Methods of the theory of singularities in the phenomenology of phase transitions

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(Submitted May 3, 1990; resubmitted after revision October 18, 1990)
Usp. Fiz. Nauk **161**, 109–147 (June 1991)

A review is presented on the methods of the theory of singularities applied to the Landau phenomenological theory of phase transitions. Constructive algorithms are presented that eliminate arbitrariness in the choice of the Landau potential and make it possible to exclude from consideration models with nonphysical results. The methods of singularity theory are illustrated by application to several real thermodynamic systems.

1. INTRODUCTION

The basis of the phenomenological theory of phase transitions was developed in a series of papers by Landau.[1-4] In those papers it was shown that in a high-symmetry phase of a crystal the equilibrium charge density distribution $\rho(\mathbf{r})$, in accordance with Curie's principle, is invariant under all the transformations of the space group G_0 of the crystal. The thermodynamic instability that arises in a phase transition brings about a symmetry-breaking deviation

$$\delta\rho(\mathrm{r}) = \int \sum_{n,\gamma} \eta_{\mathbf{k}n\gamma}\varphi_{\mathbf{k}n\gamma}(\mathrm{r})\mathrm{d}\mathbf{k}, \tag{1.1}$$

where $\mathbf{k}$ is the index of the irreducible star of the wave vectors, $\eta_{\mathbf{k}n\gamma}$ are the components of the order parameter, and $\varphi_{\mathbf{k}n\gamma}$ are the basis functions of the irreducible representations of the given star $\mathbf{k}$.

The presence of $\delta\rho(\mathbf{r})$ determines the nonequilibrium increment $\Delta\Phi$ to the thermodynamic potential:

$$\Delta\Phi = \Phi(\rho_0 + \delta\rho, P, T) - \Phi(\rho_0, P, T). \tag{1.2}$$

Because the transformation properties of $\eta_{\mathbf{k}n\gamma}$ and $\varphi_{\mathbf{k}n\gamma(\mathbf{r})}$ are identical, the nonequilibrium thermodynamic potential $\Delta\Phi$ (the Landau potential) can be considered a function only of $\eta_{\mathbf{k}n\gamma}$, and invariant with respect to G_0. The equilibrium value $\eta_{\mathbf{k}n\gamma} \equiv \eta_i$ is determined from the condition that the Landau potential be minimized with respect to the order parameters:

$$\mathrm{d}(\Delta\Phi) = \frac{\partial(\Delta\Phi)}{\partial\eta_i}\mathrm{d}\eta_i = 0,$$
$$\mathrm{d}^2(\Delta\Phi) = \frac{\partial^2(\Delta\Phi)}{\partial\eta_i\partial\eta_j}\mathrm{d}\eta_i\mathrm{d}\eta_j \geq 0. \tag{1.3}$$

The most important results obtained by the Landau theory are determined by the symmetry of the thermodynamic system. Among these results are the conclusions of Landau[1-4] that a second-order phase transition is a consequence of the spontaneous reduction of symmetry and that the behavior of the generalized susceptibility at the Curie point (the "rule of two") is general. To describe a single isolated second-order phase transition Landau proposed to use a potential of the form

$$\Phi = \alpha(T - T_c)\eta^2 + B(P, T)\eta^4. \tag{1.4}$$

In his paper,[5] Lifshitz answered the question: between which Bravais lattices are second-order phase transitions possible? Ginzburg[6] showed that the existence of a soft mode is necessary in a second-order phase transition. A more complete allowance for symmetry in the sixth-order Landau potential with a multicomponent order parameter allowed Devonshire[7] to describe phase transitions and the observed low-symmetry phases in the ferroelectric $BaTiO_3$. Dzyaloshinskiĭ predicted "weak" ferromagnetism, consisting of induced magnetization arising as a result of a symmetry-caused interaction with the antiferromagnetic order parameter,[8] and piezomagnetic and magnetoelectric effects linear in the field.[9,10] A phenomenon in which an induced polarization appears, analogous to weak ferromagnetism, was pointed out by Indenbom.[11]

Further development and application of the theory encountered difficulties related to the multidimensionality and the nonlinearity of the problems that arose, and as a result, the theory lost some popularity. However, the potential of the theory was far from exhausted. Most of the difficulties were overcome with the use of the theory of group representation. The methods proposed in the work of Gufan[12,13] and Birman,[14,15] and Michel[16,17] extended the class of systems that could be constructively described by the phenomenological theory of phase transitions. The problem of describing phase transitions within the framework of this theory breaks down naturally into two problems—the angular problem and the radial problem.[13] The angular problem involves the determination of various system characteristics that are determined only by the transformation properties of the order parameter, but not by the specific form of the thermodynamic potential (calculation of the possible low-symmetry phases, determination of the number of domains in each phase, etc.). The introduction of a number of new concepts such as the space of the order parameter components (ε is the space) the group of the various matrices of the representation (the L group), invariant subspaces (stationary vectors), and the complete rational basis of invariants

$$J_k = J_k(\eta_1, ..., \eta_n), \quad k = 1, 2, ..., m, \tag{1.5}$$

where n is the dimension of the representation, and m is the number of invariants in the basis, has made it possible to obtain a geometrically exact and final solution of the angular problem of the theory.[13,18,19]

The solution of the radial problem involves finding the equilibrium values of the order parameters, for which it is necessary to know the specific form of the thermodynamic potential. This, however cannot be done without resort to model assumptions.

Since the Landau potential is invariant with respect to

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G_0, it must be a function of the basis invariants

$$\Phi = \Phi(J_1(\vec{\eta}),\ J_2(\vec{\eta}), \ldots, J_m(\vec{\eta}), \vec{\alpha}), \tag{1.6}$$

where α is a continuous function of the external conditions. Consequently, the system of equations (1.3) can be written

$$\begin{aligned} d\Phi &= \psi_l d\eta_l = \frac{\partial\Phi}{\partial J_k}\cdot\frac{\partial J_k}{\partial\eta_l}\cdot d\eta_l = 0, \\ d^2\Phi &= \psi_{lp} d\eta_l d\eta_p \\ &= \frac{\partial^2\Phi}{\partial J_k \partial J_m}\cdot\frac{\partial J_k}{\partial\eta_l}\cdot\frac{\partial J_m}{\partial\eta_p}\cdot d\eta_l d\eta_p + \frac{\partial\Phi}{\partial J_k}\frac{\partial^2 J_k}{\partial\eta_l\partial\eta_p} d\eta_l d\eta_p . \end{aligned} \tag{1.7}$$

This form of the potential and the methods discussed in Refs. 20 and 21 reveal in the radial problem as well all the consequences issuing from the symmetry of the order parameters.

The solution of the radial problem is also related to the construction of the phase diagram, to the investigation of the dependence of the generalized susceptibility $\chi_{ij} = \delta\eta_i/\delta E_j$ on the external conditions

$$\hat{\chi}(\vec{\alpha}) = \psi^{-1}(\vec{\alpha}), \tag{1.8}$$

to the dynamics of the order parameters, which are determined by the equations of motion

$$D\cdot\Phi(\vec{\eta}, \vec{\alpha}) = 0, \tag{1.9}$$

where D is the differential operator, as well as to other topics. Examples of Eq. (1.9) are the Landau–Khalatnikov equation,[22] the Landau–Lifshitz equation,[23] and others.

To solve the problems of the phenomenological theory of phase transitions in its modern form it is thus necessary to have information on the symmetry of the Landau potential and on its nonlinearity. The symmetry of the Landau potential is determined by the transformation properties of the order parameters and can be found from experimental data. As shown above, there now exists an entire system of methods of discovering all the consequences of this symmetry.

On the other hand, the form of the Landau potential is usually selected with a great deal of arbitrariness. Moreover, within the framework of the scheme of the phenomenological theory of phase transitions discussed above, it is impossible to analyze systematically how the properties of the model depend on the choice of the nonlinearity of the Landau potential. This arbitrariness can be avoided with the use of catastrophe theory (the theory of singularities), the main ideas of which were already used in the works of Landau,[1–4,24,25] although the rigorous foundations for this theory were obtained considerably later.[26–29] The internal development of the phenomenological theory of phase transitions has prepared rich soil for the application of catastrophe theory.

Already the first significant work of R. Thom[30] on the theory of singularities led to a whole series of applied papers. The authors of some of these papers, predominantly mathematicians, attempted primarily to show the effectiveness of the methods of catastrophe theory to various fields of physics, including the phenomenological theory of phase transitions.[27,31–34] To do so they used very simple examples. In the language of catastrophe theory, these papers reformulated the theory of the critical point of a van der Waals gas,[35] the theory of the thermodynamic behavior of a uniaxial ferromagnet in an external magnetic field,[31] the model of Bragg–Williams ordering,[36] and others. The simplicity and clarity of these theoretical structures are due to the fact that the form of the Landau potential in these cases coincides exactly with the elementary catastrophe structure.

The fact is that they compiled a fairly complete dictionary for the mutual translation of the terms of the Landau theory and catastrophe theory: The phenomenological coefficients are the control parameters, the order parameter is the internal parameter, the Landau potential is the miniversal deformation of the normal form of the singularity, the equation of state is the catastrophe manifold, the dimension of the thermodynamic instability of the system is the co-rank of the singularity, and so forth (the meaning of these concepts will be clear presently).

The second group of investigators, mainly theoretical physicists, pursued other goals. First was the use of catastrophe theory to place the Landau theory on a rigorous basis, and second was the application of its methods for the description of experimentally observed phase transitions. The first goal was partially attained. With the aid of the splitting lemma (for more detail see section 2.3) it was shown[37] that the Landau potential can be considered as the asymptote of the Gibbs partition function. In the solution of this problem the question arose[38–40] as to whether catastrophe theory gives results that cannot be obtained in the Landau theory. However, it was shown by Griffiths[41] that "catastrophe theory (so far as we understand it) provides a phenomenological theory of phase transitions with results...which are very similar, if not identical, to those predicted by the Landau theory...".

Considerably more modest results were obtained in efforts to attain the second goal. In spite of the large number of papers in this direction, progress has been attained only in the description of phase transitions in simple systems such as gases, liquids, and binary mixtures.[42–44] This lack of progress is due to the fact that in these papers the methods of "elementary catastrophe theory" were used (see e.g., Refs. 26 and 27). However, in practice one mainly encounters situations that do not fit within the strict confines of this theory. Moreover, phase transitions in solid materials are accompanied, as a rule, by a change in the symmetry of the crystal. To construct the Landau potential in such a case it is necessary to use a variant of catastrophe theory that takes into account the symmetry of the system. Attempts to take symmetry into account within elementary catastrophe theory[31,45,46] have led to erroneous results (for more detail see section 5.1). An abstract theory of singularities that allowed for symmetry was already in existence. However, since it was scattered over a number of papers,[47–51] and expounded in a form difficult to deal with, most investigators have preferred to consider thermodynamic systems with trivial symmetry.

A systematic application of the theory of singularities makes it possible to avoid most of the difficulties discussed above. In this paper we shall present the basic methods and algorithms of the theory of singularities, discussing also systems with symmetry, which will allow one to construct a phenomenological model that is adequate to describe anomalies that arise in the physical properties in phase transitions in any thermodynamic system.

No less important is another role that catastrophe theory plays in the Landau theory, and this role stems from the

identity of the logic of the construction of these theories. At the basis of catastrophe theory, as at the basis of the phenomenological theory of phase transitions, lie general principles that permit answers to a number of general questions: is the Landau potential expandable in a small parameter? what role does the leading term in the expansion play? and others.

2. STRUCTURAL STABILITY

2.1. Some definitions from the theory of singularities

In this section we introduce some concepts of the theory of singularities, necessary for further discussion.

