Polyassociative thermodynamic model of A²B⁶ semiconductor melt and phase equilibria in Cd-Hg-Te system.
4. $p-T-x$ diagram of Cd-Hg-Te system

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Abstract. $p-T-x$ diagram of Cd-Hg-Te system is analyzed in the framework of the polyassociative solution model. The temperature dependence of the dissociation constant for ternary complexes, which describes the mixing effects, was determined using the low temperature data on phase equilibrium in the system. A satisfactory agreement between calculated and experimental data of various works about phase equilibrium was attained.

It was shown in our previous works [1-3] that the polyassociative model of the liquid phase can be successfully applied to the description of phase equilibrium both in binary systems Cd-Te, Hg-Te and in the range of the quasibinary CdTe-HgTe phase diagram. In the work [3], when processing the data on phase equilibrium along the quasibinary CdTe-HgTe diagram, it was shown that mixing effects in a multicomponent melt are well explained by presence of associates CdHgTe and CdHgTe$_3$ in it. For quasibinary diagram temperatures, the values of dissociation constants of mentioned complexes have been found. It has allowed describing the phase equilibria at high temperatures with a high accuracy. In this work, temperature dependences of dissociation constants for complexes CdHgTe and CdHgTe$_3$ were obtained, and using them analyzed were phase equilibria in the system for the whole range of compositions and for a wide temperature range.

Temperature dependences of the dissociation constants K_{CdHgTe}, K_{CdHgTe_3} and solid phase interacttion parameter $\alpha^S(T)$ were carried out by processing the experimental data on phase equilibria for low temperatures both for the part of the diagram enriched with metals, and in its tellurium corner.

Precomputations have shown that equilibrium curves of the phase diagram are displaced in the same way while changing the concentrations of each of associates, responsible for effects of mixing in this ternary system. It means that increase of the concentration in the melt of complexes CdHgTe or CdHgTe$_3$ each, due to the reduction of dissociation constants, results in decrease of the liquidus temperature

at the same total concentrations of a component in a liquid phase. This result is represented to be natural and corresponding to data of the theoretical analysis of behavior of the liquidus binary system depending on the degree of liquid phase dissociation, which has been performed in the generalizing work [4]. The increase in the concentration of complexes in the liquid phase displaces a liquidus line to the place of more concentrated melts, reducing the distance between it and a solidus line. For the present calculations, such information is useful, since it allows separating the composition melt where the influence of each associate on liquidus position is determinative. Proceeding from the stated reasons, the following approach of obtaining the dissociation parameters at low temperatures was formulated. In fact, the complex with the large concentration of tellurium CdHgTe$_3$ should be contained in the greater concentration in the melt enriched with a metalloid component. That's why, its formation parameters should be obtained, basing on experimental data of phase equilibrium in tellurium enriched corner of the diagram. At the same time, an influence of a complex CdHgTe should affect more essentially the equilibrium lines in the part of the diagram enriched with metals, where its formation conditions are more preferable. These conclusions have allowed getting, finally, temperature dependences of dissociation constants without using long mathematical procedures. The temperature dependences of the required parameters found by the mentioned way, as well as other thermodynamic data on the initial binary systems, found by us in [1, 2] and necessary for calculations of p–T–x equilibria in such a binary system, are shown in Table.

Table. Thermodynamic parameters of polyassociative model for Cd–Hg–Te system.

System	T^F, К	ΔS^F, e. u.	ΔC_p^{l-S}, $\frac{cal}{mole\cdot К}$	Dissociation parameters of complexes			
				ATe	ATe$_2$	A$_2$Te	A$_2$Te$_3$
Cd – Te	1365.1	8.8	1.88	$e^{78.245+\frac{1.5541\cdot10^8}{T^2}-2,289\cdot\frac{10^5}{T}}$	$e^{5.56+7.314\frac{10^6}{T^2}-1.828\cdot\frac{10^4}{T}}$	0.02	$e^{120.511+1.817\cdot\frac{10^8}{T^2}-3.12\cdot\frac{10^5}{T}}$
Hg – Te	943.1	9.25	0.98	$e^{-7.372+\frac{5591}{T}}$	$e^{53.987+2.809\cdot\frac{10^7}{T^2}-8.004\cdot\frac{10^4}{T}}$	0.6	$e^{76.249+5.641\cdot\frac{10^7}{T^2}-1.359\cdot\frac{10^5}{T}}$
Cd – Hg – Te	$K_{CdHgTe}=4\cdot10^{-3}\cdot e^{\frac{5000}{T}}$			$K_{CdHgTe_3}=8.9\cdot10^{-4}\cdot e^{\frac{-2653}{T}}$		$\alpha^S_{CdTe\cdot HgTe}=(2320-3.18T)\,\frac{cal}{mole}$	

