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Polyassociative thermodynamical model of A²B⁶ semiconductor melt and phase equilibrium in Cd-Hg-Te system: 3. Optimization of the thermodynamical functions of the model and quasi-binary structural diagram of Cd-Hg-Te system

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Abstract. Within the frames of the model of the polyassociative solutions the comparative analysis was performed of the formation parameters of multi-atom complexes in CdTe and Hg-Te systems. It was shown, that thermodynamical properties of the studied systems can be described in the supposition of the presence in the liquid phase of the ATe, A_2Te_3 , ATe_2 , A_2Te (A = Cd, Hg) and free Te, Cd, Hg atoms. In accordance with the model of polyassociative solutions the data on p-T-x equilibrium in the region of quasi-binary cross-section of Cd-Hg-Te system structural diagram were obtained. It was shown, that the mixing effects in the three-component liquid phase are satisfactorily described by the formation of CdHgTe and CdHgTe₃ associates. The good correspondence of the calculations and experiment in the high temperature part of the Cd-Hg-Te system structural diagram was achieved.

Keywords: phase equilibrium, polyassociative model.

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In our previous works [1, 2] it was shown, that the polyassociative model of the melt can be successfully applied for the description of the phase equilibrium in binary A^2B^6 systems. In this work the obtained thermodynamical information on the thermodynamical properties of the initial binary components of $Cd_xHg_{1-x}Te$ solid solution will be disseminated on the analysis of the structural diagram of ternary Cd-Hg-Te system.

Before the analysis of the interphase interaction in ternary system it is necessary to make some generalizations on the thermodynamical behavior of Hg-Te and Cd-Te systems within the frame of the model of polyassociative solutions. Mentioned above at first place refers to the melts associative composition of this related systems. According to the calculations [1], Hg-Te melt energetic state can be modeled under its consideration as consisting from the next complexes: HgTe, HgTe₂, Te₂. At the same time Cd-Te liquid phase, which provide satisfactory description of the phase equilibrium in system must consist of the following associates: CdTe, Cd₂Te, Cd₂Te₃, CdTe₂, Te₂ and free Cd and Te atoms. The increase of the number of associates in liquid Cd-Te phase is connected with the necessity to describe the liquidus of a system, the form of which is more complex than in Hg-Te system. The use in the calculations more simple representations about associative structure if mercury containing melt system nevertheless founds its reflection in lesser accuracy in the description of the liquidus of system, especially at X_{Te} values in the interval of 0.5 to 0.6 atomic parts (Fig. 1 from [1]).

The calculations of phase diagram in Hg-Te system show that the accuracy increase in the liquidus description is possible by introduction into consideration of the complex with Hg₂Te₃ composition. This associate in the highest concentration must be present in the melt with composition, which correspond to the most favorable conditions of its creation, that is at $X_{Te} = 3/5$ atomic parts. As was already mentioned, exactly in this interval the biggest differences in calculated and experimental data on the liquidus of the system are observed. Taking into account the mentioned facts, as well as considerations of the generality of the state description of A^2B^6 liquid phase system, it is necessary to correct thermodynamical model of Hg-Te melt and to



Fig. 1. Quasi-binary cross-section of the structural diagram of Cd-Hg-Te system. $+, \times, o, \Box$ – experimental data [8, 9, 10, 11].

introduce onto it the associate of Hg_2Te_3 type. Naturally this will require the reevaluation of the functional dependencies of dissociation constants on the temperature for all complexes which are present in liquid phase. Let us note that Hg_2Te_3 associate was initially was introduced in [3] during description of the mentioned above system dependence of the melt mole volume on its composition. Thus the such type correction of model considerations of Hg-Te melt associative structure can be considered as consistent and non-contradictive.

