria, solubility, liquid phase epitaxy, semiconducting II-VI materials

1. Introduction

The polyassociative liquid phase model, presented in [1], was successfully applied in order to describe the phase equilibrium in the Cd-Te and Hg-Te systems.

In [2, 3], this model was applied in order to determine the thermodynamic functions of certain complexes and to describe the phase equilibrium in the Cd-Hg-Te system. In this work, we apply this model in order to describe the p-T-x phase equilibrium in the Zn-Cd-Te ternary system. Thermodynamic data on the application of the polyassociative solutions model to the description of the melt in an A^2B^6 system [2, 3] and of the thermodynamic functions of the Zn-Te system determined in [4] served as the basis of this analysis.

2. Theory

The analysis of phase equilibrium in the Zn-Cd-Te system was based on the methodology similar to the ones used in [2, 3] for the Cd-Hg-Te system. The differences which occurred while solving the problem are indicated later in this paper.

According to the polyassociative solutions model [2, 3], the mixing effect of metallic components in the liquid phase can be triggered by the occurrence of ZnCdTe and $ZnCdTe_3$ associates in the liquid. According to the method of quasi-chemical reactions, the formation process of these complexes can be described as follows:

$$\begin{aligned} K_{\mathrm{ZnCdTe_3}}(T) &= x_{\mathrm{Cd}}x_{\mathrm{Zn}}x^3_{\mathrm{Te}}/x_{\mathrm{ZnCdTe_3}} \\ K_{\mathrm{ZnCdTe}}(T) &= x_{\mathrm{Cd}}x_{\mathrm{Zn}}x_{\mathrm{Te}}/x_{\mathrm{ZnCdTe}} \end{aligned} \tag{1}$$

where $x_{\mathrm{ZnCdTe_3}}$ and x_{ZnCdTe} are the concentrations of $ZnCdTe_3$ and ZnCdTe complexes in the melt, respectively, and $K_{\mathrm{ZnCdTe_3}}(T)$ and $K_{\mathrm{ZnCdTe}}(T)$ are the dissociation constants of these complexes.

The mass balance equations in the ternary melt in the presence of all complexes typical of initial binary systems, as well as $ZnCdTe_3$ and ZnCdTe associates, are as follows:

$$\begin{aligned} & X_{Cd}G - x_{\mathrm{CdTe}} - x_{\mathrm{CdTe_2}} - 2(x_{\mathrm{Cd_2Te_3}} + x_{\mathrm{Cd_2Te}}) - x_{\mathrm{ZnCdTe}} - x_{\mathrm{ZnCdTe_3}} - x_{\mathrm{Cd}} = 0 \\ & X_{\mathrm{Zn}}G - x_{\mathrm{ZnTe}} - x_{\mathrm{ZnTe_2}} - 2(x_{\mathrm{Zn_2Te_3}} + x_{\mathrm{Zn_2Te}}) - x_{\mathrm{ZnCdTe}} - x_{\mathrm{ZnCdTe_3}} - x_{\mathrm{Zn}} = 0 \\ & X_{\mathrm{Te}}G - x_{\mathrm{ZnTe}} - x_{\mathrm{CdTe}} - x_{\mathrm{ZnCdTe}} - 2(x_{\mathrm{ZnTe_2}} + x_{\mathrm{CdTe_2}}) - x_{\mathrm{Zn_2Te}} - x_{\mathrm{Cd_2Te}} - \\ & - 3(x_{\mathrm{Zn_2Te_3}} + x_{\mathrm{Cd_2Te_3}} + x_{\mathrm{ZnCdTe_3}}) - x_{\mathrm{Te}} = 0 \\ & G = 1 + x_{\mathrm{CdTe}} + x_{\mathrm{ZnTe}} + 2(x_{\mathrm{CdTe_2}} + x_{\mathrm{ZnTe_2}} + x_{\mathrm{Cd_2Te}} + x_{\mathrm{Zn_2Te}} + x_{\mathrm{ZnCdTe}}) + \\ & + 4(x_{\mathrm{Cd_2Te_3}} + x_{\mathrm{Zn_2Te_3}} + x_{\mathrm{ZnCdTe_3}}) \\ & X_{\mathrm{Te}} + X_{\mathrm{Zn}} + X_{\mathrm{Cd}} = 1 \\ & \sum_{i=1}^{13} x_i = 1 \end{aligned} \tag{2}$$

where X_{Zn}, X_{Te}, X_{Cd} are the atomic fractions of Zn, Te and Cd in the solution; and $x_{\mathrm{Zn_pTe_q}}$, $x_{\mathrm{Cd_pTe_q}}$ are the mole fractions of $\mathrm{Zn_pTe_q}$ and $\mathrm{Cd_pTe_q}$ complexes in the liquid phase.