The found thermodynamic parameters (Table) have allowed making calculations of liquidus and solidus lines in the system Cd-Hg-Te for all compositions of the diagram in a wide temperature range. The basic results of calculations are submitted in Figs 1-6. In Figs 1-2, together with the experimental data [5, 9, 13], the calculated system Cd-Hg-Te liquidus curves are given for various sections of the state diagram and at different temperatures in the part enriched with tellurium. If to take into account an essential differences between experimental results of various authors, which is especially distinctly observed in Fig. 2, for example, for liquidus at 500 and 550 ºC, then it is possible to consider conformity of calculations to the experiment as quite satisfactory.

In Fig. 3, the dependences of the concentration of the most numerous complexes in melts on total tellurium concentration along the section of the diagram with $Z = 0.2$ are submitted. So for chosen Z, at the tellurium concentrations in the range $X_{Te} \approx$ 0.5 at. frac., the complex HgTe as well as free atoms Hg and Te dominate as melt components whereas the concentration of other associates in the liquid phase, as a whole, does not exceed 7 %. These small concentrations of melt components insignificantly affect the position of calculated liquidus, but essentially influences on partial pressures of components. The interaction of complexes is essentially changed at enrichment of solution by tellurium, while the equilibrium temperature is decreased. So at $X_{Te} \geq$ 0.75 at. frac. multiatomic complexes HgTe$_2$, Hg$_2$Te$_3$, and CdHgTe$_3$ begin to play a dominating role in the melt, and the concentration of the two-atomic complex HgTe sharply decreases. Such a situation in a multicomponent liquid phase corresponds to the general fact that, while the temperature decreases, the concentration of multinuclear complexes should increase, whereas the content of simple associates sharply decreases. Such a change of the complexes in the melt versus temperature is responsible for the unusual shape of liquidus, and as it was discussed by us in [1], during a substantiation of enthalpy signs of free energies of associate formation and changing the associate composition of the melt versus temperature.

More difficult situation is observed when comparing the calculations to experimental data for the dependence of the grown layers composition on the initial liquid phase composition (Fig. 4). The experimental data, as a rule, are obtained in the course of crystallization of a solid solution by liquid phase epitaxy (LPE). From Fig. 4, it follows that these experimental data are grouped, basically, near respective calculated solidus lines though accuracy in the description of system behaviour for this parameter nevertheless is not so high, even considering essential difference between experimental data of various authors. Mentioned above concerns, first of all, to the practical coincidence of results obtained by various authors under rather different temperature conditions. As an example, we can compare the data [9] to the results [11] when practically from same melt a solid solution of the same composition is crystallized at the temperatures distinguished almost by
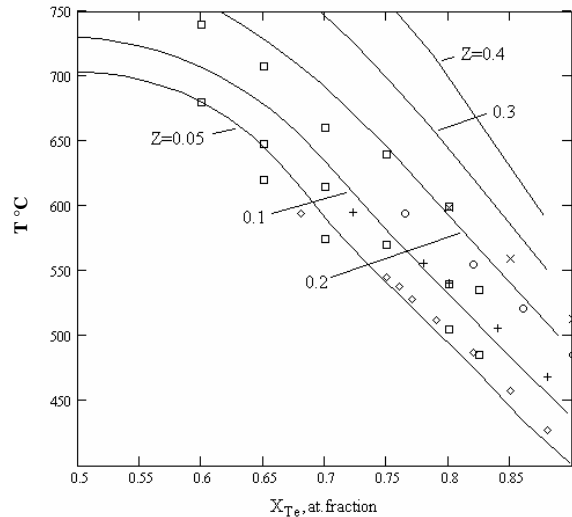

Fig. 1. Liquidus temperature of the Cd-Hg-Te system *vs* the concentration of tellurium in the melt for different values of the parameter $Z = \dfrac{X_{Cd}}{X_{Cd} + X_{Hg}}$ at Z = 0.05, 0.1, 0.2, 0.3, 0.4.