Let us consider a potential function U that is smooth, that is, infinitely differentiable, that depends on n variables $\mathbf{x} = (x_1,\dots,x_n)$ and l parameters $\vec{\alpha} = (\alpha_1,\dots,\alpha_l)$. The set of all U for fixed $\vec{\alpha}$ is called the l-parameter family of functions. A point where $dU = 0$ is called a critical point $\mathbf{x}_0$ of the function U. A critical point is called a nondegenerate, or a Morse critical point, if at this point the Hessian is $\det\|\partial^2 U/\partial x_i \partial x_j\| \neq 0$, and is called degenerate or non-Morse if $\det\|\partial^2 U/\partial x_i \partial x_j\| = 0$. If the rank of the Hessian matrix $\|\partial^2 U/\partial x_i \partial x_j\|$ at the degenerate critical point is r, then the number $n - r$ is called the co-rank of the critical point.

The multiplicity of the degeneracy of the point, μ, is the maximum number of nondegenerate critical points into which it can be decomposed. The function f is called quasihomogeneous of degree d with degrees of quasihomogeneity $q_1,\dots,q_n$ if $f(\lambda^{q_1}x_1,\dots,\lambda^{q_n}x_n) = \lambda^d f(x_1,\dots,x_n)$.

If in some space there are two objects and it is possible to specify their relative arrangement, then the most general arrangement is called their transversality. Small variations in their positions do not change qualitatively their mutual arrangement. For example, intersecting straight lines on a plane are transversal, while parallel lines are nontransversal (Fig. 1a). In this treatment it is sufficient to use this definition of transversality, without making any claims to rigor.

2.2. Structural stability and experimental reproducibility. Accidental and typical degeneracies

The notion of structural stability, introduced by Thom[30] for phenomenology, is one of the most important concepts. It is analogous to the concept of robustness (insensitivity to initial conditions) introduced previously for dynamical systems by Andronov and Pontryagin.[52,53]

Only those phenomena that have a sufficient degree of reproducibility can belong to the class of physical phenomena, that is, when experiments performed under "almost identical" conditions yield with some degree of accuracy, the same result. In other words, if we examine an ensemble of systems with as identical as possible values of the parameters that determine the external conditions of the experiment, then the properties of these systems within experimental accuracy must coincide. These systems are called structurally stable.

Since the physical phenomena that accompany a phase transition must be structurally stable, the Landau potentials that describe them also must have structural stability.

The measure of structural stability is the transversality of an object, in particular, for the Landau potential, transversality of the arrangement of its critical points. It is clear that transversal objects are structurally stable. However, a systematic modification of the arrangement of transversal objects can ultimately lead to a qualitatively different—degenerate—arrangement (Fig. 1a,b). At this critical value of the parameter that describes the variation in their mutual arrangement, they are non-transversal. Further change in this parameter again leads to transversality.

Consequently, if an experiment is conducted at a fixed value of this parameter, a nontransversal situation cannot be observable. But if the result of an investigation is the dependence of the properties of a system on this parameter, then a nontransversal system will typically be observed at a value of the parameter close to the critical value (Fig. 1c). In the case of a multiparameter variation in a transversal object a situation with a higher degeneracy can arise (Fig. 2). For fixed

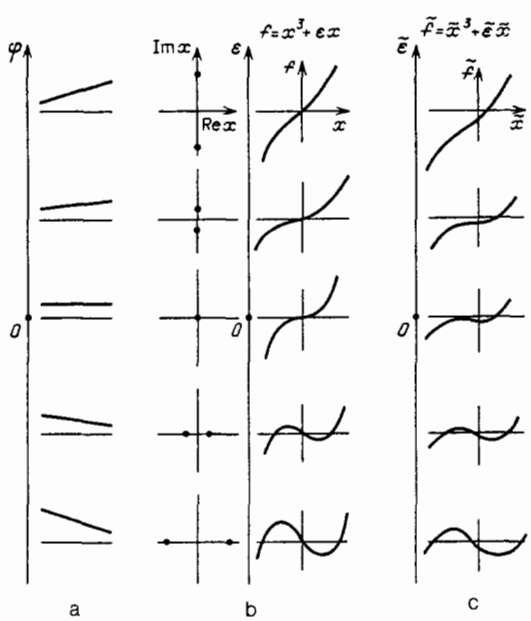

FIG. 1. Aid to understanding transversality: a) φ is the angle between straight lines; b) the positions of the extremal points are shown in the complex plane; c) "small motions" of the family of functions.

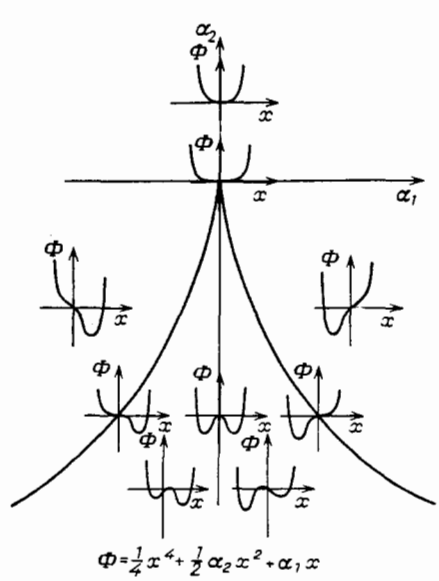

FIG. 2. Family of the cusp potential $\Phi = \alpha_1 x + \alpha_2 x^2 + x^4$. The potentials with a nontransversal arrangement of extrema are shown on the semicubic parabola $\alpha_1^2 + \alpha_2^3 = 0$.

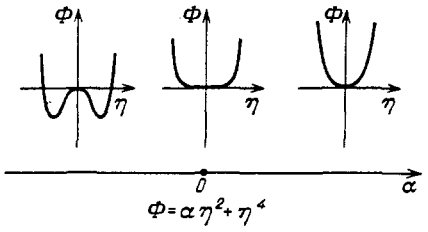

FIG. 3. Landau potential for a second-order phase transition; an example of a family of symmetric functions.

values of the external parameters only transversal objects can be observed. It follows from this argument that a regular point on a phase diagram corresponds to a morse potential; i.e., a potential that has only nondegenerate critical points. The Morse points merge at a phase stability boundary, forming a degenerate critical point.

It should, however, be noted that the route from a Morse-type Landau potential to a potential with a degenerate critical point can result in nonunique objects, since in families with the same number of control parameters one can encounter functions with different types of degenerate critical points. Therefore, the inverse route is the more correct, since the type of degenerate critical point uniquely determines the way it decays into Morse critical points. In other words, the type of degenerate critical point determines the type of singularity of the Landau potential.

Degenerate critical points of the Landau potential can arise for two reasons: First, as a nontransversal case in the variation of the control parameters. These degenerate critical points, as mentioned above, must inevitably disperse with small variations in the control parameters. Second, degenerate critical points can be a consequence of the internal nature of the thermodynamic system itself, that is, a consequence of its symmetry. These degeneracies in a typical case must be retained with small variations on the control parameters, since the Landau potential of such a system belongs to a class of functions of a specific symmetry. Therefore, slight motions of such systems must conserve their symmetry, that is, these motions must be of a special form.

An example of the first type of degenerate critical point is the Landau potential with $\alpha_1^2+\alpha_2^3$ and $\alpha_1\neq 0$, $\alpha_2<0$, shown in Fig. 2. Conversely, the potentials shown in Fig. 3 are examples of the second type. An accidental degeneracy, not due to symmetry requirements, is always related to a structural instability. Structurally unstable models in phenomenology have an attractive simplicity. They often admit of analytic solutions, and therefore have great popularity. However, these models always yield incorrect results. Examples of this sort of model are isostructural transitions without a critical point, hysteresis-free first-order phase transitions, and others.

2.3. Splitting lemma. Separation of thermodynamically unstable subsystems

One of the principal results that lie at the foundation of the theory of singularities and the phenomenological theory of phase transitions is the splitting lemma. The meaning of this lemma is the following: Since the Hessian of any smooth function $U(x_1,\dots,x_n)$ is nonzero in the vicinity of any nondegenerate critical point, the differentiable replacements

$$x_i=\varepsilon_i(y_1,\dots,y_n) \tag{2.1}$$

can transform it to a nondegenerate quadratic form

$$U=\sum_{i=1}^{n}\alpha_i y_i^2,\quad \alpha_i=\pm 1. \tag{2.2}$$

At a degenerate critical point some eigenvalues of the Hessian matrix are zero. The subspace spanned by the corresponding eigenvectors $(x_{s+1},\dots,x_n)$ is called a critical subspace, and it has dimension $n-s$, equal to the co-rank of the critical point. The rest of the variables $(x_1,\dots,x_s)$ are called Morse variables. The function $U(x_1,\dots x_n$ for this substitution (2.1) can be written in the form

$$U=\sum_{i=1}^{s}\alpha_i y_i^2+g(y_{s+1},\dots,y_n),\quad \alpha_i=\pm 1, \tag{2.3}$$

where $g(y_{s+1},\dots,y_n)$ is a function for which $dg=d^2g=0$.

The singularity of U depends only of the form of g. Addition of any number of Morse variables does not change the singularity of U. All functions with the same $g(y_{s+1},\dots,y_n)$ are called stably equivalent. We can, on the basis of the splitting lemma, prove rigorously the relation between the Landau potential and the incompletely integrated Gibbs partition function. If the energy E can be written in the form (2.3) then one can integrate the infinite-dimensional partition function

$$Z=\int\exp(-\beta E(y_1,\dots,y_n))\mathrm{d}y \tag{2.4}$$

over the Morse variables $y_1,\dots,y_s$. Thus, the problem reduces to the finite integral (usually of small dimension)

$$Z_L=Z_L(y_{s+1},\dots,y_n,\vec{\alpha}), \tag{2.5}$$

which depends on the external conditions and on the parameters. Then the Landau potential is $\Phi=\ln Z_L/\beta$. In the thermodynamic limit Z_L can be written in asymptotic form[54,55] that is completely determined by the form of $g(y_{s+1},\dots,y_n)$.

2.4. Differentiable equivalence. The action of the group of Diff ε on the space of Landau potentials

It was shown in the previous discussion that the Landau potential can be considered an m-parameter family of smooth functions of n critical variables that contains the corresponding singularity. Below we represent some important considerations that underlie a search for this family.

The requirement of structural stability allows us to analyze the Landau potential with an accuracy up to "small motions"; that is, it is necessary to consider as equivalent all the potentials in the neighborhood of a degenerate critical point that are close to a given potential in the sense of a small motion, since they lead to results that are experimentally indistinguishable. Small motions can be generated by an interchange of variables that differ only slightly from being identical. Here the question arises: How wide must be the class of transformations to which these interchanges belong?[41] It might appear at first sight that continuous interchanges might provide structural stability.

However, the smoothness of the interchange is subject to some constraints imposed by the requirement of conservation of the singularity (determined by the degenerate critical point). Indeed, it is the singularity that determines all the

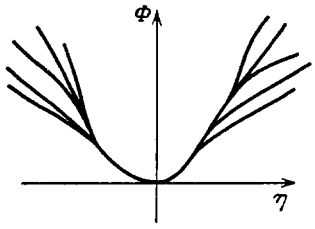

FIG. 4. Orbit of action of the group Diff ε in the space of smooth functions (it consists of all functions that have the same degenerate critical points at the origin.

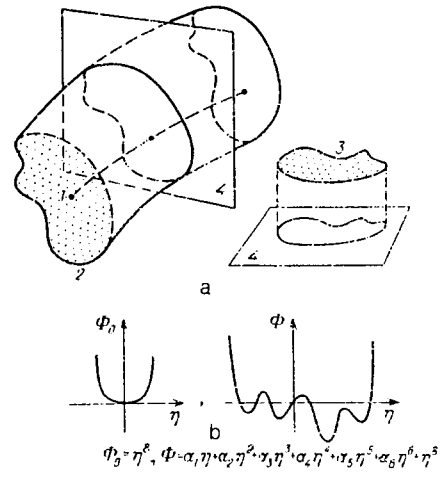

FIG. 5. Aid to understanding the deformation of the singularity of a Landau potential. a) Definition: 1) orbit of functions with a singularity; 2) nonsingular orbits; 3) representatives of the deformation; 4) deformation base. b) Example: normal form of a singularity and the representative of the deformation.

properties of a Landau potential. The decomposition of the singularity determines the phase diagram, the nature of the dependence of the components of the generalized susceptibilities on the external conditions, and other thermodynamic characteristics. Consequently, the Landau potential must be analyzed with an accuracy up to differentiable equivalence. Then the small motions are diffeomorphisms, and their smallness is provided by the first derivative, which is equal to unity.