The equations above follow from the equations describing the dependence of the mole number of every complex on the atomic and mole fraction of components in the ternary melt. Thus, Zn-Cd-Te solutions consist of the following associates:

ZnTe, Zn_2Te, $ZnTe_2$, Zn_2Te_3, CdTe, Cd_2T_4, Cd_2Te_3, $CdTe_2$, $ZnCdTe_3$, ZnCdTe and the free atoms of Zn, Cd, Te. 13 types of particles are present in the ternary liquid phase altogether.

Within the confines of the established model, the pressures of the liquid phase components are related to the concentration of non-associated atoms of Cd, Hg and Te and, therefore, must be calculated (as earlier) by Henry-Raoult's law [1–3]. The relevant data for the saturation pressure of Zn, Cd and Te with respect to their respective solutions used in the calculations are the same as in papers [1–4].

The equations of thermodynamic equilibrium between the ternary liquid phase and the solid phase, according to the theory of regular solutions and polyassociative model of melt, are as follows:

$$\begin{aligned}
&\Delta S^F_{\mathrm{CdTe}}(T^F_{\mathrm{CdTe}}-T)/RT+\ln\left(\frac{x_{\mathrm{Cd}}x_{\mathrm{Te}}}{x^{\mathrm{Sl}}_{\mathrm{Cd}}x^{\mathrm{Sl}}_{\mathrm{Te}}}\right)=\ln\gamma_{\mathrm{CdTe}}x^S_{\mathrm{CdTe}}\\
&\Delta S^F_{\mathrm{ZnTe}}(T^F_{\mathrm{ZnTe}}-T)/RT+\ln\left(\frac{x_{\mathrm{Zn}}x_{\mathrm{Te}}}{x^{\mathrm{Sl}}_{\mathrm{Zn}}x^{\mathrm{Sl}}_{\mathrm{Te}}}\right)=\ln\gamma_{\mathrm{ZnTe}}x^S_{\mathrm{ZnTe}}\\
&RT\ln\gamma_j=\alpha^S(1-x^S_j)\quad j=\mathrm{CdTe,\ ZnTe}\\
&x^S_{\mathrm{ZnTe}}+x^S_{\mathrm{CdTe}}=1
\end{aligned}\tag{3}$$

where ΔS^F_j, T^F_j are the entropy and temperature of fusion of the initial compounds, respectively; γ_j is the activity coefficient of the j^{th} component in the solid phase; and *sl* denotes the liquid phase of stoichiometric composition.

Similarly to the Cd-Hg-Te system [1–3], the parameters α^S and $K_{\mathrm{ZnCdTe_3}}$, K_{ZnCdTe} – necessary for the modeling of data on the solid phase interaction parameter between Zn and Cd in the metallic sublattice of solid solution – were fitted to experiment. The temperature dependence of these parameters was found as the best fit of p-T-x phase equilibrium to the empirical data for the ternary system.

The search for the unknown thermodynamic functions begins with the study of experimental data in the quasi-binary section of the phase diagram. The analysis of the experimental liquidus in this temperature range was carried out in [5]. In principle, the obtained data are not questionable, however, it is necessary to pay attention to the relatively low temperature range between the position of the liquidus and solidus. In the analogous Cd-Hg-Te system, for which the difference in the covalent radii between the mixing components (Cd, Hg) is small, a convex shape of the liquidus line is usually observed [2, 3]. The larger difference in the sizes of the Cd and Zn atoms in the Zn-Cd-Te system, should increase the essential temperature interval of coexistence of the two phases, as compared with the Cd-Hg-Te system. This effect was not observed experimentally [5], therefore, the experimental data seem unreliable. Nevertheless, these are the only data available and thus were taken into account in the calculations, which also considered the experimental correction.

In order to describe the system solidus, as the first approximation in choosing the value of the α^S parameter, it was assumed that for many of A^2B^6 ternary solid solutions, there exists a correlation between the mixing energy α^S and the difference in the parameters of the initial components of the crystal lattice [6]. Simultaneously, the parameter α^S must become larger in magnitude as the difference in the diameters of mutually substituted components increased. This, in turn, is the result of the elastic part of the energy increasing after the base component atom is replaced with an atom of a different diameter.

