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Polyassociative thermodynamical model of A^2B^6 semiconductor melt and P - T - X equilibria in Cd-Hg-Te system:

2. Phase equilibria in initial two-component systems. Cd-Te system

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Abstract. Phase equilibria in Cd-Hg-Te system are analyzed in the framework of the polyassociative solution model. Checking the mentioned model applicability to description of phase equilibria and search of system thermodynamical functions were realized by sequential processing the data upon phase equilibria in initial binary system using computer software. After Hg-Te system, as the next material we chose Cd-Te system. It was shown that CdTe, Cd₂Te₃, CdTe₂ and Te₂ are predominant complexes of the liquid phase in the considered system. Determined are parameters of complex creation in a liquid phase. A satisfying accordance between estimation and experimental data on P - T - X equilibria in the initial binary system Cd-Te was attained using this approach.

Keywords: phase equilibrium, polyassociative model.

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In the previous part of our work [1], using the polyassociative solution model we performed the analysis of P - T - X equilibria in the mercury-tellurium system. Attained there satisfying accordance between calculation and experimental data confirmed applicability of theoretical conceptions upon polyassociative solutions when modeling energy states in Hg-Te liquid phase. Following the set here purpose to obtain data for theoretical derivation of a state diagram for Cd-Hg-Te ternary system, it is necessary to make a theoretical analysis of phase equilibria in Cd-Te system. This system, like Hg-Te one, creates initial mixing components when forming Cd_xHg_{1-x}Te solid solution – the most important material of modern infrared electronics.

The most reliable experimental data in accordance with Refs [3-5, 11-15] concerning the liquidus of cadmium-tellurium system and vapor pressures of material main components above their own melt are depicted in Figs 1–3. Represented fragments of curves describing equilibria “temperature-pressure” differs only a little in their shape from respective data for mercury telluride. At

the same time, liquidus lines of Cd-Te system are characterized by more complex shape as compared with the case considered in [2]. Indeed, in the liquidus of the analyzed system, one can observe the presence of a strongly pronounced singular peak at temperatures close to the temperature of material melting, there are specific regions where the liquidus line has inflection points relatively to the composition coordinate axis (it means temperature interval 1250...1300 K in the part of the diagram enriched with cadmium, and the range 1150...1200 K in that enriched with tellurium). Let us note that similar sections of the liquidus cannot be observed in Hg-Te system [2-5]. Mentioned features of the system liquidus appear to be considered as an evidence of more complex melt structure as compared to the case of Hg-Te system [2-4]. These feature should find its reflection, first of all, in a more complex associative composition of Cd-Te system melt in the framework of the polyassociative solution model and be used in calculations of positions for characteristic equilibrium lines. This statement follows from the above mentioned fact that the shape of a calculated

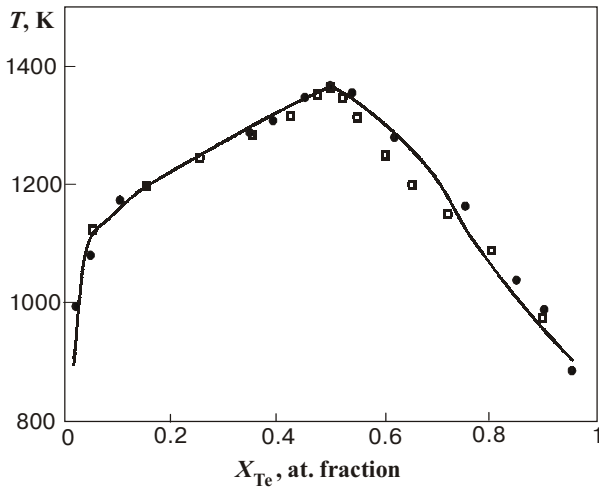


Fig. 1. Liquidus of Cd-Te system (solid line). Experimental data: □ - [10], ● - taken from [2].