One of the perspectives of polyassociative solutions application to the description of phase model equilibrium was connected with the decrease of the thermodynamical parameters number, the experimental evaluation of which is difficult or simply impossible [1]. In this respect it seems reasonable to evaluate the possibility of minimization of model parameters number at the cost of the lowering of the number of considered associates in liquid phase. In present work such attempt was performed in relation to the Te2 associate. This possibility appears if temperature dependence of the dissociation complex for complexes of A2Te3 type is considered in more complex form. Such approach enabled to exclude the two-atomic complex of tellurium from the model. For the compensation of its influence on the liquidus behavior the temperature dependencies of type $K_{mn} = \exp(A + \frac{B}{T} + \frac{C}{T^2})$ were used for dissociation parameters of A_2Te_3 , ATe_2 . The performed reevaluation of dissociation parameters, at first place

reevaluation of dissociation parameters, at first place refers to the description of the enriched by tellurium part of structural diagram of the system. At the same time for the generality of the thermodynamical analysis it considered necessary to perform additional analysis of the associative structure of liquid phase enriched by metallic components. Mentioned above refers to the presence of A2Te complex, which influence the shape of liquidus only in the enriched by metal part of the structural diagram. Indeed, it was necessary in the calculations of the liquidus of Cd-Te system in the neighborhood of the bend point of equilibrium line for the tellurium content in the melt about 0.3 atomic parts. Liquidus of Hg-Te system, in its part enriched by mercury, does not have such peculiarity, its shape is sufficiently traditional (degenerate in comparison to the structural diagram of Cd-Te system), does not have bend points, and is satisfactory described with taking into account only HgTe associate. It seems, that there is no reasons for introduction into analysis of more complex enriched by metal Hg₂Te complex. But such complex is considered necessary for the precise description of liquidus at temperatures lower than 500 K, that is at temperatures typical for the carrying out of the epitaxial growth from the enriched by metals melt. Taking into account mentioned above considerations the decision was made to introduce to the equations of phase equilibrium the component which takes into account the creation of the Hg2Te associate. Quasi-chemical equation of its formation is analogous to the equation of Cd₂Te complex formation [2]. Concluding the discussion of the associative structure of Cd-Te and Hg-Te melts, it is seemed necessary to mention the following. Calculations show, that despite the insignificant content of associates of complex composition in liquid phase, their concentration influence concentration essentially partial of components. Thus, even if their influence on the shape of liquidus of the systems is small, disregarding their contribution to the value of equilibrium pressures leads to the substantial differences of theory and experiment. This is an important argument to take them into account during modeling of the thermodynamical state of the liquid phase.

The reliability of the theoretical analysis of the phase equilibrium in Cd-Hg-Te system is determined by the final choice of the entropy value of HgTe melting. Let us remind, that the increase of this parameter from 9.25 up 14 e.u. during description of the p-T-Xequilibrium in the mentioned system enabled to achieve good correspondence of the calculations to the experiment in [1]. The analysis of the phase equilibrium in the related Cd-Te system has shown, that variations of such type are not necessary for the description of the pressure of the metallic component in this system. Proceeding from the generality of the analysis of the structural diagram in the A^2B^6 , it was decided in the consequent calculations to leave the value $\Delta S_{\text{HgTe}}^{F} = 14.0$ e.u. unchanged and corresponding to the experimental data [4], despite the decrease of the

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accuracy in the description of mercury pressure in the system [1].

Such reevaluation of the temperature dependencies of dissociation constants in Hg-Te systems, when in the melt Hg₂Te₃, Hg₂Te complexes are present was performed in the present work. The method of the search of these functions is similar to the procedure described in [1]. The corrected values of the thermodynamical parameters of Hg-Te melt were the following: $K(\text{HgTe}) = \exp(76.249 + 5591/T);$

$$K(\text{Hg}_{2}\text{Te}_{3}) = \exp(76.249 + 5.641\frac{10^{7}}{T^{2}} - 1.359\frac{10^{5}}{T});$$

$$K(\text{HgTe}_{2}) = \exp(53.987 + 2.809\frac{10^{7}}{T^{2}} - 8.004\frac{10^{5}}{T});$$

$$K(\text{Hg}_{2}\text{Te}) = 0.6.$$

Similar correction of the thermodynamical functions of the complex dissociation was performed also for the description of the state of Cd-Te liquid phase. As previously, in order to decrease the number of thermodynamical parameters Te2 complex was excluded. With such correction temperature dependencies of the dissociation constants provide satisfactory description p-T-x equilibrium in Cd-Te system and are presented by:

$$K (CdTe) = \exp(78.245 + 1.554 \frac{10^8}{T^2} - 2.289 \frac{10^5}{T});$$

$$K (CdTe_2) = \exp(5.56 + 7.314 \frac{10^6}{T^2} - 1.828 \frac{10^4}{T});$$

$$K (Cd_2Te_3) = \exp(120.511 + 1.817 \frac{10^8}{T^2} - 3.12 \frac{10^5}{T});$$

$$K (Cd_2Te) = 0.02.$$

In the consequent calculations structural diagrams of the ternary Cd-Hg-Te system the latter from the found thermodynamical functions were applied during description of the phenomena of the corresponding complexes in the liquid phase.

The presence of the two metallic components of the melt in Cd-Hg-Te liquid phase supposes the appearance of the specific, characteristic for the ternary system types of the associates. Following tested on the binary systems associative composition of the melt, and in the approximation when in the melt only multicomponent complexes with two metal atoms of A_2B_3 and A_2B type exist, it is possible to suppose, that in the considered ternary component melt the CdHgTe₃ and CdHgTe associates must be present. Such complexes must be responsible for the description of the mixing phenomenon between metal components of the liquid phase. According to the method of quasi-chemical reactions it is possible to write:

$$K_{\rm CdHgTe_3}(T) = x_{\rm Cd} \cdot x_{\rm Hg} \cdot x_{\rm Te}^3 / x_{\rm CdHgTe_3}, \qquad (1)$$

 $K_{\text{CdHgTe}}(T) = x_{\text{Cd}} \cdot x_{\text{Hg}} \cdot x_{\text{Te}} / x_{\text{CdHgTe}},$

where x_{CdHgTe_2} and x_{CdHgTe} - concentrations of CdHgTe₃ and CdHgTe complexes in melt; $K_{\rm CdHgTe_3}(T)$ and $K_{\rm CdHgTe}(T)$ – dissociation constants of complexes. In the last expression, as earlier, during record of the reaction of the mentioned complex formation the preference was given to its creation from the free atoms.

During transfer to the description of the state of ternary liquid phase the equations of the balance of the matter in the melt under presence of all of the mentioned above complexes and with taking into account of the CdHgTe₃ and CdHgTe particles can be written as:

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$$X_{Cd}G - x_{CdTe} - x_{CdTe_2} - 2(x_{Cd_2Te_3} + x_{Cd_2Te}) - x_{CdHgTe} - x_{CdHgTe_3} - x_{Cd} = 0;$$

$$X_{Hg}G - x_{HgTe} - x_{HgTe_2} - 2(x_{Hg_2Te_3} + x_{Hg_2Te}) - x_{CdHgTe} - x_{CdHgTe_3} - x_{Hg} = 0;$$

$$X_{Te}G - x_{HgTe} - x_{CdTe} - x_{CdHgTe} - 2(x_{HgTe_2} + x_{CdTe_2}) - x_{Hg_2Te} - x_{Cd_2Te} - 3(x_{Hg_2Te_3} + x_{Cd_2Te_3} + x_{Cd_2Te_3} + x_{CdHgTe_3}) - x_{Te} = 0;$$

$$G = 1 + x_{CdTe} + x_{HgTe} + 2(x_{CdTe_2} + x_{HgTe_2} + x_{Cd_2Te_3} + x_{Hg_2Te_3} + x_{CdHgTe_3});$$

$$K_{Te} + X_{Hg} + X_{Cd} = 1; \sum_{i=1}^{13} x_i = 1, \quad (2)$$

where X_{Hg} , X_{Te} , X_{Cd} – atomic parts of mercury, tellurium, cadmium in melts, $x_{\text{Hg}_p\text{Te}_a}$, $x_{\text{Cd}_p\text{Te}_a}$ - mol. parts of complexes of Hg_pTe_q and Cd_pTe_q composition in liquid phase.

Presented formula are consequence of equations which describe interconnection of the mole number for each complex with the atomic and mole part of the components of the melt. Thus in corrected model the Cd-Hg-Te melts consists from following associates: HgTe, Hg₂Te, HgTe₂, Hg₂Te₃, CdTe, Cd₂Te, Cd₂Te₃, CdTe₂, CdHgTe₃, CdHgTe and free Cd, Hg, Te atoms. General number of the particles in the melt is 13.