□ – the experimental data [13] which have been taken from the figure of the work [5]; ◊, +, ∘, × – the data [9] for Z = 0.05, 0.1, 0.2, 0.3, respectively.

30-50 K. Such a situation doesn't allow hastening with critical conclusions about applicability of the polyassociative solution model to the description of a solidus line in the system, and demands more thorough examination of a question about applicability of the equilibrium analysis for the description of the experimental data obtained by LPE methods. Really, when the calculations are compared with experimental data for the state diagram in multicomponent systems, it's necessary to be attentive. The numerous factors that influence on growing system in a real crystallization process can be the reason of a discrepancy of phase equilibrium model to experimental data [8].

When carrying out the LPE process, one of the main reasons responsible for mentioned distinctions is the absence of thermodynamic equilibrium between a binary compound substrate and a liquid three-component phase. Really, the absence of thermodynamic equilibrium in the growing system provides the realization of the crystallization process. At the same time, various initial supercoolings of an initial solution determine different growth rates which reflects on the composition of layers during crystallization. Many authors observed such influence of growing rates on layer parameters for LPE manufacturing the multicomponent solid solutions [8]. The absence of the direct control of a liquid phase liquidus temperature, from which the crystallization begins, is responsible for different growth rates of layers in each specific technological process. It quite naturally provides the various composition of grown layers. A confirmation of the fact that such kinetic effects can be essential lies in rather large values of equilibrium distribution coefficients of a solid solution main component, which were obtained in our calculations. So, for the equilibrium partial distribution coefficient, for example, cadmium, which is $K^0_{Cd} = X^{SO}_{CdTe} / 2 X^{LO}_{Cd}$, where X^{SO}_{CdTe}, X^{LO}_{Cd} are the equilibrium concentrations of cadmium in a solid and liquid phases (the factor 2 appears when

recalculating the mol. fractions into the atomic ones), it is possible to obtain the value of K^0_{Cd} in the range of 30 to 80. For such a large distribution coefficient, the diffusion rate limits of a substance supplied to the growth front can essentially reduce it. The effect of equilibrium distribution coefficient transformation into the effective one according to the model of diffusion-limited crystallization is analyzed in [12] with reference to the system Ga-In-P-As. The calculations from [12] have shown that slowness of a mass transfer to the front of growth can reduce the value of the distribution coefficient by several times. If to take into account rather high tellurium melt viscosity, the mentioned effect can be essential, and its account can provide conformity of growing phase composition calculations to experimental data. Naturally, theoretical consideration of such phenomena is beyond notions about equilibrium crystallization when compositions of contacting phases submit only to the state diagram of the system.

Mechanical strains in a film, which are caused by lattice mismatch between a layer and a massive substrate, can render an essential influence on the composition of grown layers. This effect is known in the literature as a composition-pulling effect [8]. It can influence both on a composition of growing solid solution and on the phase equilibrium temperature because of the occurrence of contact supercooling in the system. Generally, this effect is described by the coherent state diagram, which takes into account the
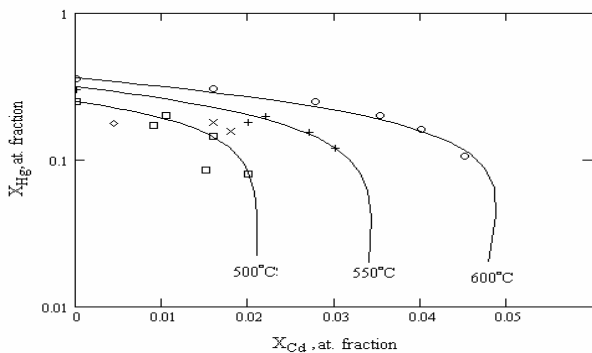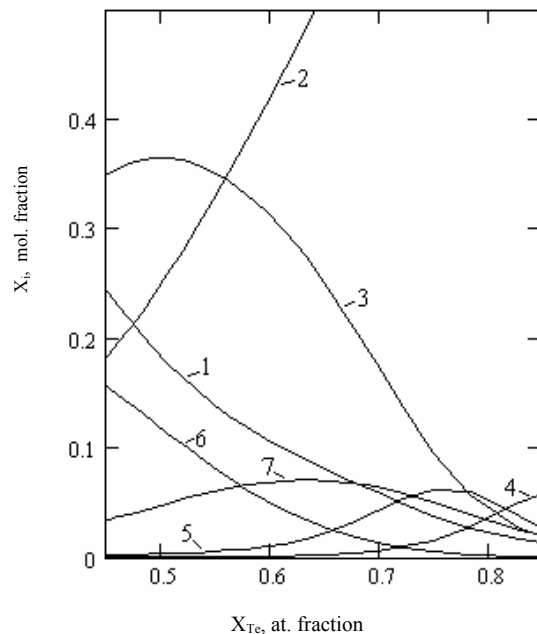