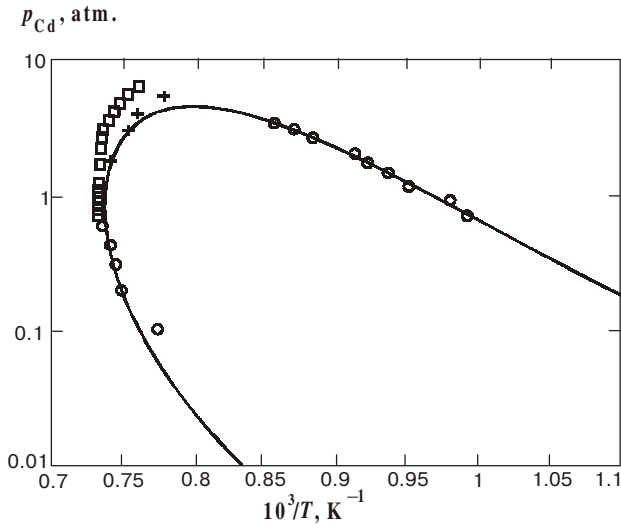


Fig. 2. Dependence of cadmium partial pressure on temperature along the three-phase equilibrium line in Cd-Te system (solid line). Experimental data: ● - [9], ○ - [2], + - [11], □ - [10].

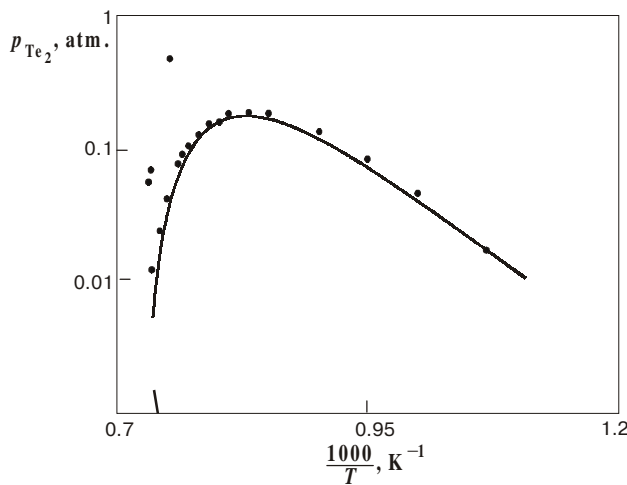


Fig. 3. Dependence of tellurium partial pressure on temperature along the three-phase equilibrium line in Cd-Te system (solid line). Experimental data: ● - [9].

liquidus for such system is mainly determined by an associate composition and to a lesser degree depends on dissociation constant values [2, 4].

In accordance with the theory of associated solutions with several complexes of various compositions in a liquid phase, interrelations between the total component content and those of creating it complexes of Cd_pTe_q composition in Cd-Te system have the following form [2]:

$$X_{Cd}G - \sum_{p=0} \sum_{q=0} p x_{Cd_pTe_q} = 0;$$

$$X_{Te}G - \sum_{p=0} \sum_{q=0} q x_{Cd_pTe_q} = 0;$$

$$G = 1 + \sum_{p=0} \sum_{q=0} (p + q - 1) x_{Cd_pTe_q}, \quad (1)$$

where X_{Cd} , X_{Te} – are atomic shares (fractions) of cadmium and tellurium in a melt, $x_{Cd_pTe_q}$ is a molar fraction of Cd_pTe_q complex in a liquid phase. Indexes p and q change from $p = 0, q = 1$ and $q = 0, p = 1$, which corresponds to free cadmium, tellurium and to the most simple complexes Te ($p = 0, q = 2$) and $CdTe$ ($p = 1, q = 1$), and then these follows along growing complexity of associate compositions.

Concentrations of associates are related to concentrations of creating them free elements due to equations of the acting mass law:

$$\frac{x_{Cd}^p x_{Te}^q}{x_{Cd_pTe_q}} = K_{pq}(T), \quad (2)$$

where K_{pq} is Cd_pTe_q complex dissociation constant.

Using approximation of an ideal associate solution, partial pressures of cadmium and tellurium over the melt can be calculated in accord with the Raoult-Henry law. This law described using concentrations of free mercury atoms, monoatomic and diatomic tellurium in a liquid phase has the following form:

$$p_{Cd} = x_{Cd} p_{Cd}^0(T);$$

$$p_{Te} = x_{Te}^2 p_{Te_2}^0(T), \quad (3)$$

where p_{Cd}^0 and $p_{Te_2}^0$ are saturation pressures of cadmium and diatomic tellurium at the given temperature. In the formulae above, as earlier [2], it is assumed that cadmium and tellurium atoms connected in liquid-phase associates do not influence on vapor pressure in the system. The latter formula takes into account the joint contribution of both atomic and diatomic forms into the total tellurium pressure in the melt.