The group Diff ε of these diffeomorphisms operates on the space of all smooth functions, and divides it into orbits. All the functions that have the same critical point belong to the same orbit (Fig. 4). In fact we shall specify a certain representative f in an orbit. The elements of Diff ε can be written in the form of vector fields v acting on ε:

$$v = \sum_i v(x_1, \ldots, x_n)\frac{\partial}{\partial x_i} \tag{2.6}$$

If we choose a diffeomorphism v that shifts f along an orbit to a nearby point g,

$$v \cdot g = f \tag{2.7}$$

in the form

$$v = v_0 + u, \quad v_0 f = f, \tag{2.8}$$

then g is expressed as

$$g = v_0 f + uf = f + uf = f + \mu_i(\mathbf{x})\frac{\partial f}{\partial x_i}, \tag{2.9}$$

where $\mu_i(\mathbf{x})$ are smooth functions.

The second term in (2.9) vanishes at a critical point, and consequently does not change the type of critical point.

The difference between Landau potentials that belong to the same orbit lies in the terms that vanish for order parameter values that describe thermodynamically stable states. In other words, all these potentials lead to equations of state that have the same solutions.

Since we are interested in Landau potentials to an accuracy up to diffeomorphisms, we can choose any representative of the orbit. For practical applications, the most convenient one is that which has the most compact form. This representative is called the normal form.

However, in order that the singularity may be found in practice, it should be considered to be in a family of functions that corresponds to the parametrization, that is, the parametrization that provides complete decomposition of this singularity into Morse critical points. The orbits on which the Diff ε group acts are mutually arranged in such a way that orbits of functions that abut an orbit of functions having a degenerate critical point, are those with critical points that arise in the decomposition of the degenerate critical point. For example, in Fig. 1b, the function $f = x^3 (\varepsilon = 0)$ belongs to the orbit with a degenerate critical point. The orbits of the function $f = x^2 + \varepsilon x$ with nondegenerate critical points ($\varepsilon \neq 0$) abut it on both sides.

The family that includes all functions, those with a singularity and those with all of its decompositions, is called the versal deformation of the singularity. The parameters of this family form a space called the deformation base. The minimum number of parameters necessary to obtain all of its decompositions is called the co-dimension of the singularity. If the co-dimension coincides with the dimension of the deformation base, then this deformation is called miniversal (Fig. 5). When the dimension of the base is higher than the co-dimension, the singularity evolves along extra parameters (this is discussed in more detail in Section 8). The deformation base includes a set of parameters for which the singularity is not completely decomposed. The set of all possible sets (strata) determine the bifurcation diagram of the singularity. At the phase stability boundaries, described with the use of a Landau potential Φ, the nondegenerate critical points merge ($d\Phi = d^2\Phi = 0$). Consequently, the phase diagram of the system is preserved in the bifurcation diagram of the singularity of the Landau potential (Fig. 6).

The bifurcation diagram of the singularity of the Landau potential means the dependence of its equilibrium values on the coefficients of the deformation base. The phase diagram is a projection of the bifurcation diagram of the singularity on the space of coefficients.

The fact that the order parameter in the phenomenological theory is always real imposes a number of constraints on the bifurcation diagram of the Landau potential. However, for the great majority of the discussions in this paper these constraints are not important.

From this analysis it can be concluded that to find the Landau potential it is first necessary to determine what degenerate critical point of maximum multiplicity it can have in the range of external conditions involved. Then from all the potentials having such a singularity it is necessary to choose the most compact, that is, it is necessary to reduce it

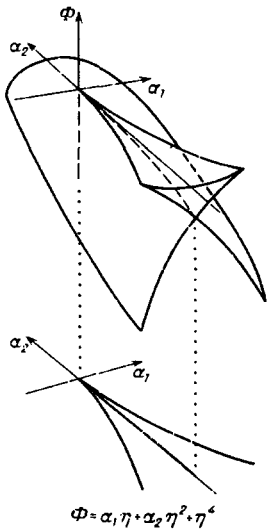

FIG. 6. Relation between the phase diagram and the bifurcation diagram of a singularity. An example of a thermodynamic potential in the neighborhood of a critical point of the liquid-vapor type.

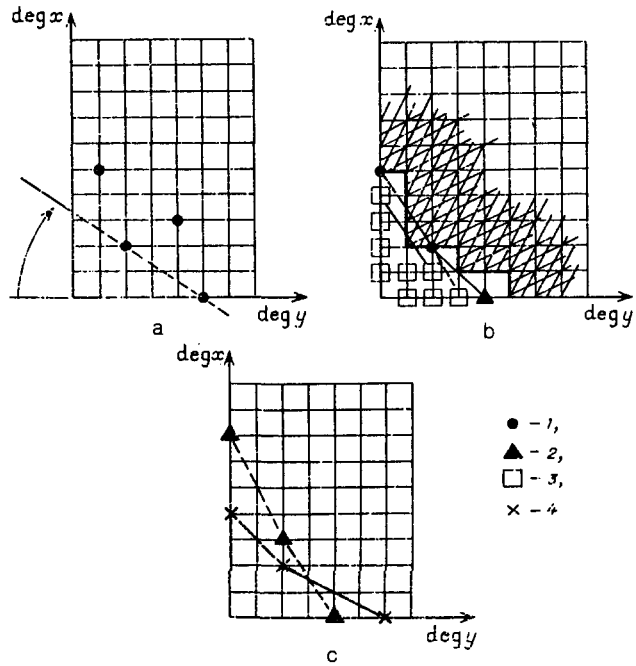

FIG. 7. Diagram relevant to the algorithm for reducing the Landau potential to normal form $f = y^5 + ax^2y^2 + bx^5y + cx^3y^4$. a) the arrow shows the rotation of Newton's ruler. b) Miniversal deformation of the normal form of the singularity $X_{1,0}$ (Ref. 28) of co-dimension 8. 1) diagonal; 2) modulus; 3) base of deformation. The monomials x^4 and xy^2 are comparable to the ideal $I_{\nabla\Phi}$. c) Globally minimal (4) and nonglobally minimal (2) normal forms.

to normal form. A miniversal deformation of the normal form of this singularity will be the desired form of the Landau potential that describes the phase transition in this region of conditions at a constant temperature.

3. ALGORITHM FOR REDUCING A SINGULARITY TO NORMAL FORM

3.1. Normal forms. Algorithm for reducing the singularity of the Landau potential to normal form

This section deals with constructive methods of reducing the Landau potential to normal form. At the present time there are many such methods. The diversity of methods to perform this operation is a result mainly of the varied complexity of the problems and the taste of the investigators.[31,32,56,57] The most general and systematic method in our opinion is the one based on the spectral sequence obtained by filtration of the Koszul complex.[28] It is not possible in this article to give a detailed and rigorous account of the spectral sequence method. Therefore, we shall briefly discuss only its algorithm.

If, in the neighborhood of a degenerate critical point, the form of the function that describes the properties of the system is not known, but a number l of parameters that depend on the external conditions are known, then this algorithm permits an exact determination of a finite number of normal forms, their form, and their miniversal deformations, one of which must be adequate to describe the properties of the system near this degenerate critical point.

The Landau potential Φ for fixed external conditions is given by a formal power series in the order parameters η:

$$\Phi = \sum_{d}^{\infty} a_d(\alpha_1, \ldots, \alpha_l)\eta^d, \tag{3.1}$$

where $d = (d_1,\ldots,d_n)$, $d_i = \deg \eta_i$.

All the polynomials in the order parameter form a ring $R[\eta]$. Ordinarily a Newton diagram is used for graphical display: Monomials in the ring are imaged by points on an exponent grid (Fig. 7a). Since all monomials are in the formal series (3.1), the potential Φ fills the entire grid. To construct the family $\tilde{\Phi}$ that contains the most degenerate critical point, it is necessary that the first q coefficients go to zero (by the implicit function theorem). It is obvious that the choice of these coefficients for a sufficiently large l is not unique. This indeterminacy is mainly what determines how many different normal forms can lay claim to being the "true" Landau potential.

In this step Φ is written as a superposition of quasihomogeneous components:

$$\tilde{\Phi} = f_0 + f_1 + f_2 + \ldots . \tag{3.2}$$

To do so one specifies on the Newton diagram the monomial of the minimum degree, lying on some coordinate axis $\eta_1^{r_1}$. A $(n-1)$-dimensional hyperplane is rotated around this monomial in the ($\deg \eta_1$, $\deg \eta_2$) plane until it passes through another monomial with nonzero coefficient (for example $\eta_1^{s_1}\eta_2^{s_2}$). Then a rotation is performed in the space $(\eta_1\eta_2\eta_3)$ to the monomial $\eta_1^{t_1}\eta_2^{t_2}\eta_3^{t_3}$, and so on until the end. As a result, the hyperplane (called Newton's ruler) passes through the monomials with nonzero coefficients

$$f_0 = a_1\eta_1^{r_1} + a_2\eta_1^{s_1}\eta_2^{s_2} + \ldots + a_n\eta_1^{i_1}\eta_2^{i_2}\ldots\eta_n^{i_n}. \tag{3.3}$$

The polynomial f_0 is called a diagonal polynomial, and it determines the partition of $\tilde{\Phi}$ into quasihomogeneous components. The latter are easy to find by moving the hyperplane parallel to the diagonal in the direction of increasing powers of the monomials.

As was shown in the previous section, differentiable equivalent Landau potentials are distinguished from one another by terms that go to zero simultaneously with the equations of state, i.e., the terms that belong to the gradient ideal $I_{\nabla\Phi}$ of the Landau potential. The elements of the gradient

ideal are polynomials that can be written as

$$\sum R_i(\vec{\eta})\frac{\partial\tilde{\Phi}}{\partial\eta_i}, \tag{3.4}$$

where $R_i(\vec{\eta})$ is an arbitrary polynomial.

Consequently, for the normal form of a potential having a given singularity, one must select the representative of the orbit of the action of the group of Diff ε that contains no terms of form (3.4). To do so we introduce the algebra U of all vector fields of the form

$$u = \sum_i R_i(\vec{\eta})\frac{\partial}{\partial\eta_i}, \quad u \in U. \tag{3.5}$$

To obtain the generators of the gradient ideal $I_{\nabla f}$ of a polynomial $f(\vec{\eta})$ it is sufficient to operate on f by the generators $\partial/\partial\eta_i$ of the algebra U. The miniversal deformation of the normal form of f is the family of polynomials in which enter all the monomials of the Q-local algebra of the singularity f, which is determined by the factor of the ring of polynomials $R[\eta]$ over the gradient ideal $I_{\nabla f}$:

$$Q = R[\vec{\eta}]/I_{\nabla f}. \tag{3.6}$$

For an infinite series this method is not constructive. In this case one used successive approximations, which converge very rapidly to the exact result. (It should be especially noted that this method has nothing to do with iterations in numerical calculations, which always given an approximate result).

First one must find the gradient ideal of f_0, by operating on it with all the fields of U:

$$I_{\nabla f_0} = R_i(\vec{\eta})\frac{\partial f_0}{\partial\eta_i}. \tag{3.7}$$

This is the first approximation to $I_{\nabla\tilde{\Phi}}$.