As was emphasized before, it is typical of the solid state to exhibit a significant difference in the lattice constant, depending on the composition. In the calculations, the value of the obtained parameter should be slightly higher than the values presented in [2, 3] for the $\mathrm{Cd}_X\mathrm{Hg}_{1-X}\mathrm{Te}$ solid solution.

3. Results and discussion

The calculations showed that a satisfactory description of the phase equilibrium for the temperatures of a quasi-binary region is reached for the following values of the required parameters: $\alpha^S \approx -500\,\mathrm{cal/mol}$, $K_{\mathrm{ZnCdTe}} \approx 2\cdot 10^{-5}$ and $K_{\mathrm{ZnCdTe_3}} \approx 3\cdot 10^{-7}$. These values of the parameters are responsible for mixing of the complexes in the melt, and their values meet the requirements discussed earlier.

Figure 1 presents the results of the calculations together with the experimental data [5] on the quasi-binary cut of the system phase diagram. In general, a good correlation between the results of calculations and the experimental data can be observed, except for $X_{\mathrm{ZnTe}} \approx 0.5-0.7$ mol frac., which corresponds to the temperature close to 1480K.

The analysis of the associative composition of the melt along the liquidus line for the system in a given temperature-concentration range shows that the shape of the liquidus depends primarily on the concentration of $\mathrm{Zn_2Te_3}$, ZnCdTe, $\mathrm{ZnCdTe_3}$ complexes and the free atoms of Zn, Cd, Te. Simultaneously, the significant difference between the calculated value and the experimental data can be explained similarly as in the case of the Zn-Te system in the same temperature range for the corner of the phase diagram enriched by tellurium (Figure 1 in [4]).

In particular, the existence of this type of calculation anomalies is related to the behavior of the $\mathrm{Zn_2Te_3}$ complex, which was responsible for the sharp maximum on the liquidus line near the melting temperature of ZnTe. It was possible to correct the liquidus of the Zn-Te system in this temperature range and thus to improve on the agreement between the calculations and experimental data on the quasi-binary diagram. However, the fact that the model does not depend on other parameters inevitably leads to a reduction in the number of data on the pressure of tellurium in the Zn-Te system. In turn, it has an adverse impact on the description of the corresponding p-T equilibrium curve in the binary systems. In fact, the analyzed shape of the experimental liquidus line was different from corresponding shapes obtained for the substituted solution of solid belonging to

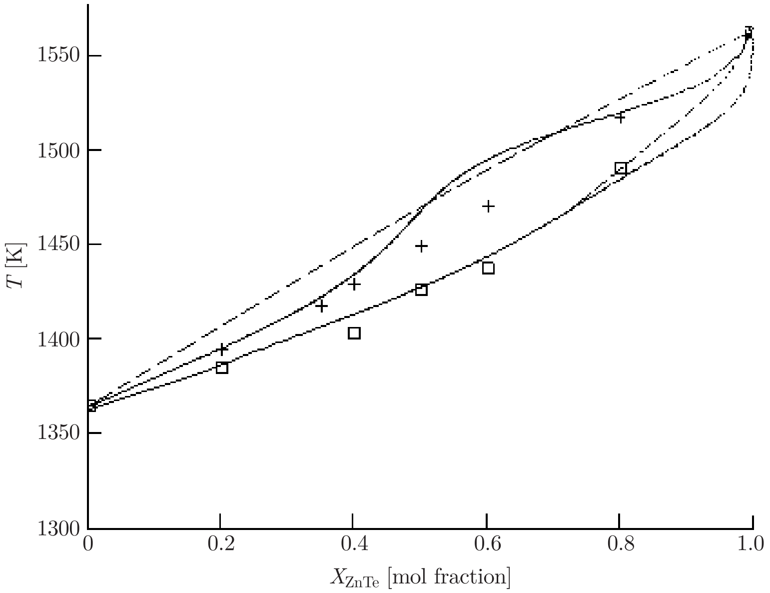

Figure 1. Phase diagram of the Zn-Cd-Te quasi-binary system. □, + are the solidus and liquidus data, according to [5]. The solid line is the line of best fit to experimental data [5]; the dotted line corresponds to a calculation with our estimations of model parameters

the same semiconductor group [7]. Figure 1 also presents the liquidus line of the quasi-binary diagram of the system, obtained by our calculations without the rigid requirements for the dissociation parameters to agree with experiments [5].

