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CALCULATION OF THE PHASES COEXISTENCE SPACES IN THE SYSTEM Hg-Mn-Te-Se

A.I. Kazakov, D.V. Burtnyi, G.V. Shapovalov. Розрахунок областей співіснування фаз в системі Hg-Mn-Te-Se. На основі моделі регулярного розчину і стандартних термодинамічних функцій, використаних для опису властивостей бінарних станів і взаємодії атомів в чотирьохкомпонентних твердих розчинах, розраховані вищі похідні вільної енергії гомогенного твердого розчину $Hg_{1-x}Mn_xTe_{1-y}Se_y$ зі змішанням в двох підгратках з другої по восьму включно. Аналітичні вирази для похідних, чисельні розрахунки і визначення нульових контурів вищих похідних проводилися на основі диференціального топологічного підходу з використанням системи комп'ютерної математики Maxima. Розраховані перетини фазової діаграми твердого розчину $Hg_{1-x}Mn_xTe_{1-y}Se_y$, критичні простори і простору співіснування фаз для різних температур. Отримані результати моделювання показують можливість утворення областей співіснування фаз другого порядку в твердих розчинах $Hg_{1-x}Mn_xTe_{1-y}Se_y$.

Ключові слова: тверді розчини, простори співіснування фаз, багатоконпонентні системи, комп'ютерне моделювання, вищі похідні

A. Kazakov, D. Burtnyi, H. Shapovalov. Calculation of the phases coexistence spaces in the system Hg-Mn-Te-Se. Based on the regular solution model and the standard thermodynamic functions used to describe the properties of binary states and the interaction of atoms in four-component solid solutions, the higher derivatives of the free energy of the homogeneous solid solution $Hg_{1-x}Mn_xTe_{1-y}Se_y$ from the second through the eighth inclusive were calculated. Analytical expressions for the derivatives, numerical calculations and determination of the zero contours of higher derivatives were carried out on the basis of a differential topological approach using the computer mathematics system of Maxima. The sections of the phase diagram of the solid solution $Hg_{1-x}Mn_xTe_{1-y}Se_y$, the critical spaces and the coexistence spaces of phases for different temperatures were calculated. The obtained simulation results show the possibility of formation the coexistence of second-order phases regions in solid solutions $Hg_{1-x}Mn_xTe_{1-y}Se_y$.

Keywords: solid solutions, coexistence spaces of phases, multicomponent systems, computer simulation, higher derivatives, free Gibbs energy

Introduction. Four-component solid solutions based on compounds of the A_2B_6 type are a good choice for creating optoelectronic devices, since they operate in a wide spectral range. But there is a possibility of loss of thermodynamic stability in solid phases in II-IV semiconductor four-component systems, which can lead to the appearance of unstable states of solid solutions. As a result, critical phenomena may exist in unstable solid phases, which lead to degradation of the properties of optoelectronic devices [1 – 5].

An important stage in the development of electronic technologies and solving problems related to the behavior of multicomponent systems was the introduction of modern methods of computer modeling into this field. This allows us to analyze thermodynamic models of multicomponent systems and predict their behavior.

In particular, computer modeling makes it possible to calculate and construct the phase diagrams necessary for the analysis of the processes of obtaining self-organized formed nanostructures, and also takes into account the possibility of the existence of bifurcation spaces and spaces of coexistence of phases of various orders.

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Objective. The aim of the paper is to calculate, on the basis of the differential topological approach [6, 7], the higher free energy derivatives of the system from the second through the eighth inclusive in four concentration parameters for analyzing the four-component solid solution $\text{Hg}_{1-x}\text{Mn}_x\text{Te}_{1-y}\text{Se}_y$ for the existence of second-order phase coexistence spaces.

Thermodynamic modeling of critical phenomena in the system Hg - Mn - Te - Se.