Fig. 2. Low-temperature liquidus of the Cd-Hg-Te system for enriched with tellurium part of the diagram. , +, ○ – experimental data [8] for temperatures 500, 550, 600 ºC, respectively; ×, ◊ – the data [10, 15] for *T* = 500 ºC.

Fig. 3. Associate concentration *vs* the total tellurium content in Cd-Hg-Te melt at Z = 0.2. 1 – Hg, 2 – Te, 3 – HgTe, 4 – $HgTe_2$, 5 – Hg_2Te_3, 6 – CdHgTe, 7 – $CdHgTe_3$.

contribution of the mechanical strains in a layer under the general condition of heterophase equilibrium [8]. In other words, the mentioned phenomenon is possible to be estimated only by comparing the calculation data obtained from the equations of the traditional state diagram and coherent one [8]. At this analysis of LPE processes in the system, it is difficult to estimate accurately the contribution of this factor into the composition change of the elastically strained layer. At the same time, a small distinction of lattice parameters of solid solution mixed components, which does not exceed 0.32 %, testifies that this contribution can be insignificant. This assumption was established by the fact that according to our data (Table) and the data [6, 7] on α^S, this parameter is in the interval of values from -1500 up to 2000 cal/mol. Such a value of the reduced excess energy of mixture α^S does not provide affinity of a condition of a solid phase to the limit of spinodal disintegration. It is known that the composition-pulling effect is the most significant, when the solid phase is thermodynamically unstable [12]. Proceeding from the mentioned facts at the following stage of calculations, it is possible to consider that the mentioned effect should not essentially displace the system from a condition of thermodynamic equilibrium. Taking into account a significant disorder of experimental data, the description of low temperature solidus in the part of the diagram enriched with tellurium can be considered as the satisfactory one.

In Fig. 5, the results of modeling of substrate CdTe dissolution in mercury at various temperatures are shown. These data are obtained at low temperatures and correspond to the part of the state diagram enriched with metals. Calculations have shown that it is possible to get satisfactory conformity of calculations to experiments in this part of the diagram at so low temperatures only by taking into consideration sharper temperature dependence of the solid phase interaction parameter. This functional dependence for the description of experimental data was as follows: $\alpha^S = (8.24 \cdot T - 19000)$ cal/mol.
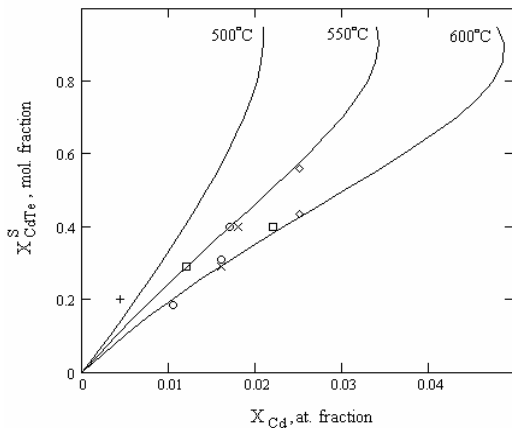
The analysis of the associate concentration in a liquid phase under conditions that are resulted in Fig. 5 has shown that the melt in practice consists completely of free atoms of mercury, tellurium and cadmium, and elementary associate HgTe and is the only liquid phase complex. Thus, its mol. fraction does not exceed 0.002 at temperatures near 500 °C, decreasing with its downturn. It means that the value of a dissociation constant of the complex in the melt under such circumstances weakly influences on the position of a calculated curve. Liquidus lines in this part of the diagram are determined by the content of free atoms of the main solution component. These values are connected, first of all, with fusion entropies of compounds and their possible temperature dependence in the temperature range from 200 to 1100 °C. In the calculations of the state diagrams in a wide temperature interval, this factor was discussed by us in [1] when analyzing the phase equilibrium in initial binary systems in a wide temperature range. Due to these amendments and use of obtained $\alpha^S(T)$, the conformity to the experiment in Fig. 5 was reached.