Within the frames of the accepted model the pressure of the melt components is connected with the concentration of the non-associated cadmium, mercury and tellurium atoms and is calculated according to the Raoult-Henry law using following formula [1, 2]:

$$p_{\rm Cd} = p_{\rm Cd}^{\rm o} \cdot x_{\rm Cd}; \quad p_{\rm Hg} = p_{\rm Hg}^{\rm o} \cdot x_{\rm Hg}; \quad p_{\rm Te_2} = p_{\rm Te_2}^{\rm o} \cdot x_{\rm Te}^2;$$

where x_i , p_i^{o} - atomic parts of free cadmium, mercury and tellurium, and also partial pressures of the mentioned components over their melts. Partial pressures of all components over own melt which were

used in calculations are presented with the respective references in [1, 2].

The equations of the heterophase equilibrium between ternary liquid and solid phases according to the theory of regular solutions and approximation of polyassociative structure of the melt are given by [1, 2, 5]:

$$\Delta S_{CdTe}^{F} (T_{CdTe}^{F} - T) / RT + \ln(\frac{x_{Cd} \cdot x_{Te}}{x_{Cd}^{Sl} \cdot x_{Te}^{Sl}}) = \ln \gamma_{CdTe} x_{CdTe}^{S};$$

$$\Delta S_{HgTe}^{F} (T_{HgTe}^{F} - T) / RT + \ln(\frac{x_{Hg} \cdot x_{Te}}{x_{Hg}^{Sl} \cdot x_{Te}^{Sl}}) = \ln \gamma_{HgTe} x_{HgTe}^{S};$$

$$RT \cdot \ln \gamma_{j} = \alpha^{S} (1 - x_{j}^{S}); \quad j = CdTe, HgTe ;$$

$$x_{HgTe}^{S} + x_{CdTe}^{S} = 1,$$

$$k_{HgTe} + x_{HgTe}^{S} = 1,$$

$$k_{HgTe} + x$$

where ΔS_j^F , T_j^F – entropies and melting temperatures of the initial substances; γ_j – activity coefficient of the *j* component in solid phase; index SI refers to the liquid phase of stoichiometric composition. According to data from [1, 2]: $x_{Cd}^{SI} = 0.0435$ at.pt., $x_{Te}^{SI} = 0.0494$ at.pt. (for Cd-Te system); $x_{Hg}^{SI} = 0.2903$ at.pt.; $x_{Te}^{SI} = 0.252$ at.pt. (for Hg-Te system).

For modeling of the solid state phase and calculation of the phase diagram the quantitative information about parameter of the solid phase interaction α^{S} between cadmium and mercury in the metallic sublattice of solid solution. This parameter, as well as K_{CdHgTe_3} , K_{CdHgTe} parameters, is necessary to consider as matching, which are determined according to the best correspondence of the calculations on p-T-x equilibrium to the experiment in the ternary system.

The search of the unknown thermodynamical functions began with the treatment of the experimental data on phase equilibrium in the region of quasi-binary cross-section of structural diagram of the system. For this part of the diagram reliable and spacious data on the liquidus and solidus of the system are available [8-11] and several experimental results on the pressure of components vapor results over the melt [11]. At the first stage of the analysis it was supposed, that the phenomena of mixture between Cd and Hg it is possible to describe by the formation of the complex of CdHgTe₃ composition. As the base for such supposition served the fact, that exactly complexes of A2B3 type are most numerous together with AB, in the neighborhood of the melting temperature of the initial binary components of the system. But calculation have shown, that, even under the substantial variation of the value of the mentioned complex dissociation parameter, to describe the liquidus of the system, even nearing to the experimental data, is impossible. Such result means, that complex of CdHgTe₃ composition can not be the only one associate responsible for the effects of components mixing in the ternary melt.