Then we find the gradient ideal $I_{\nabla f_1}$. To do so we operate on that part f_1 that did not enter into $I_{\nabla f_0}$, with all the fields of U that conserve f_0, (that is, from the stationary algebra of f_0):

$$sf_0 = 0, \quad s \in S_{f_0}. \tag{3.8}$$

The union of $I_{\nabla f_1}$ and $I_{\nabla f_0}$ gives the next approximation to the gradient ideal $I_{\nabla\tilde{\Phi}}$. The next step is obvious—to find the gradient ideal $I_{\nabla f_2}$. One operates on the part f_2 not included in the previous approximation $I_{\nabla\tilde{\Phi}}$ with fields from the stationary algebra $S_{f_0+f_1}$, i.e., so that

$$s(f_0 + f_1) = 0, \quad s \in S_{f_0+f_1}, \tag{3.9}$$

and so on.

In the neighborhood of a critical point of finite multiplicity this process reduces after a few steps to the local algebra of the singularity of the Landau potential

$$Q_{\tilde{\Phi}} = R[\vec{\eta}]/I_{\nabla\Phi}. \tag{3.10}$$

3.2. Structure of the local algebra of a singularity

The normal form of the Landau potential $\tilde{\Phi}$ consists of the diagonal and all the monomials of higher degree of quasihomogeneity that enter into the local algebra $Q_{\tilde{\Phi}}$ (Fig. 7b). All the rest of the monomials constitute the deformation base. If some linear combination of p such monomials belong to $I_{\nabla\tilde{\Phi}}$, then it is sufficient to include in the local algebra any $p-1$ of them. In this case the deformation of the normal form $\tilde{\Phi}$ is miniversal. The coefficients of the monomials of the local algebra lying on and above the diagonal f_0 are called the moduli. These coefficients, unlike those in the deformation base do not vary, and hence do not depend on the external conditions. The number ν of moduli is related to the multiplicity μ of the degenerate critical point and the codimension c by the equation

$$\mu = c + \nu + 1. \tag{3.11}$$

By means of this algorithm we obtain all the information on the miniversal deformation of the normal form of the singularity of $\tilde{\Phi}$.

3.3. Global minimality of the Landau potentials

To secure thermodynamic stability of an entire system as a whole, the Landau potential cannot permit infinite fluctuations of the order parameter, which lead to an infinite gain in energy. To obtain thermodynamic stability requires global minimality of the Landau potential,[4,24,45,46] that is, the Landau potential must always have its global minimum at finite values of the order parameters. This imposes a limitation on the class of functions to which the Landau potential can belong. In fact, all functions that belong to an orbit of Diff ε must be globally minimal. Small motions v cannot destroy this property.

The algorithm given above must be augmented with the criterion for the selection of the globally minimal normal forms of the Landau potential[58] (the "minifunctions of Vasil'ev[55]). For global minimality it is sufficient that the Newton diagram of the function at a minimum point of finite multiplicity satisfy two conditions: it intersects all the coordinate axes, and all its vertices have integral coordinates (Fig. 7c).

3.4. Variable parameters and moduli

The use of the algorithm augmented in this way as discussed in the last section, has a number of practical advantages. The most important one is that it permits one to go beyond the elementary catastrophe theory of Thom,[27,30] and moreover, there is no need to be limited by the standard lists of singularities given in the older works on mathematics.[28,55,59,60] The universal nature of the algorithm makes it possible to obtain the normal form for a thermodynamic system of any degree of complexity with any number of variable parameters. Furthermore, one can in this way divide the coefficients of the Landau potential into two groups: those that depend on the external conditions (the parameters of the deformation base) and those that do not (the moduli).

These groups of parameters play an important role. The bifurcation diagram in the space of deformation parameters determines the phase diagram and the other characteristics of a thermodynamic system. The moduli, however, determine the type of bifurcation diagram. For certain values of the moduli the normal form is degenerate. These values divide the space of moduli into parts. Different parts of this space correspond to the normal forms of the same type, but with qualitative differences in the bifurcation diagrams.

Variation of the moduli in the phenomenological theory of phase transitions is not permitted, since it leads to the

possibility of them taking on the segregated values. The corresponding normal forms then belong to another type.

Along with the advantages of this algorithm in the phenomenological theory of phase transitions, there is an important drawback. In this form it is applicable only to Landau potentials with trivial symmetry, those that describe the liquid-vapor type of phase transitions, transitions in binary mixtures, and the like. However, most phase transitions in solids are accompanied by changes in the symmetry of the system. Consequently, the algorithm for reduction to the normal form of the Landau potentials that describe these transitions must take into account the transformation properties of the order parameter.

4. DETAILS OF THE ALGORITHM FOR THE REDUCTION OF A SINGULARITY TO THE NORMAL FORM, WITH ALLOWANCE FOR SYMMETRY

4.1. Symmetry of the Landau potential and the details of the algorithm for the reduction of a singularity to normal form. Equivalent Diffeomorphisms, vector fields on the manifold of orbits

In the construction of the normal form of a function with allowance for symmetry there is a temptation to proceed in the following way: first construct the normal form by the method outlined in section 3.1, and then keep only those terms that are invariant under the symmetry group of the system.[31,45,46] However, this way of constructing the normal form is not applicable for many reasons. The normal form found in this manner will be symmetric for functions of general form. But it will not be the normal form for a symmetric function. The symmetry of this normal form is accidental and not characteristic, since any smooth replacement of variables in the class of functions of a general form inevitably will break the symmetry of the normal form. Consequently, in the reduction to normal form of functions that are invariant under the group G_0 the symmetry must not be broken.

The Landau potentials $\tilde{\Phi}$ that belong to the same orbit action of Diff ε must have the same symmetry. For this to occur it is necessary first, that $\tilde{\Phi}$ be polynomials in the invariants of the complete rational basis (1.5), and second, the diffeomorphisms of Diff ε must be equivalent. In this case the generators of the algebra of the vector fields must have the form[49]

$$u_k = \sum_{i=1}^{n} \nabla_i J_k \frac{\partial}{\partial \eta_i}, \quad k = 1, 2, \ldots, m, \tag{4.1}$$

where J_k are the basis invariants.

For L-groups generated by reflections[61,62] all the basis invariants are algebraically independent. The number of them coincides with the dimension of the representation τ of the space group G_0, i.e., $m = n$. Then the algebra of the vector fields, U^G, also has n independent generators. For L-groups that are not generated by reflections, $m - n$ algebraically dependent invariants are included in addition to the n independent ones. In this case there are $m - n$ relations,

$$F_j(J_1, \ldots, J_m) = 0, \quad j = 1, 2, \ldots, m-n, \tag{4.2}$$

called syzygies, between the invariants of the basis.

The dimension of the corresponding algebra U_G is higher than the dimension of the representation, n, and the number of invariants, m.

Besides fields of the form (4.1) it is necessary to include

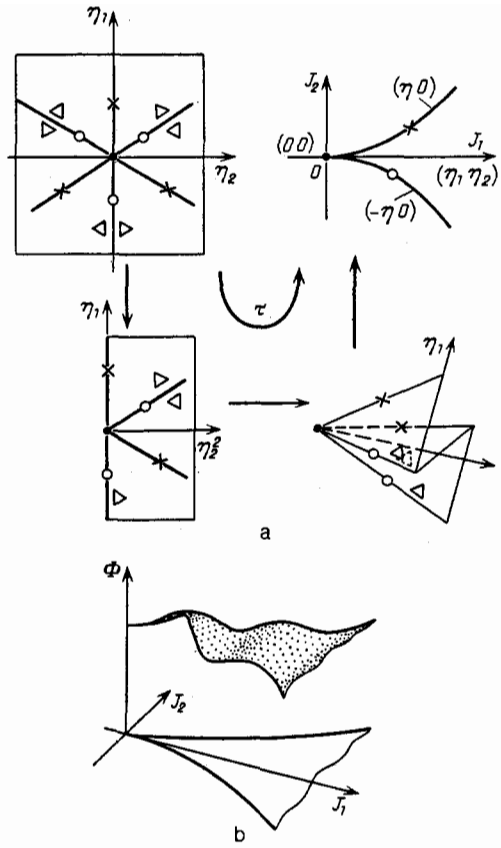

FIG. 8. Description of symmetric singularities. a) space and manifold M of orbits for the group $L = C_{3v}$; $M_{C_{3v}}$ is the image of the mapping τ: $J_1 = \eta_1^2 + \eta_2^2$, $J_2 = \eta_1^3 - 3\eta_1\eta_2^2$. b) Graph of the Landau potential invariant with respect to the group $L = C_{3v}$.

in U^G all their commutators. The form of the complete rational basis of invariants (1.5) gives the mapping from the space of the components of the order parameters ε in the space of invariants, J, the image of which is called the manifold M of orbits of the action of the L-group on ε (Refs. 16,17,63,64). The manifold M of orbits consists of submanifolds (strata) of various dimensions corresponding to the phases of different symmetry (Fig. 8a). The Landau potential is a family of functions that are defined on this manifold (Fig. 8b). In this sense the description of symmetric singularities is analogous to the description of boundary singularities.[28,65,66]

It is obvious that reduction to normal form on the manifold M of orbits is more convenient than on ε space. Then the generator (4.1) of the algebra U^G can be written as[49]

$$V_k = \sum_{i,l} \nabla_i J_k \nabla_l J_l \frac{\partial}{\partial J_l}. \tag{4.3}$$

Let us point out other distinctions between the symmetric case and the nonsymmetric case. If the order parameter that describes the phase transition transforms according to an irreducible representation of the group G_0, then the meaning of the term quasihomogeneous reduces to the meaning of homogeneous, since the invariants are homogeneous in the components of the order parameter. Quasihomogeneity obtains only between irreducible components of a reducible representation. The co-rank of the singularity of the Landau potential is equal to the dimension of the order parameter.

4.2. An example of a cubic ferroelastic

Let us illustrate the algorithm for the reduction to normal form of a Landau potential that describes the thermodynamic behavior of a cubic ferroelastic. We consider a phase transition in a crystal of class O_h, which brings about spontaneous uniaxial strain. The matrices of the corresponding two-dimensional representation of the group $G_0 = O_h$ form the group $L = C_{3v}$. The components of the order parameter $(\eta_1\eta_2)$ are expressed in terms of the diagonal components u_{ii} of the strain tensor in the form of symmetric linear combinations:

$$\eta_1 = \frac{1}{\sqrt{6}}\cdot(2u_{zz} - u_{xx} - u_{yy}),$$
$$\eta_2 = \frac{1}{\sqrt{2}}\cdot(u_{xx} - u_{yy}). \tag{4.4}$$

The complete rational basis of invariants consists of two polynomials

$$J_1 = \eta_1^2 + \eta_2^2,$$
$$J_2 = \eta_1^3 - 3\eta_1\eta_2^2. \tag{4.5}$$

The generators of the algebra of vector fields $U^{C_{3v}}$ are

$$u_1 = \eta_1\frac{\partial}{\partial\eta_1} + \eta_2\frac{\partial}{\partial\eta_2},$$
$$u_2 = (\eta_1^2 - \eta_2^2)\frac{\partial}{\partial\eta_1} - 2\eta_1\eta_2\frac{\partial}{\partial\eta_2}. \tag{4.6}$$

The manifold M of orbits of the group $L = C_{3v}$ is shown in Fig. 8a. Then reduction of the Landau potential to normal form will be carried out on this manifold. The generators of $U^{C_{3v}}$ are written as

$$V_1 = J_1\frac{\partial}{\partial J_1} + J_2\frac{\partial}{\partial J_2},$$
$$V_2 = J_2\frac{\partial}{\partial J_1} + J_1^2\frac{\partial}{\partial J_2}. \tag{4.7}$$

The expansion of the landau potential in a formal Taylor series in powers of the invariants of the complete rational basis of invariants has the form

$$\Phi = \Phi_0 + a_1J_1 + b_1J_2 + a_2J_1^2 + c_1J_1J_2 + b_2J_2^2 + \dots \ . \tag{4.8}$$