The search for the temperature dependence of the K_{ZnCdTe}, $K_{\mathrm{ZnCdTe_3}}$ dissociation constants and for the mutual interaction parameter in the solid phase, $\alpha^S(T)$, was performed by calculating the experimental data of the phase equilibrium for the Te-enriched diagram corner. The calculations were made on the basis of a similar problem solved for the Cd-Hg-Te system [2, 3]. However, here, in order to achieve a satisfactory description of experimental data [5], it was necessary to assume a more complex temperature dependence, $K_{\mathrm{ZnCdTe_3}}(T)$, *i.e.* $K_{\mathrm{ZnCdTe_3}}(T) = \exp(A - B/T + C/T^2)$. Otherwise, it would have been difficult to describe the liquidus in the range of $X_{\mathrm{Te}} \approx 0.6 - 0.75$ at. frac.

The practical application of the calculations is related to the thermodynamic description of the low-temperature LPE process in the system. This would require paying careful attention to the low-temperature ranges in the analysis of the phase equilibrium. Therefore, in this work, the thermodynamic functions of the Cd-Te system were slightly corrected. In other words, in order to achieve a more accurate description of the experimental data [8] in the typical temperature range of LPE (500–600°C), the temperature dependence of the dissociation constant of $\mathrm{CdTe_2}$ was specified more accurately. This complex prevails in this temperature range and thus determines the shape of the liquidus in this parameter range. All thermodynamic parameters of the model necessary for the analysis are presented in Table 1.

Table 1. Thermodynamic parameters of the polyassociative model for Zn-Cd-Te systems

System	T^F, K	$\Delta S^F \cdot 4.183$, $\frac{J}{\mathrm{mol \cdot K}}$	Dissociation parameters of complexes			
			ATe	ATe_2	A_2Te	A_2Te_3
Zn-Te	1563.0	10.58	$e^{1551.2+3.641 \cdot \frac{10^9}{T^2} - 4.759 \cdot \frac{10^6}{T}}$	$e^{32.445+5.090 \cdot \frac{10^7}{T^2} - 8.753 \cdot \frac{10^4}{T}}$	$e^{1169.5+2.929 \cdot \frac{10^9}{T^2} - 3.712 \cdot \frac{10^6}{T}}$	$e^{106.03+2.337 \cdot \frac{10^8}{T^2} - 3.299 \cdot \frac{10^5}{T}}$
Cd-Te	1365.1	8.8	$e^{78.245+1.5541 \cdot \frac{10^8}{T^2} - 2.289 \cdot \frac{10^5}{T}}$	$e^{5.56+7.314 \cdot \frac{10^6}{T^2} - 1.828 \cdot \frac{10^4}{T}}$	0.02	$e^{120.511+1.817 \cdot \frac{10^8}{T^2} - 3.12 \cdot \frac{10^5}{T}}$
Zn-Cd-Te	$K_{\mathrm{ZnCdTe}} = e^{-22.365 + \frac{21612.1}{T}}$		$K_{\mathrm{ZnCdTe_3}} = e^{-25.579 - 1.107 \cdot \frac{10^7}{T^2} + 2.322 \cdot \frac{10^4}{T}}$		$\alpha^S_{\mathrm{ZnTe \times CdTe}} = (2320 - 3.18T) \cdot 4.183 \frac{J}{\mathrm{mol}}$	

The thermodynamic parameters presented in Table 1 enabled us to calculate the p-T-x equilibrium lines in the Zn-Cd-Te system in a wide temperature range. The results of the analysis are presented in Figures 2–4. The data calculated for the liquidus of the Zn-Cd-Te system for different sections of the diagram in Te-enriched part are presented in Figures 2–3 together with data from [5].