In Fig. 6, temperature dependences of partial pressure along lines of $p - T - x$ equilibrium versus composition of a solid solution $Cd_xHg_{1-x}Te$ are submitted. Considering the significant disorder of experimental data [7, 14] and not high reliability of their production at high temperatures, the conformity of calculations to experiment can be considered as satisfactory.

Successful application of the theory of the associated solutions with several complexes of different compositions to the description of phase equilibrium in a system allows making the following conclusion. Really, the polyassociative solution model is the attempt to expand the use of ideal solution laws to a set of multicomponent systems. Thus, it was considered that the deviation from Raoult's law and the deviation of liquidus lines from ideal solutions predicted by the model is caused only by incorrect calculation of number of particles
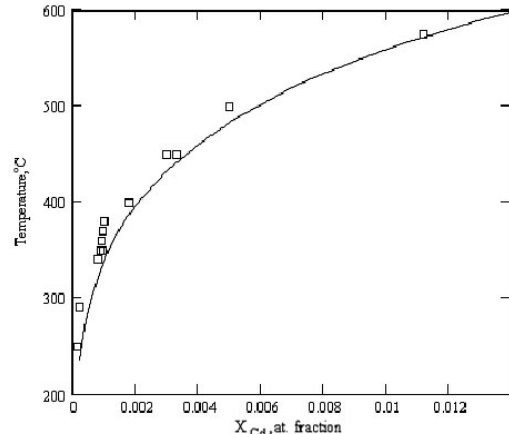

Fig. 4. Cadmium concentration in the solid solution versus that in the initial liquid phase. $+ - [15]$ for $T = 450$ °C; $\times$, $\circ$ $-$ [10, 11] for $T = 500$ °C; , $\diamond - [9]$ for $T = 550$ °C.

Fig. 5. CdTe substrate solubility in liquid mercury at various temperatures. Experimental data are taken from Fig. of [6].
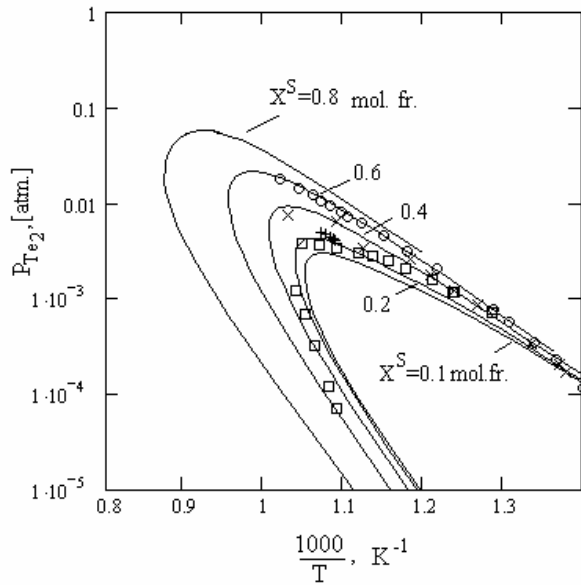
Fig. 6. Partial pressure of tellurium along a three-phase curves for various solid solutions $Cd_xHg_{1-x}Te$. X^S_{CdTe} = 0.1, 0.2, 0.4, 0.6, 0.8 mol. frac. , +, ×, ∘ – experimental data [7, 14] for X^S_{CdTe} = 0.1, 0.2, 0.4, 0.6 mol. frac.

existing in melt, whereas the approximation of ideal liquid phase remains acceptable. The reality of such an approach to the description of multicomponent systems has been stated in [16] when modeling the thermodynamic functions of organic materials. It is possible to assume that the approach with use of several associates in the melt can replace Lewis' standard method based on the application of activity coefficients when modeling the complex systems with strong interaction.