If the experiment admits the possibility of varying four external conditions, such as the temperature, the pressure, the concentrations of two different admixtures, then by the appropriate choice of parameters it is possible to set to zero four coefficients of the terms of lowest degree in expansion (4.8). As we have already noted, this choice may be nonunique. Depending on the kind of choice, one can obtain normal forms at different singularities. In this case the coefficients a_1, b_1, c_1, and a_2 go to zero. The partition into homogeneous parts $f_0, f_1, f_2, \dots$ of the remaining "tail" of the series (4.8) is shown in Fig. 9. The operation of the equivalent vector fields (4.7) on the diagonal $f_0 = J_1^3 + J_2^2$ gives the generators of the gradient ideal I_{Vf_0}:

$$V_1f_0 = 3J_1^3 + 2J_2^2 \in I_{\nabla f_0},$$
$$V_2f_0 = 5J_1^2J_2 \in I_{\nabla f_0}. \tag{4.9}$$

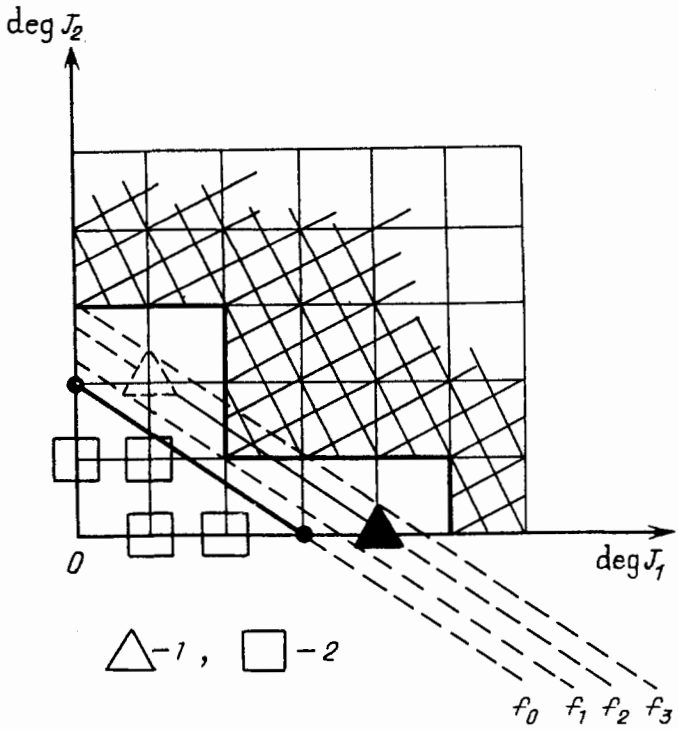

FIG. 9. Miniversal deformation of the normal form of the singularity of the Landau potential invariant with respect to the group $L = C_{3v}$. The dashed lines indicate the quasihomogeneous components; the gradient ideal is cross-hatched. 1) modulus; 2) deformation base.

The gradient ideal $I_{\nabla\Phi}$ consists of all polynomials of the form

$$P = P_1(J_1, J_2)(J_1^3 + J_2^2) + P_2(J_1, J_2)J_1^2J_2, \tag{4.10}$$

where P_1 and P_2 are arbitrary polynomials invariant under $L = C_{3v}$.

The local algebra $Q = R(J_1, J_2)/J_{\nabla\Phi}$ of the singularity of the Landau potential includes the terms (see Fig. 9).

$$Q = \{1, J_1, J_2, J_1^2, J_1J_2, J_1^3, J_2^2, gJ_1^4 + J_1J_2^2\}, \tag{4.11}$$

where $g \neq 3/2$.

Consequently, a miniversal deformation of a normal form describing a phase transition in this ferroelastic with variations of four external conditions is written as

$$\Phi = a_1J_1 + b_1J_2 + a_2J_1^2 + c_{12}J_1J_2 + J_2^2 + J_1^3 + gJ_1^4 + J_1J_2^2. \tag{4.12}$$

We note that the linear combination $gJ_1^4 + J_1J_2^2$, in the local algebra lies above the diagonal f_0 (Fig. 9). By the definition given in section 3.2, the coefficient g is a modulus and does not depend on the external conditions.

5. CONSTRUCTION OF PHENEMOLOGICAL MODELS WITH A MULTICOMPONENT ORDER PARAMETER

5.1. Structurally stable thermodynamic potentials describing phase transitions with a multicomponent order parameter: a) The group $L = C_{3v}$; b) the group $L = O_h$, (cubic ferroelectrics and ferromagnets; c) the group $L = C_4$ (gadolinium molybdate)

a) *The group* $L = C_{3v}$. The group $L = C_{3v}$, considered in the last section, is very popular in the phenomenological theory of phase transitions (see, e.g., Refs. 13, 18, 19). Such

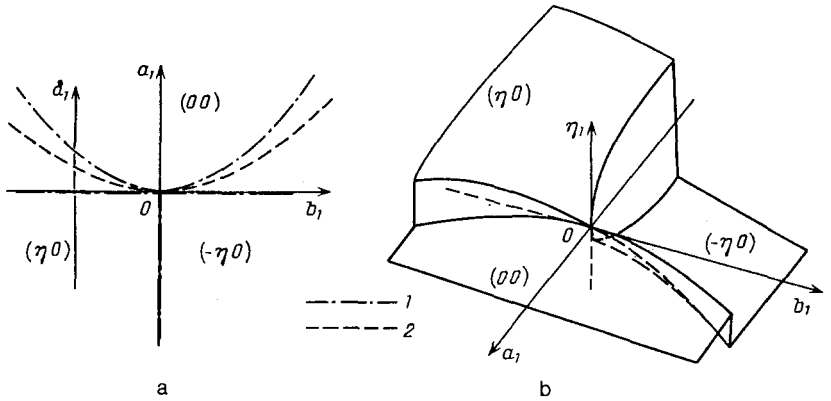

FIG. 10. Dependence of the bifurcation diagram (a) the manifold of states (b) on the modulus b_1 for the potential (5.1). 1) Phase stability boundary; 2) second-order phase transition.

a two-dimensional representation is frequently encountered in the description of phase transitions with wave vector k from various points of the Brillouin zone having very different space group symmetries (see, e.g., Refs 67–71). However, some widely used Landau potentials with the group $L = C_{3v}$ are incorrect from the point of view of the theory of singularities. Let us see where we are led in an attempt to describe phase transitions in the space of two varying external conditions (such as the temperature and pressure) by expanding Φ to fourth degree in a series in the small order parameter

$$\Phi = a_1 J_1 + b_1 J_2 + a_2 J_1^2. \tag{5.1}$$

The symmetry of the order parameter admits the existence of three low-symmetry phases: the phase $(\eta 0)$, in which $\eta_1 > 0$ and $\eta_2 = 0$, the phase $(-\eta)$, in which $\eta_1 < 0$ and $\eta_2 = 0$, and the regular phase $(\eta_1\eta_2)$, in which $\eta_1 \neq \eta_2 \neq 0$. The form of the bifurcation diagram of potential (5.1) as a function of the modulus b_1 is shown in Fig. 10a. The manifold of states called in catastrophe theory the catastrophe manifold or the catastrophe surface[26,27,31] (the dependence of the values of the component η_1 of the order parameter on the phenomenological coefficients) is shown in Fig. 10b.

The results found within the framework of this model (5.1) are nonphysical. In fact, as the parameter b_1 is varied the component η_1 of the order parameter undergoes a finite jump at the point $b_1 = 0$; even though the boundaries of the phases (η_0) and $(-\eta_0)$ coincide. These facts cannot be interpreted as a first-order phase transition or as two second-order transitions through an intermediate phase $(\eta_1\eta_2)$.

It follows from the theory of singularities that this model is structurally unstable. Any small motion in the class of functions that are invariant under $L = C_{3v}$ results in a qualitative change in the results. As the theory of singularities shows, when two external conditions are varied, the Landau potential, which is invariant under $L = C_{3v}$, goes over into the form

$$\Phi = a_1 J_1 + b_1 J_2 + J_1^2 + b_2 J_2^2, \tag{5.2}$$

where a_1 and b_1 are the variable parameters and $b_2 \neq 0$ is a modulus. The phase diagram and the manifold of states of model (5.2) are shown in Fig. 11a and 11b, respectively. On the phase diagram there is a region of stability of the phase of lowest symmetry $(\eta_1\eta_2)$, which abuts the phase $(\eta 0)$ and the phase $(-\eta 0)$ along a line of second-order phase transitions. These results are structurally stable and are not altered with small motions.

b) *The group* $L = O_h$ (cubic ferroelectrics and ferromagnetics). It is possible to adduce many more examples similar to the ones considered. One of them could be the Landau potential with the space group $L = O_h$. The potential with these transformation properties for the order parameter usually describes phase transitions in the ferroelectrics of the type of $BaTiO_3$,[7,72,73] cubic ferromagnets of the type RFe_2 of RCo_2, where R is a rare-earth ion,[74,75] and other systems. The series expansion to the sixth degree that is used for this is

$$\Phi = a_1 J_1 + a_2 J_1^2 + a_3 J_1^3 + b_1 J_2 + d_1 J_3 + c_{12} J_1 J_2, \tag{5.3}$$

where $J_1 = \eta_1^2 + \eta_2^2 + \eta_3^2$, $J_2 = \eta_1^2\eta_2^2 + \eta_2^2\eta_3^2 + \eta_1^2\eta_3^2$, and $J_3 = \eta_1^2\eta_2^2\eta_3^2$ have a form similar to the deformation of the normal form of co-dimension two. The corresponding phase diagram must be two-dimensional. An attempt to vary the third parameter (a modulus) in model (5.3) leads to unphysical, structurally unstable results. However, the

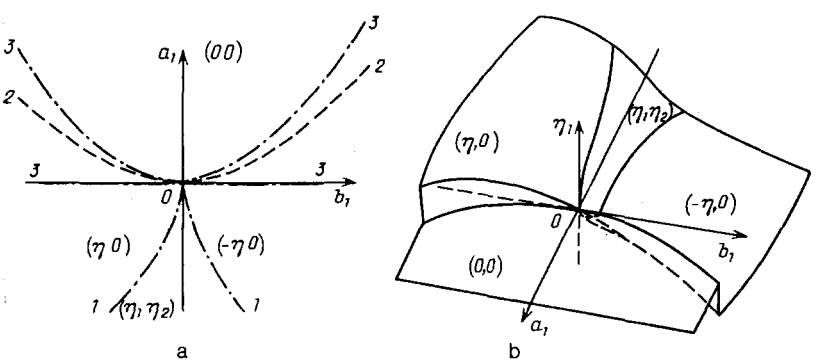

FIG. 11. Phase diagram (a) and manifold (b) for the potential (5.2). 1) Second-order phase transition; 2) first-order phase transition; 3) phase stability boundary.

phase diagram in the space of the three external conditions (temperature, pressure, and the concentration of an isomorphic admixture) is of practical interest for these compounds. To describe the experiment one needs a normal form of the singularity of the Landau potential with a co-dimension of three and, consequently, a degree no less than eight.

c) *The group* $L = C_4$ (gadolinium molybdate). A still higher degeneracy occurs in the variation of the modulus in the Landau potential with the group $L = C_4$ (for example, the primary order parameter that describes the phase transition in gadolinium molybdate has this symmetry[76,77]).