Data upon cadmium and diatomic tellurium saturated vapor pressure at high temperatures were taken from [3]:

$$\lg p_{Cd}^0(\text{atm.}) = -\frac{5317}{T} + 5.119; T > 594K;$$

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

Expressions (2), and (3) are described using concentrations of respective melt components, that is reflected in them is the revealed earlier in [2,7,8] property that the associate melt in A^2B^6 system is ideal.

To have a complete description of P - T - X equilibrium in a two-component system, Exps (1) to (3) should be supplemented with an equation of crystal-melt equilibrium. According to [5,6,9] this expression takes the following form:

$$\Delta S^F (T^F - T) + RT \ln \frac{x_{Cd}^{St} x_{Te}^{St}}{x_{Cd}^{St} x_{Te}^{St}} = 0. \quad (4)$$

where T^F and ΔS^F are temperature and entropy of melting CdTe. The index St related to the liquid phase of a stoichiometric composition.

In the represented expression, when describing the crystal-melt equilibrium, preference was given to the simplest quasi-chemical crystallization reaction of the type $(Cd)_L + (Te)_L = (CdTe)_S$ as it was made in the first chapter.

Following the estimations made by us in [2], difference in specific heats between solid and liquid phases at high temperatures in A^2B^6 systems influences very weakly on a calculated position of heterophase equilibrium lines. In accord with our estimations made when analyzing Hg-Te system, neglect of the difference between specific heats of contacting phase introduces the error less than 3 K into the liquidus position. Therefore, at the currently calculation stage, as in the case of Hg-Te system, we neglected this difference in specific heats in our analysis. As a consequence, this term is absent in the formulae (4).

When calculating three-phase equilibrium lines, as initial parameters we took the following values of temperature and entropy: $T^F = 1365$ K, $\Delta S^F = 8.8$ e.u. [3,4].

Our theoretical study of dominating associate compositions present in liquid phase was realized using mentioned main regularities in behavior of heterophase equilibrium equation solutions corresponding to the model of polyassociative solutions applying the method described earlier in the first part. This procedure was begun from processing the data upon phase equilibria in the diagram state part enriched with metal. The complex form of the system liquidus having an inflexion point in that diagram range cannot be described by a monotonically increasing dependence for the dissociation constant of the simplest CdTe complex on temperature. To attain a satisfactory description of the liquidus line in this region, it is necessary to consider a presence of a complex with more complicated composition. Cd_2Te is the most probable candidate for that. In reality, the only associate with a high atomic content of the solvent can be present in the melt in large amounts and, as a consequence, affect essentially the position of equilibrium calculated lines. Following the mentioned earlier principle of increasing

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concentrations for complexes with complicated compositions with decreasing temperature in the system, the appearance of a multi-atomic complex with a considerable concentration was found by us at low temperatures. Accordingly to data obtained, to satisfactorily describe the system liquidus, it was quite sufficient to take the following dependence of the dissociation constant on temperature of CdTe complex creation

$$K(CdTe) = \exp(64.53 - 1.946 \cdot 10^5 / T + 1.34 \cdot 10^7 / T^2).$$

At the same time, the dissociation constant of Cd_2Te complex was independent from temperature, and its value was $K(Cd_2Te) = 0.015$. This complex with complicated composition influenced the equilibrium line behavior at temperatures lower than 1100 K, and its concentration became practically negligible with the following temperature increase.

It is necessary to note that in the search of dissociation constant functional dependences on temperature, we performed also the respective correction of complex content in the liquid phase of the stoichiometric composition, that is of x^{St} parameters in Eq. (4). The latter values should provide not only the required system liquidus line behavior, but describe the gas phase component pressures at the material melt temperature, too. x_i^{St} values satisfying these requirements had the following magnitudes: $x_{Cd} = 0.0463$ mol. fraction and $x_{Te} = 0.04351$ mol. fraction. These data were obtained using joint solving the equations of gas-melt equilibrium (3) and conditions of melt component balance, when the liquid phase composition in Eqs (1) corresponds to the stoichiometric one ($X_{Cd}^{St} = X_{Te}^{St} = 0.5$ at. fraction).