In conclusion, it is necessary to note that the dissociation parameters of Cd-Hg-Te melt complexes are self-connected. In practice, it means that it is impossible to take any of dissociation parameters from the data in Table and estimate by using it the concentration of one specific complex, ignoring thus the presence of other associates in the melt. Really, the concentrations of complexes are interconnected through the equations of quasi-chemical reactions, and the condition of the balance of substance and change in the concentration of one of the complexes inevitably causes the variation of the others. Such a situation is not new and is typical for thermodynamic calculations on phase equilibrium for other multicomponent systems, even when they are carried out with use of other models of solutions [8]. Nevertheless, ignoring this circumstance, especially when applying the polyassociative solution model with a set of complexes in the melt, will inevitably yield an incorrectness in use of the model and lead to essential mistakes in calculation results. Thus, it can be asserted that the model of polyassociative solutions with the dissociation parameters found in the work is capable to

describe successfully $p – T – x$ equilibrium in system Cd-Hg-Te. Attempts to achieve higher accuracy in the description of technological processes for preparing materials according to equilibrium thermodynamics due to a variation of dissociation parameters were inefficient. Obviously, it is possible to assert that the accuracy of calculations based on representations about the equilibrium phase diagram is achieved. It seems, a perspective way to increase the reliability of calculations is connected with the transition to kinetic non-equilibrium models considering process of crystallization, proceeding in time and when occurring the external factors. The developed thermodynamic model of phase equilibrium can be successfully applied as the first approximation for the choice of growth conditions of a solid solution $Cd_xHg_{1-x}Te$ with a necessary composition.

References

1. P.P. Moskvin, L.V. Rashkovets'kyi, S.V. Kavertsev // *Semiconductor Physics, Quantum Electronics & Optoelectronics* 5, p. 378-384 (2002).
2. P.P. Moskvin, L.V. Rashkovets'kyi, S.V. Kavertsev // *Ibid.* 6(1), p. 23-27 (2003).
3. P.P. Moskvin, L.V. Rashkovets'kyi, O.V. Stronski //*Ibid.* 8(2), p. 81-85 (2005).
4. V.M. Glazov, L.M. Pavlova, *Chemical thermodynamics and phase equilibria.* Metallurgiya, Moscow, 1988 (in Russian).
5. T. Tung, C.-H. Su, P.-K. Liao, R.F. Brebrick // *Vac. Sci. Technol.* 21, p. 117-124 (1982).
6. R.F. Brebrick // *J. Crystal Growth*, 86, p. 39-48 (1988).
7. T. Tung, L. Golonka, R.F. Brebrick // *Electrochem. Soc.* 128, p. 451-456 (1981).
8. V.V. Kuznetsov, P.P. Moskvin, V.S. Sorokin, *Nonequilibrium phenomenon at liquid heteroepitaxy of semiconductor solid solutions.* Metallurgiya, Moscow, 1991 (in Russian).
9. T.C. Harman // *Electron. Mater* 9, p. 945-961 (1980).
10. J.E. Bowers, J.L. Schmit, C.J. Speerschneider, R.B. Maciolek // *IEEE Trans. Electron. Devices* ED27, p. 25 (1980).
11. R. Kikuchi //*Vac. Sci. Technol.* 21, p. 129-132 (1982).
12. V.V. Kuznetsov, P.P. Moskvin, V.S. Sorokin // *J. Cryst. Growth* 66, p. 562-574 (1984).
13. K.L. Lawly, *Texas Instruments Technical Report*, Contract N 79-C-1099 (10 February, 1980).
14. J.P. Schwartz, T. Tung, R.F. Brebrick // *Electrochem. Soc.* 128, p. 438-451 (1981).
15. C.C. Wang, S.H. Shin, M. Chu, M. Lanir, A.H.B. Vanderwyck // *Electrochem. Soc.* 127, p. 175-179 (1980).
16. A.L. Vasnetsova, G.P. Gladyshev, *Ecological biophysical chemistry.* Nauka, Moscow, 1989 (in Russian).