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The theory of phase diagrams of thermodynamic systems with symmetry 3*m*

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ABSTRACT

Within the framework of the phenomenological theory of the second-order phase transitions for the crystals undergoing structural transformations, induced by irreducible representations with symmetry group $\mathcal{L}=3m$, all possible types of phase diagrams are constructed. Conditions of realization of each type of phase diagrams are found in the approach of the thermodynamic potential of the sixth power of expansion on order parameter components. The equations for calculation of tricritical and triple point coordinates are received. In the case of spinel-type structure, qualitative agreement between the results of theoretical calculations of phase diagrams and experimental phase diagrams is observed.

1. Introduction

For the first time in his works Landau gave two-dimensional phase diagrams in which N ($N>3$) phases adjoin in a singular point vicinity in a plane of two thermodynamic parameters (temperature, pressure, concentration of components, etc.). Thus, the Gibbs' phase rule "is broken" [1–4]. Diagrams with $N=4$, 5 are presented in figures in works [1,2]. These Landau's results have been reproduced later in many fundamental theoretical calculations in the analysis of various types of thermodynamic potentials (see, for example, [4–7]). It has been established that these special "*N*-phase" points in terms of Gibbs' classical thermodynamics are multicritical ones.

Multicritical points in the theoretical calculations are obtained at strictly defined relationships between the coefficients of Landau's model of thermodynamic potential. When these relationships are not fulfilled, multicritical points are split. This process is accompanied by a transformation of the phase diagram into usual phase diagrams, studied by classical thermodynamics [7,8]. Therefore, we can assume that Landau's phase diagrams are metadiagrams from which a variety of phase diagrams are derived and studied in the traditional Gibbs' thermodynamics.

For the first time the phenomenon of a multicritical point splitting was observed in the study of the thermodynamic potential which is invariant concerning transformation group $\mathcal{L}=3m$ (C_{3v}) [7]. In general a space group of the structure of substance is a group of symmetry of a thermodynamic potential G_0 [1,2]. However, if we consider that phase transitions are induced by one irreducible representation of group G_0, then real symmetry group of a thermodynamic potential will be a factor-group G_0/G_1 (where G_1 is a kernel of critical irreducible representation), which is isomorphic to some point group $\mathcal{L}$ [4]. Many papers in which the results obtained in [7] were used and developed were published later (see e.g. [4–6,9,10]). However, all possible types of phase diagrams have not been received in these studies because of the limitations of methods used.

In this report we present the results of a complete analysis of the thermodynamic potential of the sixth power of expansion on order parameter with symmetry $\mathcal{L}=3m$ (C_{3v}); we have established theoretically all possible types of phase diagrams. The potential of such symmetry describes the phase transformations in many classes of materials, including intermetallic compounds, peroxides, spinels, garnets, perovskites, etc. [7].

2. The thermodynamic potential and the types of extremes induced by symmetry

We represent Landau's thermodynamic potential as follows:

$$\Phi=\alpha_1 I_1+\alpha_2 I_1^2+\alpha_3 I_1^3+\beta_1 I_2+I_2^2+\delta_1 I_1 I_2$$

where I_1 and I_2 are invariants, consisting of two components η_1 and η_2 of an order parameter

$$I_1=\eta_1^2+\eta_2^2,\quad I_2=\eta_1^3-3\eta_1\eta_2^2$$

The order parameter components are transformed by a two-dimensional irreducible representation of the point group with symmetry $\mathcal{L}=3m$ (C_{3v}).

Possible types of phases are defined by solution types of the system ($\partial\Phi/\partial\eta_1=0$ and $\partial\Phi/\partial\eta_2=0$) of necessary conditions of the thermodynamic potential minimum as a function of η_1 and η_2.

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Introducing the designations $\Phi_1=\partial\Phi/\partial I_1$ and $\Phi_2=\partial\Phi/\partial I_2$, we note that the following types of solutions of this system and the corresponding types of phases different by symmetry are possible [7]:

1. $\eta_1=\eta_2=0$—highly symmetric phase (I);
2. $\eta_1=-2\Phi_1/3\Phi_2\neq 0$, $\eta_2=0$—one-parametrical phase, there are two possibilities: $\eta_1<0$ (phase II) and $\eta_1>0$ (phase III);
3. $\eta_1\neq 0$, $\eta_2\neq 0$, $\Phi_1=\Phi_2=0$—two-parametrical phase (IV).

The total degeneracy (i.e. the number of different domains) of phases II (III) and IV is equal to 3 and 6, respectively. These solutions, however, should satisfy sufficient conditions of minimum Φ as well, i.e. conditions of thermodynamic stability. For phase I they are reduced to the inequality $\alpha_1>0$. One-parametrical phases conditions of thermodynamic stability look like

$$\begin{cases}\eta_1\cdot[24(\alpha_3+1)\eta_1^3+15\delta_1\eta_1^2+8\alpha_2\eta_1+3\beta_1]>0\\ \eta_1\cdot(2\eta_1^3+\delta_1\eta_1^2+\beta_1)<0\end{cases}$$

To analyze the conditions of existence of phase IV it is more convenient to consider the potential Φ as a function of invariants; $\Phi=f(I_1,I_2)$. Equations $\Phi_1=\Phi_2=0$ give two possible values I_1 and I_2, but it can be shown that sufficient conditions of minimum are satisfied by only one of them. We have

$$I_1=\frac{-\gamma+\sqrt{\gamma^2-24\alpha_3(2\alpha_1-\beta_1\delta_1)}}{12\alpha_3},\quad I_2=-\frac{\beta_1+\delta_1 I_1}{2}$$

where $\gamma\equiv 4\alpha_2-\delta_1^2$.