Principle difficulties in calculations become to arise in attempts to describe P - T - X equilibria in the diagram state part enriched with tellurium. It is necessary to note here that we have already observed the similar situation when describing phase equilibria in Hg-Te system at temperatures close to the compound melt temperature, that is at tellurium concentration in the melt, X_{Te} , at the level of 0.5-0.65 at. fraction. It was in this temperature-concentration diagram region that one could observe the worst correspondence between the theoretical and experimental data. In this case restrictions of the theoretical model were related to the necessity of providing a high tellurium pressure above the melt that is reached due to a high dissociation degree of the liquid phase. Simultaneously, one should require sufficiently sharp liquidus behavior under these conditions. On the contrary, the latter implied some increase of the melt dissociation degree. In [2] this contradiction was solved by applying $HgTe_2$ complex dissociation constant rather sharply increasing with temperature.

Our attempt to describe the liquidus line in this temperature range for Cd-Te system by using the same approach as well as Te_2 , CdTe and $CdTe_2$ set of associates did not result in desired outcomes. On the liquidus curve, we observed the clearly pronounced peak at satisfactory description of P - T equilibria in the most critical temperature range. An attempt to correct dissociation constants

in the model of polyassociative solutions did not result in essential improvement of correspondence between calculations and experiment. The only way out from this situation, which would not contradict to the physical basis of the model of the associated liquid phase, we saw in introduction into consideration one liquid-phase complex more. This associate should provide sharpness of the liquidus line drop, when the melt compositions are close to the equiatomic one, if we keep, at the same time, the necessary component pressure in the system. Let us note that it is higher association degree of the liquid phase, which is an attribute of arising the sharp peak in the system liquidus line [6].

Cd_2Te_3 complex is the most suitable in this situation. This associate has the form $CdTe_{1.5}$ that calculated using the atomic ratio per one cadmium atom in the liquid-phase complex. Therefore, its appearance with the maximum concentration in the melt should be expected just in the vicinity of the equiatomic composition of this liquid phase, that is in the actual diagram state concentration range. Mentioned considerations found its corroboration in calculations made, when the liquidus lines and vapor pressure were estimated taking into account the presence of associates Te_2 , $CdTe$, Cd_2Te , Cd_2Te_3 and $CdTe_2$ in the melt. For instance, depicted in Figs 1–3 are the results of the liquidus calculation and partial pressures of tellurium and cadmium along the line of three-phase equilibrium in the system. The best correspondence between calculated and experimental data was observed when using the following melt association thermodynamical functions of temperature:

$$K(Cd_2Te) = \exp(7.659 - 4.319 \cdot 10^4 / T + 2.194 \cdot 10^7 / T^2);$$

$$K(CdTe) = 3.7 \exp(-5419 / T); K(Te_2) = 5$$

According to data of these figures, we can state that the obtained set of thermodynamical functions and the model of polyassociative solutions itself, in the whole, provides good correspondence between calculated and experimental data. In this case, the observed discrepancy in estimations does not exceed 10...15 K, which is fully acceptable for the thermodynamical analysis.

It is necessary to note especially that the found temperature dependence of $K(Cd_2Te_3)$ parameter has a tendency to reduce with decreasing temperature from the melting point of the compound. This result corresponds to physical principles of the model and is related to increasing probability for melt components to create complexes with decreasing temperature. At the same time, at temperatures below 1000 K, this functional dependence begin to grow a little. However, this temperature behavior of the function considered does not contradict to general regularities of complex creation in the liquid phase, which was discussed in the first part in more details. Indeed, starting from 1000 K with decreasing temperature, the liquidus shape is essentially influenced by $CdTe_2$ associate, the concentration of which considerably grows with approaching to the tellurium corner of the state diagram. Such competitive interaction between associates with

decreasing temperature was also observed in Hg-Te system, when describing liquidus in the metal-enriched part of the state diagram. A satisfactory correspondence between experiment and estimations for this material was observed when the dissociation constant of HgTe diatomic complex grew with decreasing temperature, while $K(HgTe_2)$ constant was decreased. This appearance of temperature dependences for complex dissociation constants provided a total growth of multiatomic $HgTe_2$ associates with decreasing temperature and simultaneous reduction of the simple associate HgTe content.