When analyzing the four-component solid solution $\text{Hg}_{1-x}\text{Mn}_x\text{Te}_{1-y}\text{Se}_y$ as a system in which several phases are assumed, the condition for the existence of two phases that are in equilibrium is used [6, 7], by means of which the existence of second-order phase coexistence spaces is verified:

$$\frac{d^2G}{dx^2} = \frac{d^3G}{dx^3} = 0; \quad \frac{d^4G}{dx^4} > 0. \quad (1)$$

For the analysis of a multicomponent system, a thermodynamic model was used in which the free Gibbs energy for a four-component solution was considered as a mixture of four hypothetical binary compounds in the form [6]:

$$G = G(X_{AC} X_{BC} X_{AD} X_{BD}), \quad (2)$$

where G – free energy of the system, X_{ij} – the concentration of binary components.

The state functions of such a solid solution can be described using the indicated concentrations X_{ij} . The basis of the regular solution model is the assumption of the random distribution of heterogeneous atoms that form a solid substitutional solution along the sites of the corresponding sublattices. Accordingly, the expression for the concentrations of the binary components takes the form:

$$X_{AC} = (1-x)(1-y), \quad X_{BC} = x(1-y), \quad X_{AD} = (1-x)y, \quad X_{BD} = xy, \quad (3)$$

where x and y – concentration parameters.

To assess the possibility of the emergence of critical spaces and coexistence spaces in the solid solution under consideration, analytical expressions for higher derivatives of the potential energy of the system are obtained and investigated.

The higher derivatives for the free Gibbs energy of the solid solution $\text{Hg}_{1-x}\text{Mn}_x\text{Te}_{1-y}\text{Se}_y$ by the concentration parameters are calculated by matrix-vector differentiation of multidimensional systems. To obtain matrices of higher derivatives, the method of direct sums was used [8].

The higher derivatives of the free energy of the system under consideration were obtained by the following algorithm. In the framework of the regular solution model [6, 7], the second derivatives of the free Gibbs free energy μ_{ij} of the solid solution $\text{Hg}_{1-x}\text{Mn}_x\text{Te}_{1-y}\text{Se}_y$ were obtained, of which an A_2 matrix of 4×4 dimensions was formed:

$$A_2 = \begin{vmatrix} \mu_{11} & \mu_{12} & \mu_{13} & \mu_{14} \\ \mu_{21} & \mu_{22} & \mu_{23} & \mu_{24} \\ \mu_{31} & \mu_{32} & \mu_{33} & \mu_{34} \\ \mu_{41} & \mu_{42} & \mu_{43} & \mu_{44} \end{vmatrix}, \quad (4)$$

Further, the matrix A_2 was differentiated in four corresponding concentrations X_{ij} . As a result of differentiation, four fourth-order partial derivatives of the third order of 4×4 were obtained. Then, using the method of direct sums, the block-diagonal matrix of the total third derivative of the free energy of the system under investigation was formed:

$$A_3 = \begin{vmatrix} \frac{dA_2}{dX_{AC}} & 0 & 0 & 0 \\ 0 & \frac{dA_2}{dX_{AD}} & 0 & 0 \\ 0 & 0 & \frac{dA_2}{dX_{BC}} & 0 \\ 0 & 0 & 0 & \frac{dA_2}{dX_{BD}} \end{vmatrix}, \quad (5)$$

The determinant of the obtained matrix A_3 is defined as the sum of the determinants of the matrices of partial derivatives located on the main diagonal:

$$\det A_3 = \det A_{13} + \det A_{23} + \det A_{33} + \det A_{43}, \quad (6)$$

where

$$A_{13} = \frac{dA_2}{dX_{AC}}; \quad A_{23} = \frac{dA_2}{dX_{AD}}; \quad A_{33} = \frac{dA_2}{dX_{BD}}; \quad A_{43} = \frac{dA_2}{dX_{BC}}. \quad (7)$$

Preparation of higher order system free energy derived from the fourth to the eighth, and the related determinants $\det A_i$, where i is the order of the derivative was performed using the same algorithm. Analytical expressions of higher derivatives were obtained using Maxima computer mathematics [9].