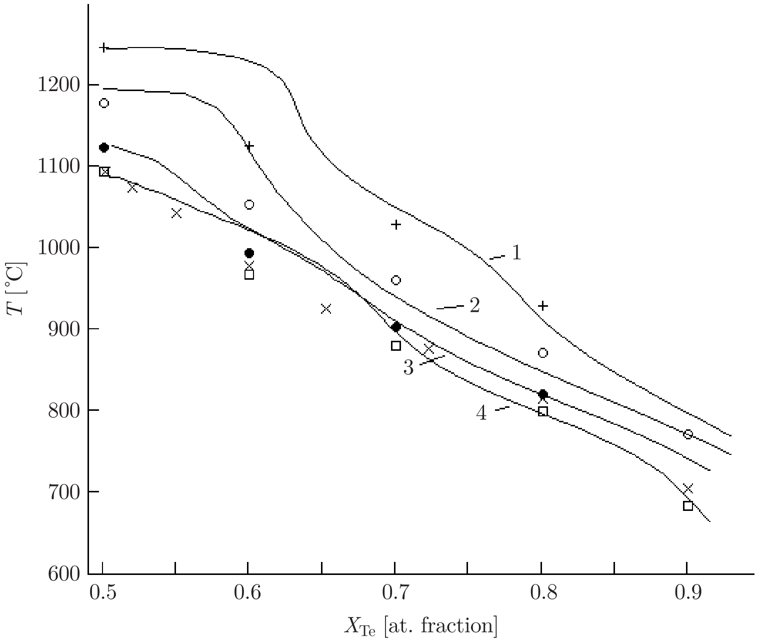

Figure 2. Liquidus temperature of the Zn-Cd-Te systems depending on the tellurium content in the melt for different values of $Z = \frac{X_{\mathrm{Zn}}}{X_{\mathrm{Cd}}}$. Curve 1 and + are the results of calculations and experimental data [5], respectively, for $Z = 4$; curve 2 and ○ correspond to the data obtained for $Z = 1$; curve 3 and ● correspond to the data for $Z = 0.25$; and curve 4, × and □ correspond to the data for the Cd-Te system [5, 9]

If we assume the experimental data [5] to be reliable, the correlation between the calculations and experiment can be deemed satisfactory. It should also be emphasized that in the case of the quasi-binary equilibrium diagram section, the inaccuracy in the liquidus calculation did not exceed 15–20K, which is acceptable in thermodynamic calculations using a multiparameter thermodynamic model. The accuracy of the description of liquidus significantly increased with a decrease in temperature and for the liquid-phase contents different from $X_{\mathrm{Te}} \approx 0.6 - 0.75$ at. frac.

Our attention was drawn by the course of the liquidus line at high temperatures in Figure 3, which was related to the occurrence of a maximum for $X_{\mathrm{Te}} \approx 0.6$ at. frac. (line 2). The analysis of the results of the calculation showed that this maximum was caused by a metal substitution effect, *i.e.* cadmium was substituted for zinc as the solvent in the liquid phase.

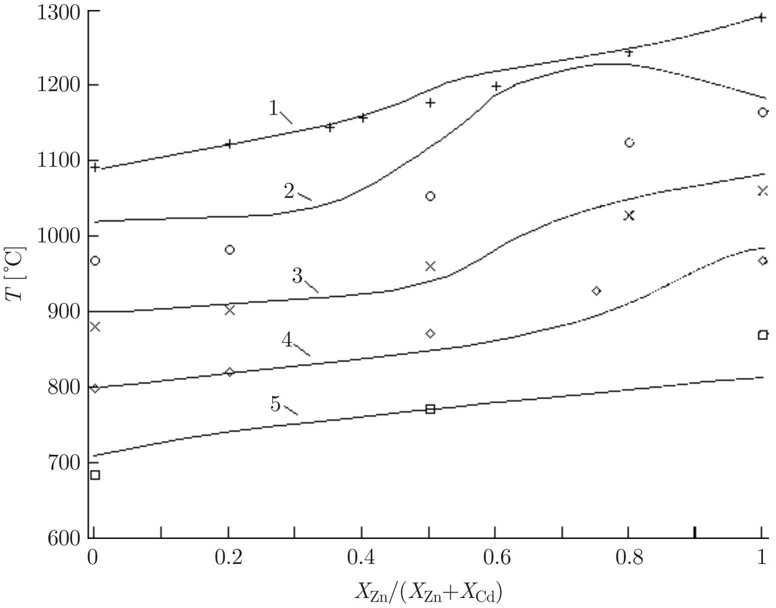

Figure 3. Liquidus temperature of the Zn-Cd-Te systems versus the relative content of metals in the liquid phase $Z = \frac{X_{Zn}}{(X_{Cd}+X_{Zn})}$ for various total concentrations of tellurium in the melt. The data corresponds to the corner of the phase diagram enriched by tellurium. For 1 and +, the quasi-binary sections of the diagram $X_{Te} = 0.5$at. frac.; for 2 and ○, $X_{Te} = 0.6$at. frac.; for 3 and ×, $X_{Te} = 0.7$at. frac.; for 4 and ◇, $X_{Te} = 0.8$at. frac.; for 5 and □, $X_{Te} = 0.9$at. frac.; Experimental data from [5] is shown

In fact, in the process of enrichment by zinc of solid phase during growth of layer, its concentration in the initial liquid phase should also increase. However, the substitution of cadmium by zinc atoms should lead to a significant increase of the melting temperature of the system. A further increase in the concentration of zinc in the solid solution should lead to an increase in the concentration of cadmium in the melt and to a leveling-off of its influence.

