PHENOMENOLOGICAL THEORY OF THE SYMMETRY OF ORDERED PHASES

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Abstract

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PHENOMENOLOGICAL THEORY OF THE SYMMETRY OF ORDERED PHASES

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In paper (^{1}) it was shown that all phases arising in phase transitions of the first or second kind, accompanied by a lowering of symmetry, can be divided into two groups. These are, first, ordinary phases, whose translational symmetry does not change upon variation, within the single-phase region, of the external thermodynamic parameters. Secondly, there are the so-called modulated structures—phases whose identity periods, expressed in terms of an integer number of interatomic distances, change upon variation, within the single-phase region, of the external thermodynamic parameters. As an example of phases of the second type one may cite helicoidal magnetic structures. In (^{1}) it was also shown that a necessary condition for the existence of ordinary phases (phases of the first type) is a definite restriction on the subgroup of translations. The formulation of this restriction coincides with E. M. Lifshitz' s criterion, derived for a much more special case of a second-order phase transition and under the assumption that the free energy can be expanded in a Taylor series in powers of the long-range order parameter (^{2}). We note that all the results obtained in (^{1}) are valid independently of the type of phase transition and of the condition that the free energy be expandable in a series in the long-range-order parameters, since they were obtained using only symmetry properties. However, the results of (^{1}) make it possible to find only the translation subgroup of a stable phase. Below a method is proposed that makes it possible to establish the complete symmetry of stable phases of type I.

For simplicity let us consider the case of ordering in binary substitutional solutions which, in the disordered state, have one of the 14 lattices without a basis (Bravais lattices). The state of the solution is characterized by the form of the function $n(\mathbf{R})$—the probability of finding an atom of one kind at the sites $\mathbf{R}$ of the lattice (atoms of the other kind are found at the site $\mathbf{R}$ with probability $1 - n(\mathbf{R})$). The function $n(\mathbf{R})$ describes the crystal structure of the phase and can be represented in the form of a Fourier series

$$n(\mathbf{R}) = n_0 + \sum_{(s)} \sum_{j_s} \left(x^{(s)}(j_s) \exp(i\mathbf{k}_{j_s}\mathbf{R}) + \text{c.c.} \right), \qquad (1)$$

where $x^{(s)}(j_s)$ are Fourier coefficients; $\mathbf{k}_{j_s}$ are the wave vectors of the star s, defined in the first Brillouin zone of the disordered solution. The summation is carried out over the different stars s and over the vectors $\mathbf{k}_j^s$ within each star. The restriction on the translation subgroup of ordinary phases established in (^{1}) consists in the following requirement:

1. The group of all wave vectors $\mathbf{k}_{j_s}$ appearing in (1) must contain symmetry elements intersecting at a single point.

However, in order to find the symmetry of superstructures one must know not only the form of all wave vectors appearing in (1) (the translation subgroup), but also the relations between the Fourier coefficients $x^{(s)}(j_s)$, which determine the rotation and reflection transformations (the crystal class). The action of rotation and reflection transformations on $n(\mathbf{R})$ reduces to the pre-

to the formation of coefficients $x^{(s)}(j_s)$, belonging to one star s, from one another. In this case the coefficients $x^{(s)}(j_s)$ transform in exactly the same way as the corresponding exponents $\exp(ik_{j_s}R)$. Hence it follows that a definite symmetry of the function $n(R)$ with respect to rotations and reflections presupposes the existence of corresponding relations (coupling equations) between the Fourier coefficients $x^{(s)}(j_s)$. The latter means that the number of independent coefficients $x^{(s)}(j_s)$ is always less than or equal to the number of exponents appearing in (1). In addition, one more necessary condition must be fulfilled.

II. The maximum number of different values of $n(R)$, not related to one another by translational symmetry, each of which may be changed arbitrarily while preserving the symmetry of the stable superstructure, must be equal to the full number of its independent parameters $x^{(s)}(j_s)$.

As already mentioned, the symmetry of a superstructure with respect to rotations and reflections is determined only by the relations between the coefficients $x^{(s)}(j_s)$ within each of the stars s. Relations between the coefficients $x^{(s)}(j_s)$ and $x^{(s')}(j_{s'})$, belonging to different stars, do not affect the symmetry. On the other hand, the symmetry of $n(R)$ always coincides with the symmetry of $n^2(R)$. Hence there follows one more condition for the stability of an ordered phase.

III. The relations between the coefficients at the exponents obtained by squaring (1) must coincide with the corresponding relations between the coefficients $x^{(s)}(j_s)$ in (1), belonging to the same star.

In the limiting case, when the number of coupling equations between the coefficients $x^{(s)}(j_s) = \eta_s \alpha^{(s)}(j_s)$ is maximal (η_s is the long-range order parameter, $\alpha^{(s)}(j_s)$ are coefficients satisfying the normalization condition

$$\sum_{(j_s)} |\alpha^{(s)}(j_s)|^2 = 1),$$

then all coefficients $x^{(s)}(j_s)$ depend on the external thermodynamic parameters only through the long-range order parameter η_s. The coefficients $\alpha^{(s)}(j_s)$ within the single-phase region are constants. This special case is, apparently, the most widespread. The latter is connected with the circumstance that the conditions for a minimum of the free energy consist in the requirement of extremality only with respect to the parameters η_s (their number is equal to or less than the number of stars), and not with respect to all coefficients $x^{(s)}(j_s)$. The extremum conditions for these coefficients $x^{(s)}(j_s)$ are satisfied identically owing to the symmetry of the system, and not to its dynamical properties.

From all that has been set forth it is clear that the determination of the functions $n(R)$ should begin with the determination of the wave vectors k_{j_s} satisfying criterion I. After this it is necessary to find the coupling equations between the coefficients $x^{(s)}(j_s)$ in (1) by successively adding to the function $n(R)$ all the symmetry elements of the crystallographic class (rotations and reflections) of the disordered phase. From the functions thus obtained one must exclude those which do not satisfy criteria II and III. The restrictions imposed by conditions I-III prove to be so stringent that the number of functions $n(R)$ (superstructures) satisfying them usually does not exceed ten.

It should be noted that all the results obtained above are also applicable to the cases of multiatomic lattices. The only difference will be that the expansion (1) is carried out not in exponents, but in functions of irreducible representations of the space group (“Bloch functions”) $u_\sigma(j_s, h_p)\exp(ik_{j_s}R)$, where h_p is a vector numbering the position of the species p within the unit cell, and σ is the number of the irreducible representation. The quantities $u_\sigma(j_s, h_p)$ can be found by the usual method with the aid of the projection operator of the group of the wave vector k_{j_s} (see, for example, (3)).

Thus, the method developed here makes it possible to find all stable superstructures without any assumptions whatsoever about the analytic properties of the free energy as a function of the long-range-order parameters and about the type of phase transition. The theory uses only information about the structure of the disordered phase.

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Note: Figure translations are in progress. See original paper for figures.