After obtaining analytical expressions for the determinants of the matrices of the free energy derivatives of the system under consideration, the positions of the zero contours of the considered derivatives were calculated.

For this, the values of the concentration parameters x and y in the range from 0 to 1 in 0.1 increments were substituted into the expressions for the corresponding determinants, after which the condition $\det A_i=0$ was checked. Further, the areas in which the values of the corresponding determinants take positive and negative values were determined. Positive values were marked by light areas, negative values – darker.

Results. By calculating the positions of the zero contours, the analytical expressions for the total derivatives of the Gibbs free energy of the four-component solid solution $Hg_{1-x}Mn_xTe_{1-y}Se_y$, the phase diagrams of the studied system of the position of the areas of coexistence of the derivatives with allowance for (1) are numerically determined and plotted. Also their zero contours from the second to the eighth derivative inclusive for the temperature range of 800...1000 K were determined.

In the simulation, the values of the quasibinary interaction parameters in solid solutions and crystal-physical parameters of binary systems were used (Table):

Parameters of the interaction in the solid phase for quasibinary systems

Solid solution	Interaction Parameters	Parameter value α_{sj-lk} , J/mole
$Hg_{1-x}Mn_xTe_{1-y}Se_y$	$\alpha_{13}=\alpha_{HgSe-MnSe}$	16000[8]
	$\alpha_{24}=\alpha_{HgTe-MnTe}$	14200[8]
	$\alpha_{12}=\alpha_{MnTe-MnSe}$	900[8]
	$\alpha_{34}=\alpha_{HgTe-HgSe}$	2933[8]

In Fig. 1 – 4 are graphical representations of the positions of the zero contours of the derivatives of the free Gibbs energy in the $Hg_{1-x}Mn_xTe_{1-y}Se_y$ system in terms of the concentration parameters, starting with the second derivative and the eighth derivative inclusive for the 800 K temperature and the second-order phase coexistence spaces (Fig. 4, b) The area of positive values of the derivative is shown in dark color and, accordingly, the lighter one is the area of negative values.

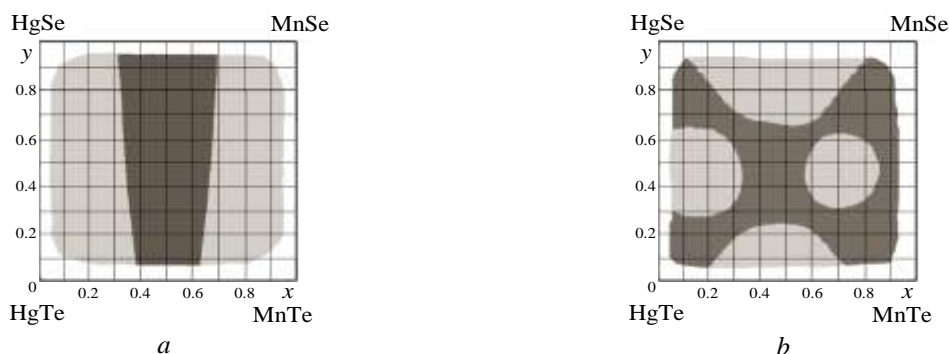


Fig. 1. Graphical representations of the positions of the zero contours of the second derivative (a) and the third derivative (b) of the free energy in the Hg-Mn-Te-Se system at the cross section for the existence of solid solutions of the phase diagram