The group $L = C_4$ is not generated by reflections. The basis of the invariants consists of three polynomials in the components of the order parameter ($\eta_1 = r\sin\varphi$, $\eta_2 = r\cos\varphi$):

$$J_1 = r^2, \quad J_2 = r^4\cos 4\varphi, \quad J_3 = r^4\sin 4\varphi. \tag{5.4}$$

The invariants are related by the syzygy

$$J_1^4 = J_2^2 + J_3^2. \tag{5.5}$$

An expansion of Φ in a series in powers of the invariants (5.4) to the fourth degree

$$\Phi = a_1J_1 + b_1J_2 + d_1J_3 + J_1^2 \tag{5.6}$$

coincides in form with the deformation of the normal form K of a singularity of co-dimension codim $K = 1$, in which a_1 is a variable parameter and b_1 and d_1 are moduli. Variation of both moduli led Galam and Hatch[78] to the paradoxical conclusion that a) either there exists an isostructural phase transition without a critical point of the liquid-vapor type, with the attendant possibility that the critical point might be circumvented, or b) some regions of the phase diagram are forbidden because of the symmetry of the problem. However, a structurally stable model of a potential that is invariant under the group $L = C_4$, unlike (5.6), removes this contradiction. Figure 12a,b shows the corresponding dependence of the one-dimensional phase diagram of the model (5.6) on the moduli b_1 and d_1 and the phase diagram of a miniversal deformation of the normal form

$$\tilde{\Phi} = a_1J_1 + b_1J_2 + d_1J_3 + J_1^2 + gJ_2^2, \tag{5.7}$$

where a_1, b_1, and d_1, are variable parameters and g is a modulus. At each point of the line $b_1 = d_1 = 0$ of the model (5.6) there coexist an infinite number of solutions of the equation of state of the type $(\eta_1\eta_2)$ ($\eta_1 \neq 0$, $\eta_2 \neq 0$, $\eta_1 \neq \eta_2$). In the stable model the "filament" $b_1 = d_1 = 0$ is split into a cone with an astroid base, within which two isostructural low-symmetry phases $(\eta_1\eta_2)$ coexist. The isostructural phase transition takes place on the surface that joins the opposite edges of the cone; these edges, in turn, are lines of critical points of the liquid-vapor type.

In this way, the reduction of the thermodynamic potential Φ to a structurally stable form eliminates the nonphysical results.

5.2. Models of the theory of static concentration waves and their normal forms

The constructive use of the methods of the theory of singularities with allowance for symmetry in the description of phase transitions is not confined to the Landau theory. These methods can also be used with success in some microscopic theories of phase transitions—for example in the Gorskii–Bragg–Williams (GBW) theory of the ordering of alloys or in the theory of static concentration waves (SCW). In Refs. 79–81 the authors have formulated the problem of constructing the normal form of the singularity of a model thermodynamic potential for a theory of the GBW- or SCW-type in the neighborhood of a given critical point. This approach automatically includes a test of the potentials of the theory of static concentration waves for structural stability, and, consequently, a test of the physicalness of the results. Moreover, with this approach one can convert the transcendental equations of the theory to algebraic equations, which considerably simplifies the applications—construction of the phase diagram, the dependences of the components of the order parameter on the external conditions, etc.

In particular, Gufan[79] has examined the thermodynamic potential of the theory of static concentration waves for binary alloys:[81]

$$F = \frac{1}{2}\sum_{R,R'} V(R - R')n(R') + T\sum(n(R)\ln n(R) - (1 + n(R))\ln(1 - n(R))), \tag{5.8}$$

$$\sum_R n(R) = cN = N_A,$$

where c is the concentration of atoms of type A.
After introducing symmetric coordinates $\eta_i = \Sigma_k\, \alpha_{ik}^{-1} p_k$ and the normalization conditions

$$\sum_{i=1}^{m} p_i = \sum_{i,k} \alpha_{ik}\eta_k = cm \tag{5.9}$$

and recognizing that in the factorization of a commuting representation into irreducible representations each representation appears only once, one can reduce the potential (5.8) to

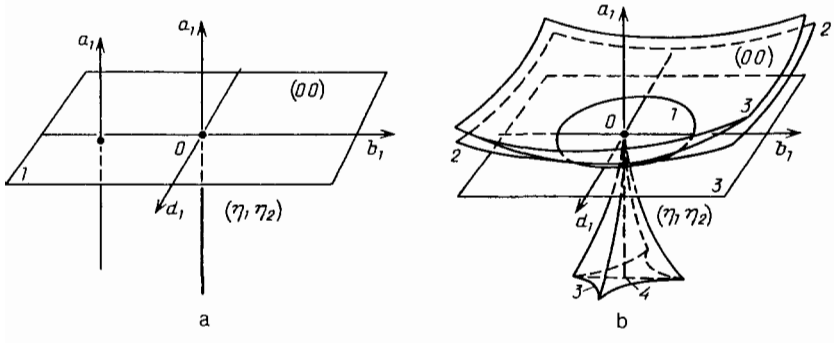

FIG. 12. a) "Phase diagram" of model (5.6); b) phase diagram of the structurally stable model (5.7). 1) second-order phase transition; 2) first-order phase transition; 3) phase stability boundary; 4) isostructural phase transition.

$$f = \frac{\Sigma m}{NT} \cdot F$$

$$= \omega_1 c + \omega_{11} c^2 - \sum_{i=1}^{s} \omega_{ii} \eta_i^2 + \sum_{i=1}^{w} [p_i \ln p_i - (1 - p_i) \ln(1 - p_i)], \tag{5.10}$$

where $\omega_{ij} = W_{ij}/T$, and W_{ij} are the energy parameters of the theory. The possibility of the decomposition of a solid solution was not taken into account in Refs. 79–81, and consequently the concentration c is considered an external condition and not a minimization parameter. For $T \gg 1$ and $c \neq 0$ or 1, there exists on the line

$$-2\omega_{ii} + \frac{1}{c(1-c)} = 0$$

a single degenerate critical point $c = 1/2$, in the neighborhood of which the potential (5.10) is expanded in a formal series. The number of variable external conditions for each model (5.10) is fixed. In addition to the concentration, only the various ω_{ii} are involved. In other respects the algorithm for reduction to normal form is no different in this case from that put forth in section 4.1. In Refs. 79–81 the normal forms of the singularities of potentials of static concentration waves were obtained for the cases of three and four sublattices equivalent in paraphrase, and a structurally stable model was constructed that describes the ordering of hydrogen in HfV_2H_4, a compound with the structure of the cubic Laves phase.

6. LOCAL NATURE OF THE PHENOMENOLOGICAL THEORY OF PHASE TRANSITIONS

6.1. Types of order parameters and the co-rank of the singularity of the Landau potential

In the usual formulation of the problem the nonequilibrium probability density $\delta\rho(\mathbf{r})$ is expanded in terms of the basis functions of the irreducible representations of the space group G_0 [see Eq. (1.1)]. The coefficient of any of the basis functions in this expansion is understood as being the only critical mode out of all of the generalized internal coordinates that are condensed in the phase transition. The co-rank of the singularity of the thermodynamic potential is taken to be equal to the dimension of the irreducible representation that induces the phase transition; that is, for these transitions the Landau potential is a non-Morse function only over one of the linear combinations comprised of all possible physical quantities that transform by this irreducible representation. As a result of the interaction with the linear combination (usually called the proper order parameter), induced deviations of other noncritical degrees of freedom arise. If the transformation properties of these degrees of freedom are the same as those of the proper order parameter, then they are called pseudo-proper order parameters (see, e.g., Refs. 83 and 84). Nonzero components of an order parameter of another symmetry can arise in the field of the proper order parameter if there exist mixed invariants that are linear in these components.[85,13] The inclusion of nonintrinsic and pseudointrinsic order parameters leads to a singularity that is stably equivalent to the original singularity.[27,28]

Actually, situations are frequently encountered where the phase transitions occur as a result of the critical behavior of several modes of the same symmetry. These order parameters have been called quasi-proper.[86] It is not possible to distinguish the proper order parameter among the critical modes, since they are all on an equal footing. In this situation unusual effects can occur (for more detail, see section 8). Here the singularity differs qualitatively from that which can exist in the case of a single critical mode and has a co-rank that is higher than the dimension of the corresponding representation.

6.2. Local nature of the phenomenological theory of phase transitions

In considering the Landau potential from the point of view of the theory of singularities it is necessary to introduce some important corrections to the now-traditional understanding of this concept.

Since the Landau potential is not known *a priori*, it is frequently represented as a Taylor series that must converge to some hypothetical "true" potential. Inclusion of the successive terms of the expansion is regarded as an increase in the accuracy of the approximation to the true value of the potential. In such an analysis, as in perturbation theory, a small order parameter is required.

Not only is an expansion in a small parameter not needed in the theory of singularities, but there is no limitation at all on the size of the order parameter. The number of variable parameters in an experiment is in fact determined by the maximum possible degree of singularity of the "true" thermodynamic potential. If this potential is given by a converging series, then with the apparatus of the theory of singularities smooth nonlinear interchanges of the order parameter can convert it to a polynomial of finite degree. This polynomial is equivalent to the "true" potential with an accuracy to terms that vanish exactly along with the gradient of the potential. An interchange of the variables that effect this reduction is expressed by some generally unknown, infinite series.

The potential that is obtained in this manner leads by definition to results that coincide qualitatively with those of the "true" potential.

The theory of singularities imposes a limit on the degree of localization. That is, the Landau potential must describe a phase transition in the region of external conditions that allows merging of all the observable singularities in a single point. In this case all that has been said previously is applicable. If the region of external conditions is such that this cannot be done, it is necessary to use the generalization to the case of multisingularity presented in Ref. 87. Nevertheless, the requirement of locality must be satisfied near each of the remaining isolated singularities.

Thus, not only does the application of the theory of singularities not require an expansion in a small parameter, it also helps to avoid errors and "paradoxes" that arise in a theory with a small order parameter.

In this same context we must understand the discarding of unimportant terms in the expansion for the description of an isolated second-order phase transition[4] with the use of the potential (1.4). The result of the expansion (1.4) then coincides with the normal form with a single variable parameter, and therefore for a local description of a second-order phase transition it is sufficient to use either of them. (Following Ginzberg and his coworkers[88,89] we shall assume that we can almost always ignore a sharp increase in the probability of fluctuations in the order parameter on the real temperature scale.)

Already a small increase in the number of variable external parameters with codim > 1 and in the dimension of the representation that induces the phase transition (co-rank higher than 1) will bring about results in the theory of singularities that are quite different from those obtained in a theory with a small order parameter. Moreover, the phenomenological theory of second-order phase transitions has long ago outgrown the problem of the description of an isolated second-order phase transition. The object of study of the theory has already become the description of the entire system of phase transitions observed in some region of external conditions.

7. PHASE TRANSITIONS WITH A QUASI-INTRINSIC ORDER PARAMETER. MODEL OF A FERROELECTRIC OF THE KDP TYPE

The preceding discussions of the co-rank of a singularity must be augmented with an investigation of the thermodynamic behavior of a system during a phase transition with a quasi-proper order parameter. The structures of the admissible low-symmetry phases in this case are the same as in a phase transition describable by a single critical mode. Nonetheless, there are differences in the thermodynamics of the transition. In the first place, they are expressed in the appearance of isostructural phase transitions within the low-symmetry phases, these phase transitions being accompanied by anomalies in the dependences of the order parameters and the generalized susceptibilities on the external conditions. Some anomalies in these dependences, although they are not very conspicuous, occur in the supercritical region of isostructural phase transitions.

Below we use for illustration the model of a ferroelectric crystal of the potassium dihydrogen phosphate (KDP) group. The unit cell of KDP has been well described in Refs. 73 and 90. The lowering of the symmetry in KDP is given by the representation $\tau_3(\mathbf{k}=0)$ of the group $I\bar{4}2m(D_{2d}^{12})$. The component of the polarization vector P_z, along the c-axis, joining the K and P ions, as well as a number of other degrees of freedom transform according to this representation. Among these degrees of freedom is the symmetric x-coordinate, which is responsible for the ordering of the protons in the O–H–O bonds that join the two upper and the two lower oxygen ions in the PO_4^{3-} tetrahedron. Even though the polarization is due to a displacement of the heavy ions, KDP is usually regarded as an order-disorder type of ferroelectric, and the phonon degrees of freedom are accounted for in a pseudointrinsic way.[91–93] In general, P_z and x form a reducible order parameter, $\eta = P_z$ and $\xi = x$, on which the Landau potential depends, and there are no real grounds not to take into account the criticality of the two coordinates.