Other situation was observed during consideration of CdHgTe complex. In this case the calculated curve of liquidus is the neighborhood of the experiments, when $K_{\rm CdHgTe} \approx 4 \cdot 10^{-4}$. Under that the maximal concentration of the mentioned complex was not bigger than 0.25 mol. pt. For the description of the behavior of the systems solidus, as the first approximation was chosen the ideal assumption for the description of the solid phase components of the melt, that is the values of the α^{S} parameter in Eq. (3) was varied in the neighborhood of zero. Such range of the searched parameter change does not contradict the data from the milestone works [6, 7] and is seen acceptable from the theoretical positions of the regular solutions model [12]. Indeed, insignificant difference in the periods of the crystalline lattice of initial mixing components (CdTe and HgTe) supposes small contribution of the elastic component of the mixing energy into total energy of solid state. It is known, that exactly this component gives main contribution to the excess energy of the components mixing in solid phase [12]. Preliminary calculations with the mentioned parameters has shown, that high temperature part of the diagram is quite adequately described by the regular approximation for the solid phase with α^{S} parameter insignificantly deviating from zero. At the same time the effects of the mixing of the melt metallic components must be described at first place, by associate of CdHgTe composition, also the use in the analysis of the CdHgTe₃ complex also enables to control the liquidus of the quasi-binary cross-section near HgTe.

The calculation results has shown, that satisfactory description of the equilibrium lines at temperatures of quasi-binary cross-section is achieved under the following values of the searched parameters: $\alpha^{s} \approx -1500 \text{ cal./mol.}$; $K_{\text{CdHgTe}} \approx 3 \cdot 10^{-4}$ and $K_{\text{CdHgTe}_{3}} \approx 5 \cdot 10^{-3}$.

In Fig. 1 the calculation results for the quasi-binary structural of the diagram Cd-Hg-Te system with the respective experimental data are presented [8-11]. The good correspondence of the calculations with the experimental results on the liquidus and solidus of the system are presented. In Fig. 2 jointly with the experiments from paper [9] the data on the components pressure over the melt along the quasi-binary cross section are presented. Taking into account the small accuracy of the correspondence of the calculations to the experiment also in this situation can be considered satisfactory.

In Fig. 3, the concentrations of the main associates in the melt along liquidus line along the considered crosssection are presented. It is seen from the figure, that the behavior of the equilibrium line mainly is determined by the HgTe, CdTe, Hg₂Te₃, Cd₂Te₃, CdHgTe, CdHgTe₃ complexes content in the melt. It is necessary to note,



Fig. 2. Pressure of components along quasi-binary crosssection of structural diagram of Cd-Hg-Te system. 1, 2, 3 – refers to the pressure of mercury, cadmium and tellurium. Experimental data [11].

that, content of the complexes which are responsible for the effects of metallic components mixing, is enough essential and commensurable with the associate concentration in the initial two-component phases. The last one can be interpreted as the confirmation of the substantial deviation of the mixed liquid components behavior from the predicted by the model of the ideal solutions, also the shape of the lines of the quasi-binary cross-section is traditional. The last fact sometimes is interpreted as testimony of the proximity of the systems



Fig. 3. Content of prevailing associates in the melt along quasibinary cross-section of the structural diagram of Cd-Hg-Te system. 1 - Hg; 2 - Te; 3 - CdTe; 4 - HgTe; $5 - \text{Cd}_2\text{Te}_3$; 6 - CdHgTe; $7 - \text{Hg}_2\text{Te}_3$; $8 - \text{CdHgTe}_3$; $9 - \text{Hg}_2\text{Te}$; $10 - \text{CdTe}_2$.

thermodynamical state to that one, described by the model of ideal solutions. Such statement does not find its justification by our analysis and calculations.

The final parameters search of the temperature dependencies of the ternary associates dissociation constants and value of the parameter of solid phase interacttion will be performed in the next part of the work. As a base for the consequent analysis will serve the data on the low temperature fragments of structural diagram (data on liquid phase epitaxy), as for the enriched by metal part of the diagram as well for its tellurium part.

Thus, the results obtained enable to state, that the model of the polyassociative solutions is capable to satisfactory description of the phase equilibrium in the region of the quasi-binary cross-section of the A^2B^6 ternary systems. Obtained in this work thermodynamical functions of the dissociation of a melt components are applicable for the description of the high-temperature phase equilibrium in Cd-Hg-Te system.

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