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Model of polyassosiative solutions and its application for the analysis of p–T–x equilibrium in iron-like oxide solutions and A^2B^6 semiconductor systems

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ABSTRACT

This work is the analysis of phase equilibria using the thermodynamic model of solutions, in which it is assumed that the strong interaction between the liquid phase components is due to the presence of atomic complexes of different compositions (polyassociative solutions model—PAS model). It is an analysis of its effectiveness and validity when creating p–T–x phase diagrams for A^2B^6 semiconductor compounds, as well as for magnetic oxide solid solutions crystallizing to a spinel structure.

The theoretical analysis results were compared with the experimental ones. Conclusions were drawn regarding the effectiveness of the PAS model, application restrictions were discussed, and long-term perspective application directions in the analysis of phase equilibrium were identified.

1. Introduction

The basis for selecting the conditions for crystallizing out solid solutions from the liquid phase is the data on phase equilibrium in these systems. The reliability of this data has an impact on the validity of creating different crystallization models. It is precisely, on the basis of thermodynamic models describing the system's equilibrium state, that technological processes for creating materials with desired properties are predicted.

The theme of this paper is to analyze the creation of phase diagrams for A^2B^6 semiconductor compounds as well as magnetic solid solutions with a spinel structure based on the PAS model. These materials are widely used as active environments for creating the latest optoelectronic devices, and also in magnetic technologies [1–9]. This analysis is based on the assumption that in a liquid solution complexes of different compositions exist—polyassociative solutions model (PAS model). So far, the most widely used model to characterize the p–T–x phase equilibrium of these systems has been the associative solutions model. The assumption concerning the weak dissociation of these compounds at the melting point and the existence of AB complexes in the liquid phase can only explain the basic characteristics of phase equilibrium [10–13]. In particular, it refers to such characteristics as follows:

- the presence of a single sharp liquidus maximum of the solution at the melting point,
- there is considerable liquidus asymmetry in the phase diagram with regard to the composition of the alloy enriched with metallic and metalloid components. These characteristic features are more clear in compounds beginning with *HgTe*, through CdTe–ZnTe (Fig. 1.1) and
- intensive interaction of the alloy's components with the gas phase, due to the significant vapor pressure of each component at high temperatures.

The basic criterion during the development of the thermodynamic model of interaction between the liquid phase components in these systems was the assumption concerning the presence of a single complex in the binary liquid phase, while the relatively weak interaction between this complex and the free atoms of the basic substance was described by a sub-regular approximation [10–14].

It should be noted that using the regular solutions model for calculations leads to a symmetric distribution of the liquidus curve in comparison to an equiatomic composition. Furthermore,

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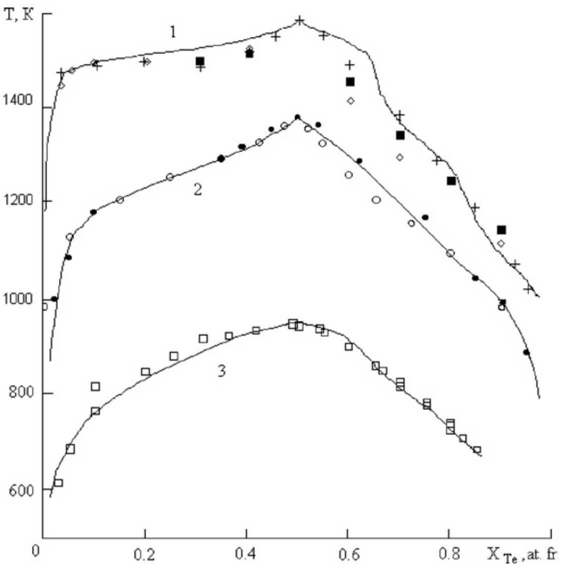

Fig. 1.1. The liquidus of the Zn–Te (1), Cd–Te(2) and Hg–Te(3) systems. +, ◇, □—the data of work [5] for the Zn–Te system; *o*, *o*, ■—the data of works [1–3] for the Cd–Te and Hg–Te systems.

it is necessary to include in the calculations, the excess energies derived from the mixing of the components which are dependent on phase composition. In many cases, a good agreement with the experiment was obtained, not only by introducing concentration dependent component mixing parameters, but also by allowing the possibility of the existence of various thermodynamic functions to describe the equilibrium state [15]. This second approach is not a convincing argument to describe the equilibrium state in the liquid phase, in which, at certain concentrations thermodynamic function discontinuities appear. Thus, a better solution for describing the equilibrium state in a wide range of concentrations is to assume the existence of many complexes in the liquid phase (PAS model).