The matrices of the corresponding reducible representation $\tau = \tau_3 \oplus \tau_3$ form the group $L = C_2$. In the complete rational basis of invariants we find three functions

$$J_1 = \eta^2, \quad J_2 = \xi^2, \quad J_3 = \eta\xi, \tag{7.1}$$

related by a syzygy of the form

$$J_3^2 = J_1 J_2. \tag{7.2}$$

To obtain the Landau potential Φ that gives a qualitatively correct description of experiment, it is necessary to bring together all the observable singularities into a single degenerate critical point and find the normal form of the corresponding singularity. The equivalent vector fields (4.1) for the reduction of Φ to normal form in the case $L = C_2$ are written as

$$V_1 = \eta\frac{\partial}{\partial\eta},$$

$$V_2 = \xi\frac{\partial}{\partial\xi}, \tag{7.3}$$

$$V_3 = \eta\frac{\partial}{\partial\xi} + \xi\frac{\partial}{\partial\eta}.$$

In addition to the fields (7.3), the commutator

$$V_4 = [V_2 V_3] = \eta\frac{\partial}{\partial\xi} - \xi\frac{\partial}{\partial\eta}. \tag{7.4}$$

also enters into the algebra U^{C_2}.

As shown in Refs. 21 and 86, a miniversal deformation of the normal form of fourth degree and co-dimension of three

$$\Phi = a_1 J_1 + b_1 J_2 + d_1 J_3 + J_1^2 + J_2^2 + g J_1 J_2, \tag{7.5}$$

besides describing a second-order phase transition from the phase (00) ($\eta = 0$, $\xi = 0$) into the phase ($\eta\xi$) ($\eta \neq 0$, $\xi \neq 0$), also describes an isostructural transition within the low-symmetry phase. The phase diagram of model (7.5) is depicted in Fig. 13. The order parameter undergoes a bend on the thermodynamic path that passes through the supercritical region of an isostructural phase transition, and on the curve of the generalized susceptibility as a function of the temperature there is an anomaly of the "plateau" type. A similar anomaly is observed on the temperature dependence of the dielectric permittivity of KDP. However, as is known from experiment,[94] the ferroelectric phase transition in KDP, with the admixture of a small amount of deuterium becomes a first order transition, close to a second-order phase transition. The thermodynamic path of a KDP crystal in the temperature/deuterium-content space passes through the tricritical point. To reveal this tricritical point on the phase diagram, it is necessary that at least one of the coefficients of the invariants of fourth degree in the order parameter be variable. If we take the coefficient a_2 as the variable parameter, with $J_1^2 = \eta^4$, then the diagonal f_0 has the form

$$f_0 = \eta^6 + \eta^2\xi^2. \tag{7.6}$$

The use of the algorithm given in section 4 gives, as a

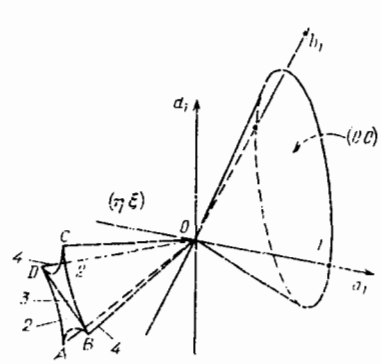

FIG. 13. Phase diagram of model (7.5). 1) second-order phase transition; 2) phase stability boundaries; 3) isostructural phase transition; 4) lines of critical points of the liquid-vapor type. Inside the cone OABCD two isostructural phases with symmetry $(\eta_1\eta_2)$ coexist.

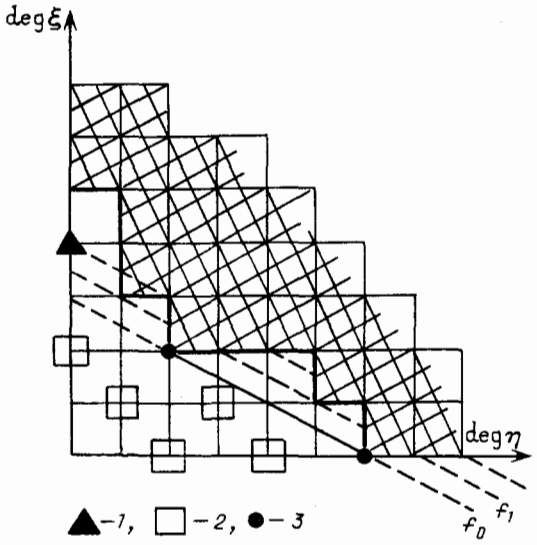

FIG. 14. Miniversal deformation of the normal form of the singularity of a Landau potential with a quasi-proper order parameter. The dashed lines show the quasi-homogeneous components; the gradient ideal is cross-hatched. 1) modulus; 2) deformation base; 3) diagonal f_0.

result of a miniversal deformation of the normal form (Fig. 14),

$$\Phi = a_1 J_1 + b_1 J_2 + d_1 J_3 + a_2 J_1^2 + c_{13} J_1 J_3 + J_1 J_2 + J_1^3 + g_1 J_2^2, \tag{7.7}$$

where a_1, b_1, d_1, a_2, and c_{13} are variable parameters and g_1 is a modulus. The phase diagram of model (7.7) is five-dimensional. Its typical three-dimensional and two-dimensional cross sections are shown in Fig. 15. On the two-dimensional cross section the line of second-order phase transitions $(00) \to (\eta\xi)$ and the tricritical point B turn into a line of first-order phase transitions. Within the phase $(\eta\xi)$, as in model (7.5), passes a line of isostructural phase transitions, which terminates at a tricritical point of the liquid-vapor type. The thermodynamic path $\alpha\alpha'$, which corresponds to KDP, intersects the line of $(00) \to (\eta\xi)$ phase transitions near the tricritical point and passes through the subcritical region of isostructural phase transitions. Figure 16 demonstrates the dependence of the generalized susceptibility

$$\chi_{\eta\eta} = \Phi_{\xi\xi}'' / [\Phi_{\eta\eta}'' \Phi_{\xi\xi}'' - (\Phi_{\eta\xi}'')^2]\big|_{\Phi_i = 0} \tag{7.8}$$

on the temperature along the path $\alpha\alpha'$. Deuterization leads to a change in the thermodynamic path from $\alpha\alpha'$ to $\beta\beta'$. The new path intersects the line of first-order phase transitions and passes far from the supercritical region of isostructural phase transitions. The "plateau" on the curve of the susceptibility as a function of the temperature vanishes. A variation in the third external condition, the hydrostatic pressure for example, is equivalent to motion along the third coordinate of the three-dimensional cross section of the complete phase diagram. On the temperature-deuterization plane this shows up in a separation of the critical point of the isostructural phase transitions from the line of the ferroelectric phase transition, and consequently, in an elongation of the "plateau" of the susceptibility. This elongation has been observed experimentally in KDP with an increase in the hydrostatic pressure.[95]

The thermodynamic behavior in the supercritical region of isostructural phase transitions induced by a quasi-proper order parameter thus provides an explanation for the presence and evolution of the "plateau" on the temperature dependence of ε in KDP. We note that this type of isostructural phase transition differs from that studied in Ref. 96. The hysteresis of such a transition contracts as the high-symmetry phase is approached. Below the critical point the isostructural phase transition must be accompanied by a jump from the state with large polarization and a proton subsystem with a low degree of order to a state with a small polarization and a high degree of hydrogen order. By analogy with the structural phase transition that occurs with a change of order parameter, this isostructural phase transition should be called a transition with a "quasi-change" in the order parameter. Transitions of this type should be encountered frequently, for example in piezoelectrics,[86] weak ferromagnets,[97] and multicomponent alloys.[98]

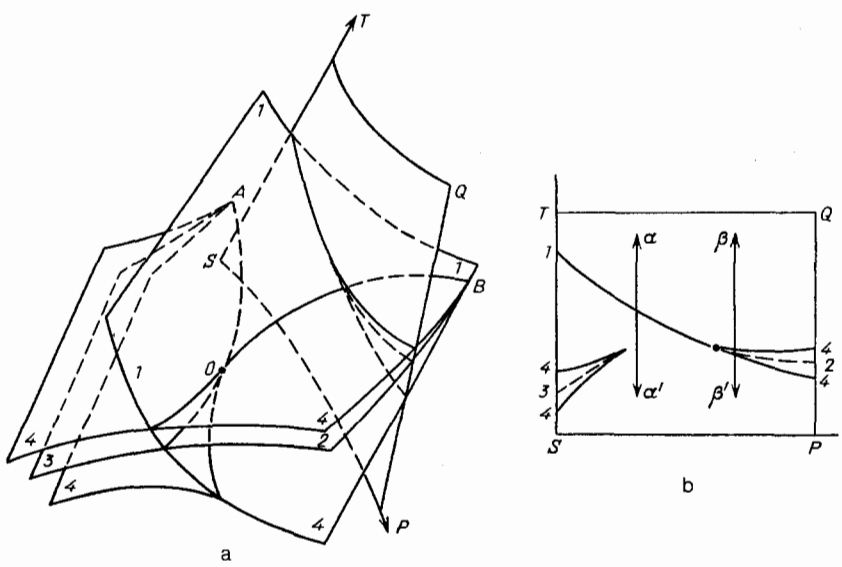

FIG. 15. Typical cross sections of the phase diagram of model (7.7). a) three-dimensional cross section; b) two-dimensional cross section TSPQ. 1) second-order phase transition; 2) first-order phase transition; 3) isostructural phase transition; 4) phase stability boundaries; OB is the line of tricritical points; AO is the line of critical points of the liquid-vapor type.

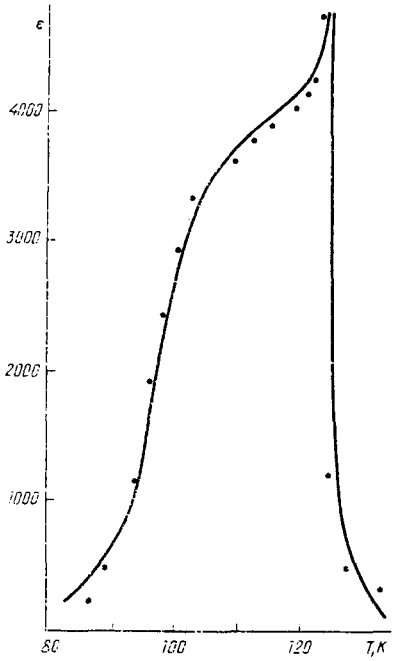

FIG. 16. Temperature dependence of the dielectric permittivity of a KDP crystal. The points represent experimental results; the line represents the theory (calculation with the model) (7.7).

8. RESTRUCTURING OF PHASE DIAGRAMS AND OF THE CRITERIA FOR NONLINEARITY OF THE LANDAU POTENTIAL

8.1. Restructuring of phase diagrams and of the criteria for determining the co-dimensionality of the "true" singularity of the thermodynamic potential

Up to this point in this paper we have posed the question: What sort of singularities can the Landau potential have for a fixed number of variable parameters that determine the external conditions? However, the problem of determining the "true" Landau potential can be formulated in another way.

In some region of the external conditions the type of singularity of the Landau potential is determined by the degree of "nonrigidity" along the generalized internal coordinates of the thermodynamically unstable subsystem of the crystal. In other words, the thermodynamic system in general has a specific singularity that depends only on its internal nature. Therefore, the following question seems valid: which singularities of the Landau potential of this system can be observed experimentally for various numbers of variable parameters?

Let us consider the Landau potential of a system that has a singularity K of co-dimension c. Depending on the number l of variable parameters, one can in practice obtain three qualitatively different cases.

If the number of experimentally variable external conditions is $l < c$, then at some points of the space of the variable parameters one will typically find singularities of co-dimension l, entering into the decomposition of a singularity K due to the internal nature of the system.