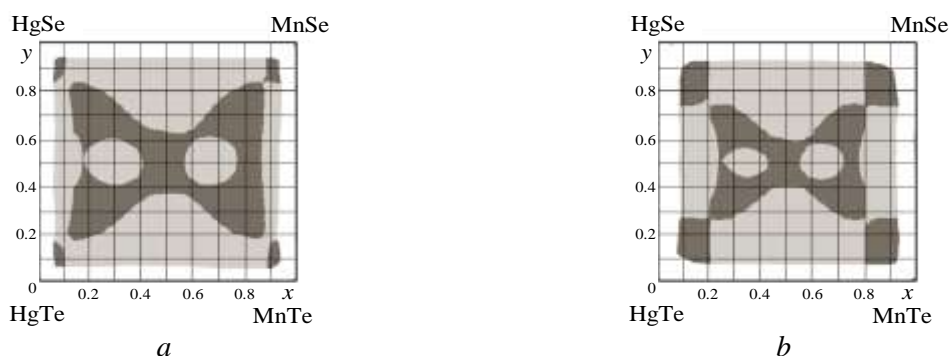


Fig. 2. Graphical images of the positions of the zero contours of the fourth derivative (a) and the fifth derivative (b) of free energy in the Hg-Mn-Te-Se system at the cross section for the existence of solid solutions of the phase diagram

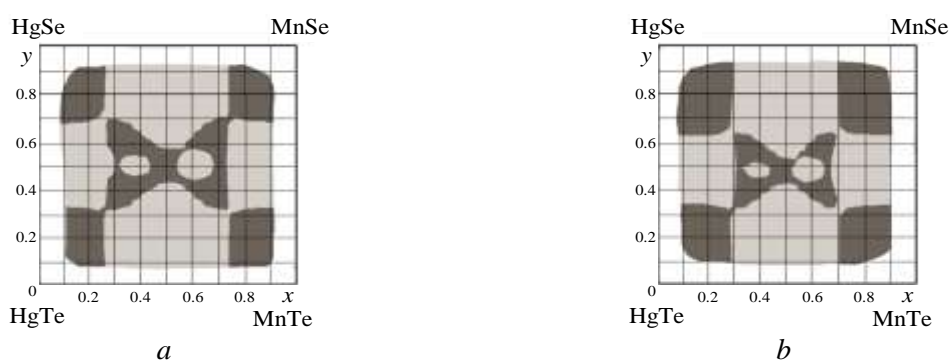


Fig. 3. Graphical representations of the positions of the zero contours of the sixth derivative (a) and the seventh derivative (b) of the free energy in the Hg-Mn-Te-Se system on the cross section for the existence of solid solutions of the phase diagram

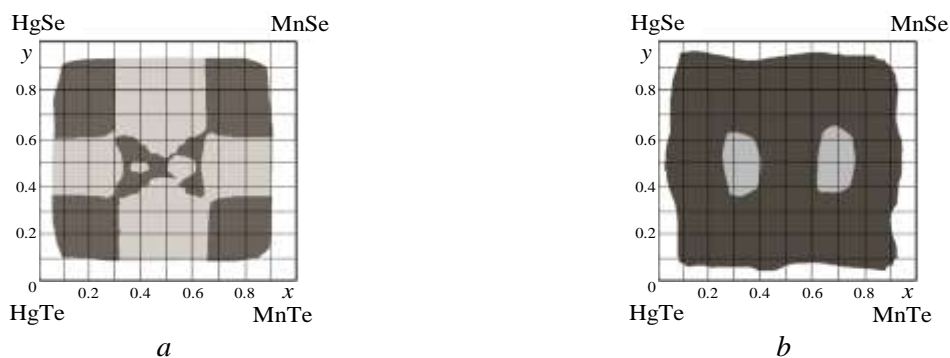


Fig. 4. Graphical representations of the positions of the zero contours of the eighth derivative (a) of free energy in the Hg-Mn-Te-Se system on the cross section for the existence of solid solutions of the phase diagram and second-order phase coexistence spaces (b, shown in a lighter color)

Conclusion. The considered procedure for calculating of higher derivatives of free energy with respect to four concentration parameters makes it possible to correctly estimate the position of the second-order phase coexistence spaces in multicomponent solid solutions. The constructed thermodynamic model of the solid solution $\text{Hg}_{1-x}\text{Mn}_x\text{Te}_{1-y}\text{Se}_y$ can also be used to predict the formation and coexistence of three and four different phases in the solid solution considered.

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