The assumption of a multicomplex composition in a liquid solution allows for the simplification of a complicated description of the component activity coefficients in the sub-regular solution model, which is also physically difficult to interpret [24].

The positive side of such an approach is the possibility to make use of parameters specified for binary systems while analyzing the phase equilibrium of multicomponent systems. It should also be noted that in several papers [15,16] the thermodynamic phase equilibrium description is presented only in *T–x* coordinates, and does not take the gas phase into consideration. However, disregarding the gas phase during analysis limits the scope of the information about the equilibrium state of the whole system, and cannot prove the validity of all assumptions adopted in the model.

It should also be noted that the regular solution model can be used when the deviation of the system from the state, described by the ideal solution model, is not too big and does not exceed the value of a few *RT* [17].

This situation also occurs in the phase equilibrium descriptions of oxide systems, crystallizing to a spinel structure. Phase diagrams for the Fe–O, Mn–O, and Mn–Fe–O systems [7–9] are characterized by similar traits as indicated by the A^2B^6 semiconductor systems above. That is why the purpose of this paper is to demonstrate the superiority of the PAS model for the thermodynamic analysis of the *p–T–x* phase equilibrium in A^2B^6 semiconductor systems, and oxide materials which crystalize to a spinel structure.

2. Theoretical assumptions in the PAS model

The thermodynamic description model of the liquid phase with several complexes of different compositions was first presented in [17]. Based on the assumption that significant attractive forces exist between the atoms of the substances being mixed, which leads to the formation of complexes (associates), the basic mathematical expressions were derived, which related their concentrations and formation parameters to the total component content and the main thermodynamic functions of the solution. This model assumes that the lifetime of such complexes is longer than the lifetime of their components in a free state.

According to the PAS model for *A–B* binary systems, the relationship between the concentration of an A_pB_q type complex in a solution and the general component content can be written as follows [1–10,17]:

$$X_BG-\sum_{p=0}\sum_{q=1}qx_{A_pB_q}=0;$$

$$X_AG-\sum_{p=1}\sum_{q=0}px_{A_pB_q}=0;$$

$$G=1+\sum_{p=0}\sum_{q=0}(p+q-1)x_{A_pB_q} \qquad (1.1)$$

where X_A and X_B are the atomic parts of the alloy's metallic and metalloid components, $x_{A_pB_q}$ is the molar composition of the A_pB_q complex and *p* and *q* are the indices that represent the composition of the complex for each of the reviewed systems.

For quasi-chemical reactions which create liquid phase complexes, the law of conservation of mass can be written as

$$\frac{x_A^px_B^q}{x_{A_pB_q}}=K_{pq}(T) \qquad (1.2)$$

where K_{pq} is the dissociation constant for the A_pB_q complex.

According to the PAS model, the *T–x* phase equilibrium in the *A–B* binary system can be described as follows [1–9]:

$$\Delta S^F_{AB}(T^F_{AB}-T)/RT+\int_T^{T^F}dT''\int_{T^F}^{T}\frac{\Delta C_P}{T'}dT'+\ln\left(\frac{x_Ax_B}{x_A^{Sl}x_B^{Sl}}\right)=0 \qquad (1.3)$$

where ΔS^F_{AB} and T^F_{AB} are the melting entropy and the melting temperature of the *AB* compound, respectively. x_A, x_B is the concentration of free atoms of components *A* and *B* respectively, *T* is the temperature and *Sl* is the superscript that indicates a liquid phase of stoichiometric composition, $\Delta C_P=C_A^L+C_B^L-C_{AB}^S$. C_i,C_{AB} is the molar heat capacity of the components in the liquid phase and compound.

The integral in Eq. (1.3) takes into account the difference in the molar heat capacity of the inputs and outputs in the liquid and solid phases, depending on the chemical reaction creating the substance: $A(l)+B(l)=AB(s)$. The immediate (direct) calculations performed in [1–6] by using the thermodynamic properties of individual substance, showed that the magnitude of this component in the equation has negligibly small value in comparison with the other members of this equation, i.e.

$$\Delta S^F_{AB}(T^F_{AB}-T)/RT,\ \ln\left(\frac{x_Ax_B}{x_A^{Sl}x_B^{Sl}}\right)$$

This allowed to be ignored in subsequent phase equilibrium calculations. For further calculations, it seems that it is necessary to draw attention to the following properties of the PAS model, as indicated in [17], where it is shown that all liquid phase complexes are in a thermodynamic equilibrium state with each other and the phases with which they are in contact. The formation of the solid phase can also be described by other equations, using different combinations of other complexes. To serve as an example, the reactions which create magnetite