An increase in the range of melting temperature related to the substitution of the two metals and the ensuing extreme dependence of the solubility of the nonmetallic components have been observed before, for example in Ga-In-P, Ga-In-P-As and Al-Ga-P-As [6].

In the equilibrium diagram, in the range where the substitution of the main component of the melt (the solvent) takes place, the shape of the liquidus line depends strongly on different model parameters applied to describe the liquid phase. Thus, it might be rather difficult to achieve high accuracy in this part of the diagram [6]. To a degree, these theoretical assumptions can be applied to explain a decrease in the accuracy of the description of the phase equilibrium in the specific temperature-concentration areas of the system.

Figure 4 presents the temperature dependence of the general vapor pressure along the three-phase equilibrium line, on the composition of the solid solution of $Zn_XCd_{1-X}Te$. Taking into account the significant discrepancy in the experimental

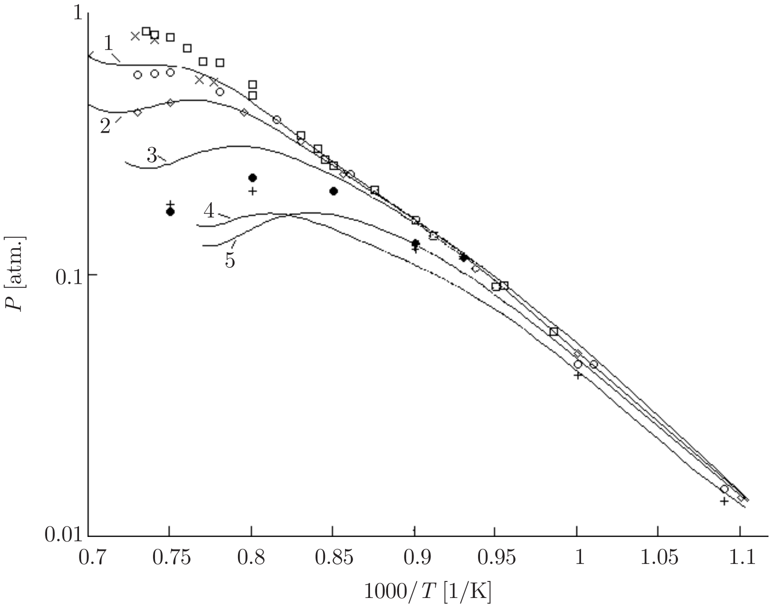

Figure 4. General pressure of the components in the system along the line of the three-phase equilibrium for various compositions of the $\mathrm{Zn}_X\mathrm{Cd}_{1-X}\mathrm{Te}$ solid solution. The melt was enriched by tellurium. 1 and × correspond to the data [10, 11] for $X^S_{\mathrm{ZnTe}} = 1.0$mol frac.; 2 and ○ to $X^S_{\mathrm{ZnTe}} = 0.9$mol frac.; 3 and ◇ to $X^S_{\mathrm{ZnTe}} = 0.7$mol frac.; 4 and ● to $X^S_{\mathrm{ZnTe}} = 0.25$mol frac.; 5 and + to $X^S_{\mathrm{ZnTe}} = 0.1$mol frac.; ○, ◇, ● and + are the experimental data taken from the figures in [12]

data [5, 10, 11] and their poor reliability at high temperatures, the correlation between the calculations and experimental results can be deemed satisfactory.

4. Conclusions

The obtained results allowed us to conclude that the polyassociative solutions model with the given parameters satisfactorily describes the p-T-x equilibrium in the Zn-Cd-Te system. The data obtained by means of this model can be used as the first approximation for selecting the initial conditions of crystallization for the solid solution of $\mathrm{Zn}_X\mathrm{Cd}_{1-X}\mathrm{Te}$ with the composition fixed in advance.

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