Thus, an l-dimensional phase diagram will contain in some l-dimensional cross section the complete bifurcation diagram of the singularity K.

When $l = c$, then at some point in the space of the variable parameters, one should typically find the singularity K. The phase diagram contains this singularity in the complete bifurcation diagram.

Finally, if $l > c$, the singularity K will evolve, or in other words it will be seen, not at a single point, but on some $(l - c)$-dimensional manifold θ. Singularities of co-dimension higher than c will not be found, since they are not permitted by the internal nature of the thermodynamic system. The bifurcation diagram in this case will be a result of the evolution of the bifurcation diagram of the singularity K along θ. This results in an unusual phase diagram with a number of external parameters not less than c.

However, an unresolved question remains: What sort of typical cross sections of the bifurcation diagram occur in the first and the third cases? The answer to this question is given by the theory of the restructuring of phase diagrams,[28,49,54] the essence of which is presented below.

The topology of the nonsingular level of the Landau potential with a completely decomposed singularity is described by the monodromy group of the singularity, which is a generalization of the permutation group (the Galois group) of the roots of the polynomial in one variable

$$x^n + a_1 x^{n-1} + a_2 x^{n-2} + \ldots + a_n = 0. \tag{8.1}$$

It is known from the theorem of Vieta that the coefficients of a polynomial can be expressed in terms of x_i:

$$a_1 = -\sum_{i=1}^{n} x_i,\ a_2 = \sum_{i \neq j}^{n} x_i x_j,\ \ldots,\ a_n = \prod_{i=1}^{n} x_i, \tag{8.2}$$

at the center of gravity of the roots of $a_1 = 0$.

It is obvious that the a_i are invariant with respect to permutations of x_i. The same is true of the coefficients of the Landau potential, which are invariant with respect to permutations of the solutions of the equations of state under the operations of the monodromy group G_M, and consequently, are the invariants of G_M. The coefficient α_0 in the monomial of the highest quasi-homogeneous degree l_0, by analogy with a_2 in (8.1), will be the quadratic invariant $\alpha_0 = I^{(2)}_{G_M}(x_1, \ldots, x_n)$. The restructuring of the bifurcation diagram can be described by some function t of the variable conditions, where t preserves the singularity K. For this purpose, the function t must be a Morse function (nonsingular) and invariant under the monodromy group. However, since the monodromy group operates in different ways on the solutions of the equations of state (representing them) and on the "extra" variable parameters τ_i (which are invariant under this group) the nondegenerate quadratic form of both of them is

$$t = \alpha_0 + \sum_{i=1}^{p} \sigma_i \tau_i^2,\ \ \sigma_i = \pm 1. \tag{8.3}$$

If $l = c$ and there are no "extra" variable parameters, then

$$t = \alpha_0. \tag{8.4}$$

The bifurcation diagram, and, consequently, the phase diagrams are reconstructed with t equal to a constant. Therefore, in order to obtain a typical cross section of the bifurcation diagram of the singularity K for $L < c$ it is necessary to reduce it transversally to a $(c - l)$-dimensional space of the coefficients of the Landau potential with monomials of the observed degree of quasi-homogeneity. This provides the

structural stability of the phase diagrams that are obtained.

For $l > c$ quite unusual objects typically will be found on the cross sections of dimension $\dim \geqslant c$ of the bifurcation diagram. Points with the singularity K of the Landau potential can be typically found on the c-dimensional cross section. In the dimensionalities $c+1$, $c+2, \ldots$, $c+l-1$, the phase diagram will contain, respectively, 1-, 2-, ..., and $l-1$-dimensional spheres, hyperboloids, and paraboloids (or parts of them), filled with points with the singularity K.

The fact that it is possible to have one or several points with the singularity K of the Landau potential on phase diagrams of dimension $l = c$ makes it possible to formulate the criteria of the limitation of its nonlinearity.

Let two points with a singularity of co-dimension d occur on a d-dimensional phase diagram. If, when one more variable parameter is changed these points merge and disappear, leaving a stratum of lower co-dimension, then the Landau potential has a singularity of maximum co-dimension d. It should be noted, however, that this criterion can be used constructively only in a very small number of thermodynamic systems. A serious limitation comes from the experimental possibilities that allow simultaneous control of only a small number of variable external parameters. Therefore, one can determine the singularity of a thermodynamic potential due to its internal nature only for sufficiently "rigid" systems. For these, the maximum co-dimension is usually small, as, for example in some chalcogenides of the rare-earth metals.

8.2. Restructuring of a phase diagram in the neighborhood of a critical point of the liquid-vapor type

The SmS crystal undergoes an isostructural phase transition[99] that terminates at $T \sim 700$ K at a critical point of the liquid-vapor type, in the neighborhood of which the system is well described by a cusp potential (a Λ_3 singularity).[45,46] In addition to a high-temperature critical point at $T \sim 500$–600 K, there is also a low-temperature critical point[100,101] at $T \sim 90$–170 K in the continuous series of solid solutions of $Sm_{1-x}R_xS$ (R = La, Gd, Y) with concentrations $x \sim 0.15$ and at standard pressure. An increase in the pressure causes a merging of the critical points, which disappear after joining together (Fig. 17). It has been shown[102] that an increase in the degree of nonlinearity of the thermodynamic potential does not permit a description of such a phase diagram. However, regarding it as a restructuring of the phase diagram for the cusp potential

$$\Phi = \alpha_1 x + \alpha_2 x^2 + x^4, \quad t = \alpha_2 - \tau^2, \tag{8.5}$$

one can describe the entire set of experiments in this region of external conditions. The variable x has the meaning of an effective volume. A similar situation is observed on the P–T–x diagrams of the intermetallics $Ce_{0.9-x}Th_{0.1}R_x$ (R = Th,

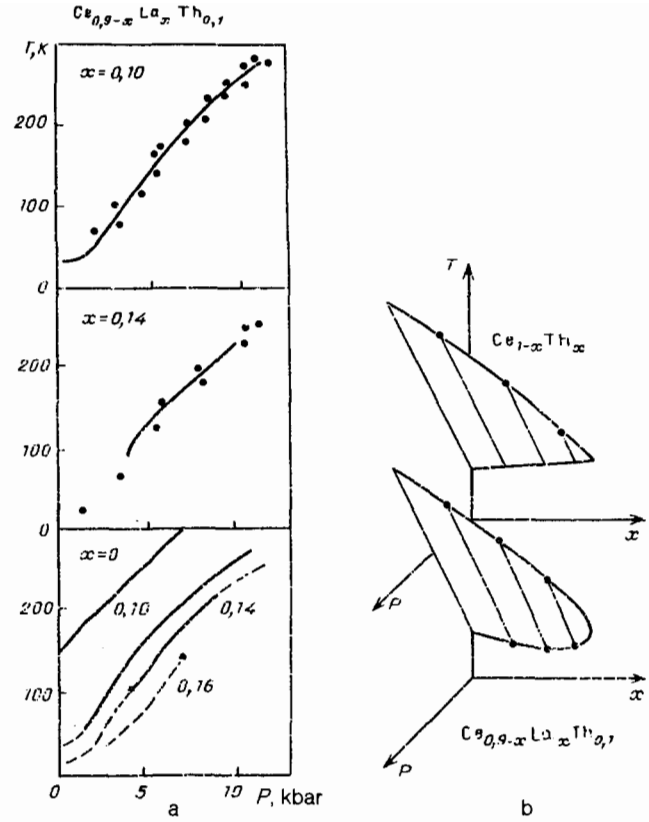

FIG. 18. Phase diagram of the compound $Ce_{0.9-x}La_xTh_{0.1}$. a) set of T-P-x diagrams for various concentrations of lanthanum; b) schematic T-P-x diagram from Ref. 13.

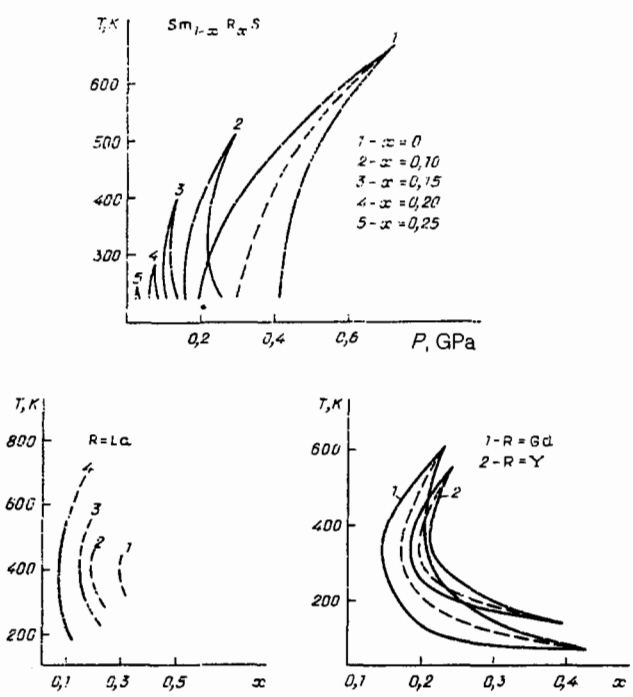

FIG. 17. Phase diagrams of the compounds $Sm_{1-x}R_xS$ (Refs. 100, 101).

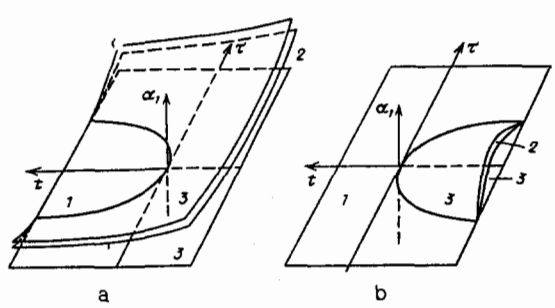

FIG. 19. Phase diagram of the potential (8.6) in the space of three external conditions. a) $t = a_2 + \tau^2$; b) $t = a_2 - \tau^2$. 1) second-order phase transition; 2) first order phase transition; 3) phase stability lines.

Er, La, Sc, Dy, Yb, Lu, Gd, Eu) (Ref. 103; Fig. 18a,b). Other examples of thermodynamic systems for which one can observe a multiplication of singularities are some liquid mixtures, in particular guaiacol-glycerine with an admixture of water, nicotine and water, and others,[104] where the region of stratification is limited in temperature by the two critical points. As the pressure is changed this region contracts, the critical points approach each other and merge, and thereafter the system is of a single phase.

It should be especially emphasized that restructuring of phase diagrams is determined by a change along the coefficient of the leading term of the quasi-homogeneity, and not of the term in the Landau potential quadratic in the order parameters. For example, restructurings of a phase diagram near a tricritical point in the space of the three external conditions are described by the potential

$$\Phi = \alpha_1\eta^2 + \alpha_2\eta^4 + \eta^6, \quad t = \alpha_2 \pm \tau^2 \tag{8.6}$$

and are shown in Fig. 19.

9. CONCLUSIONS

Singularities of families of smooth functions show real promise of occupying in the future a place in the Landau theory analogous to the concept of the space group representations. The unification of the theory of representations with the theory of singularities is an apparatus for exhibiting universality in the physics of phase transitions and by its means it will be possible to account for the identical thermodynamic behavior of very different systems, regardless of the physical nature of the order parameter.

In this paper we have come nowhere near to examining all the methods of the theory of singularities whose application to the phenomenology of phase transitions can be of interest. This field of mathematics is still young, and is developing extremely rapidly. (One indication of this fast development is the excellent review in Ref. 105, the material of which is not reflected in this paper). Therefore, there are still grounds to assume that the influence of this field of mathematics will be to extend the range of effective solutions of problems in the theory of phase transitions.

The authors wish to express their deep thanks to V. I. Arnol'd, V. V. Goryunov, and V. A. Vasil'ev for their inestimable assistance in the work and to S. M. Chudinov for his constant support and attention to this work.

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Translated by J. R. Anderson