For the existence of phase IV it is necessary and enough that the following three conditions are fulfilled:

$$I_1>0,\quad \tau\equiv\gamma^2-24\alpha_3(2\alpha_1-\beta_1\delta_1)>0,\quad \theta\equiv I_1^3-I_2^2\geq 0$$

The last requirement is caused by the necessity of existence of the real values η_2, corresponding to the pair I_1 and I_2. These conditions correspond to a set of lines (in the phase diagram in coordinates "α_1–β_1"), which restrict the region of existence of a two-parametrical phase. The equations of these three lines are

1. $I_1=0$—straight line $\alpha_1=(\delta_1/2)\beta_1$ (this line is not present in the diagram if $\gamma<0$),
2. $\tau=0$—straight line $\alpha_1=(\delta_1/2)\beta_1+\gamma^2/48\alpha_3$,
3. $\theta=0$—curve (in general, not continuous)

$$\alpha_1=\tfrac{1}{2}(\delta_1\beta_1-\gamma I_1)-3\alpha_3 I_1^2 \tag{1}$$

where I_1 are those roots of the equation

$$4I_1^3-\delta_1^2 I_1^2-2\beta_1\delta_1 I_1-\beta_1^2=0 \tag{2}$$

which satisfy the condition

$$12\alpha_3 I_1+\gamma\geq 0 \tag{3}$$

3. Types of the phase diagrams

The geometric meaning of condition (3) lies in the fact that branches of the curve $\theta=0$ may end up on the line $\tau=0$, but may not cross it. If $\beta_1=0$, from (2) we have double value $I_1=0$, and, according to (1), two branches of the curve $\theta=0$ converge in the multicritical point with coordinates $\alpha_1=\beta_1=0$. In this unique point, stability regions of one-, two-parametrical and highly symmetric phases adjoin. But according to (3) it is possible only if $\gamma>0$. If $\gamma<0$, phase IV does not exist neither at all (since the condition (3) is never fulfilled) or (if $\alpha_3>0$) the branches of the curve $\theta=0$ converge in the specified point. It means that the multicritical point is split and the branches of the curve $\theta=0$ end up on the line $\tau=0$. So, the general conditions of the multicritical point splitting are the following inequalities:

$$\begin{cases}\gamma<0\\ \alpha_3>0\end{cases} \tag{4}$$

Ordinates of the points of breakage may be obtained from the equation

$$\alpha_1^2-\frac{\gamma}{24\alpha_3}(4\alpha_2+\delta_1^2)\cdot\alpha_1+\left(\frac{\gamma}{24\alpha_3}\right)^2\cdot\frac{3\alpha_3(4\alpha_2+\delta_1^2)^2+4\delta_1^2\gamma}{12\alpha_3}=0 \tag{5}$$

(abscisses are found by substituting the ordinates into the equation $\tau=0$).

For the case of $\gamma>0$ and $\delta_1>0$ the scheme of the lines limiting the region of stability of phase IV and the corresponding phase diagram with the multicritical point are shown in Fig. 1(a, b). It is seen that if $\alpha_1>0$ then phase I is stable (alone or in combination with phase II or III). If $\alpha_1<0$ then phase IV is stable, the transition from one-parametrical phases into which is the second-order one. If $\delta_1<0$, the region of phase IV is shifted in the opposite direction. The module increase of this coefficient (other conditions being equal) enlarges the asymmetry of the phase diagram. The case of $\delta_1=0$ corresponds to the symmetrical diagram.

If conditions (4) are fulfilled, then the combination of signs of equation (5) roots specifies the type of the multicritical point

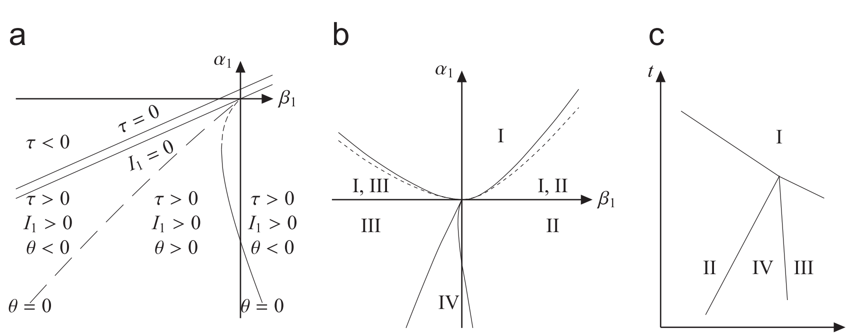

Fig. 1. The scheme of lines (a), theoretical phase diagram with a multicritical point (b) and experimental phase diagram of spinel solid solution $Cu_{1-x}Ni_xCr_2O_4$ [11] in the coordinates "temperature (t)–concentration (x)" (c). Here and further on the sites of curve $\theta=0$ corresponding to different roots of Eq. (2) are designated on schemes by different kinds of dashing. On phase diagrams continuous lines designate borders of thermodynamic stability of phases, and dashed lines designate the first-order phase transitions.