Solving the task of reaching a satisfactory correspondence between the theory and experiment is also possible by using more sophisticated approximating functions for the temperature dependence of $CdTe_2$ complex dissociation constant. Such an attempt was undertaken in this work. However, the obtained dependence was not monotonic and had the clear peak in its temperature curve. But taking into account that the most widely used in practice are functional dependences of the form used in this work and keeping in the mind just the model of polyassociative solutions, we decided to introduce into consideration one complex more, namely Cd_2Te_3 .

Depicted in Fig. 4 are calculated dependences of complex concentrations in the melt along the liquidus line of Cd-Te system. In the framework of chosen approximation applied to considered here liquid-phase complexes, principal tendencies of changing their concentrations seem to be quite natural. As it was expected, the most intricate picture of associate interaction is observed in Te-enriched part of the state diagram. It is the place where Te_2 , Cd_2Te_3 and $CdTe_2$ complexes arise in considerable concentrations. In this case, while the fraction of the diatomic tellurium complex begins to influence the liquidus

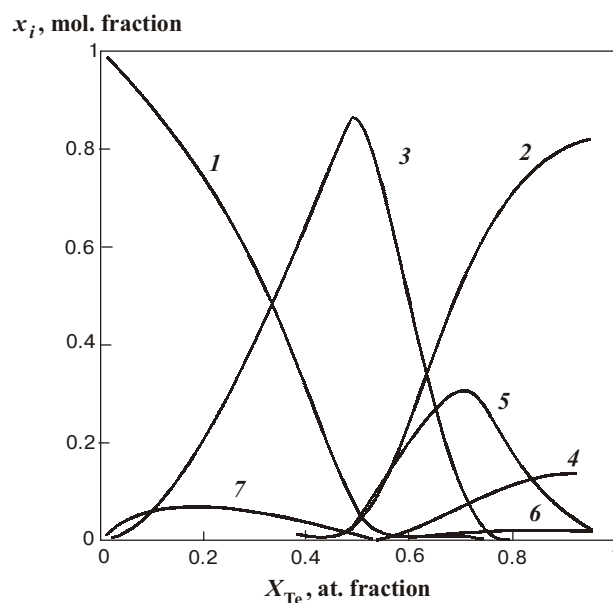


Fig. 4. Dependence of a concentration inherent to complexes in the melt on the total Te content in the liquid phase along the liquidus line for Cd-Te system: 1 – Cd; 2 – Te; 3 – CdTe; 4 – Te_2 ; 5 – Cd_2Te_3 ; 6 – $CdTe_2$; 7 – Cd_2Te .

line shape at $X_{Te} > 0.5$ and monotonically grows in the liquid phase, a similar concentration dependences for Cd_2Te_3 and $CdTe_2$ have an extremum character (Fig. 4). As it should be expected, the gross composition of the liquid phase corresponding to maximum concentrations of above complexes is close to the equiatomic melt ones. Let us note that, even at presence of Te_2 , Cd_2Te_3 , Cd_2Te and $CdTe_2$ associates, the most numerous complex in the melt is $CdTe$ one. It is the complex that determines the main parameters of three-phase equilibrium lines in the system. At the same time, as follows from Fig. 4, the only $CdTe$ complex could not provide liquidus asymmetry in the metal- and metalloids-enriched state diagram part relatively to the equiatomic composition. Therefore, taking into account these complex liquid-phase associates is necessary in the framework of the developed model.

There were undertaken several attempts in this work to increase accuracy in description P - T - X equilibria using the more correct choice of functional dependences for dissociation constants. However, it turned out that even an essential variation could not change considerably P - T dependence behavior. This fact testifies to essential stability of the model relatively to any parameter choice, which is a positive property. At the same time, to further increase the description reliability, one should, apparently, revise effectively the associate composition of the melt or take another measures.

Thus, in the work, we quantitatively proved the applicability of the polyassociative solution model to description of phase equilibria in semiconductor system Cd-Te. We found compositions and parameters of complex creation in Cd-Te liquid phase and developed a theoretical basis for construction of P - T - X equilibrium lines for the three-component Cd-Hg-Te system. Our next work in this cycle will be devoted to solving this general problem.

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