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Abstract

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SOME QUESTIONS IN THE THEORY OF ORDERING IN CRYSTALS

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It is generally assumed that, under configurational ordering in alloys, superstructures possessing a definite crystallographic symmetry are always formed. It is also assumed that ordered phases in equilibrium possess an unchanged crystallographic symmetry within some range of variation of the thermodynamic parameters. Although such an assumption appears, at first sight, obvious, it is highly desirable to clarify the conditions under which it is valid.

For simplicity, let us consider the case of configurational ordering in binary alloys with one of the simple lattices (Bravais lattices) in the disordered state. All the conclusions that will be obtained below are also valid for more complicated lattices, and may likewise be extended to the case of magnetic ordering.

The free energy F of an ordering two-component alloy is a functional of the atomic-density distribution function $\rho(\mathbf{r})$ of one of the components, where $\mathbf{r}$ is the radius vector of the sites of the crystal lattice.

The function $\rho_0(\mathbf{r})$, characterizing the periodic structure of an equilibrium alloy, can be expanded in a Fourier series

$$\rho_0(\mathbf{r}) = c + \sum_{(j)} \left(\alpha(\mathbf{k}_{0j}) \exp(i\mathbf{k}_{0j}\mathbf{r}) + \text{c.c.}\right), \tag{1}$$

where c is the atomic concentration of the alloy; the summation in (1) is carried out over a discrete system of wave vectors $\mathbf{k}_{0j}$ in the reciprocal space of the lattice of the disordered alloy. Correspondingly, the free energy of such a system will have the form

$$F_0 = F(\{\rho_0(\mathbf{r})\}) = F(\dots \mathbf{k}_{0j} \dots). \tag{2}$$

Since, by assumption, the function $\rho_0(\mathbf{r})$ ensures the absolute minimum of the free energy, the relation

$$F(\{\rho_0(\mathbf{r})\}) = F(\dots \mathbf{k}_{0j} \dots) \leq F(\{\rho(\mathbf{r})\}) = F(\dots \mathbf{k}_{0j} \dots, \mathbf{k}_m),$$

holds, where the function $\rho(\mathbf{r})$ differs from $\rho_0(\mathbf{r})$ by replacing the vector $\mathbf{k}_{0m}$ with $\mathbf{k}_m$ in the exponent

$$\rho(\mathbf{r}) = c + \sum_{j\neq m}{}' \left(\alpha(\mathbf{k}_{0j})e^{i\mathbf{k}_{0j}\mathbf{r}} + \text{c.c.}\right) + \left(\alpha(\mathbf{k}_{0m})e^{i\mathbf{k}_m\mathbf{r}} + \text{c.c.}\right). \tag{3}$$

It follows immediately from this that, for the value $\mathbf{k}_m = \mathbf{k}_{0m}$, which ensures the minimum of the free energy, the equality

$$\left.\frac{\partial F(\mathbf{k}_m; T, \rho, \mu)}{\partial \mathbf{k}_m}\right|_{k_m=\mathbf{k}_{0m}} = 0, \tag{4}$$

is valid.

where T, p, μ are the temperature, pressure, and chemical potential of the system. Equation (4) is, in essence, an equality determining the dependence of the vector $\mathbf{k}_{0m}$ on the thermodynamic parameters of the system,

$$\mathbf{k}_{0m} = \mathbf{k}_{0m}(T, p, \mu). \tag{5}$$

However, the existence of a phase with an unchanged crystal structure over an interval of thermodynamic parameters requires that $\mathbf{k}_{0m}$ be independent of these parameters. Otherwise the translational symmetry of the alloy will change.*

In turn, the requirement that $\mathbf{k}_{0m}$ be independent of T, p, μ reduces to the requirement that equation (4) at the point $\mathbf{k}_{0m}$ become an identity by virtue of symmetry. As shown in [1–3], gradients of the form (4) are identically zero at those points of reciprocal space for which the small group has symmetry elements intersecting at one point. This conclusion applies to all vectors $\mathbf{k}_{0j}$, since a similar proof can be carried out for each of them. The symmetry criterion formulated for the wave-vector group coincides with the criterion of E. M. Lifshitz [4] in the theory of second-order phase transitions. In those cases where the absolute minimum of the free energy at given T, p, μ is realized for some other points $\mathbf{k}_{0j}$ that do not possess the indicated symmetry properties, a small change in the thermodynamic parameters leads to small changes in $\mathbf{k}_{0j}$, which ensure the minimum of the free energy for the new values of the parameters. The latter, in turn, causes a change in the translational symmetry of the system. Taking the above into account, for any Bravais lattice one can write the most general form of the density function whose symmetry remains unchanged under variation of the parameters. Such a function describes the state of the system that is usually called a phase.

Let us consider an alloy which in the disordered state has an f.c.c. lattice. For such an alloy, the density function that does not change its symmetry under variation of p, T, μ must include vectors satisfying the symmetry criterion, with

coordinates in units of the reciprocal-lattice vectors $4\pi\mathbf{a}_1^*, 4\pi\mathbf{a}_2^*, 4\pi\mathbf{a}_3^*$: (1/2 0 0), (0 1/2 0); (0 0 1/2); (1/4 1/4 1/4), ($\bar{1}$/4 1/4 1/4), (1/4 $\bar{1}$/4 1/4), (1/4 1/4 $\bar{1}$/4), (1/4 0 1/2), (1/2 1/4 0), (0 1/2 1/4), ($\bar{1}$/4 0 1/2), (1/2 $\bar{1}$/4 0), (0 1/2 $\bar{1}$/4), where $\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*$ are the basis vectors of the reciprocal lattice conjugate to the basic cubic vectors of the face-centered cube $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$. Accordingly the density has the form

$$\rho(\mathbf{r}) = c + \alpha_1 e^{i2\pi x} + \alpha_2 e^{i2\pi y} + \alpha_3 e^{i2\pi z} + \beta_1 e^{i\pi(x+y+z)} +$$

$$+\beta_2 e^{i\pi(-x+y+z)} + \beta_3 e^{i\pi(x-y+z)} + \beta_4 e^{i\pi(x+y-z)} + \big(\gamma_1 e^{i\pi(x+2z)} +$$

$$+\gamma_2 e^{i\pi(2x+y)} + \gamma_3 e^{i\pi(2y+z)} + \gamma_4 e^{i\pi(-x+2z)} + \gamma_5 e^{i\pi(2x-y)} +$$

$$+\gamma_6 e^{i\pi(2y-z)} + \text{c.c.}\big), \tag{6}$$

where x, y, z are the coordinates of a lattice site, $\mathbf{r} = x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3$, and the constants of the form α_j, β_j, and γ_j are Fourier coefficients, playing the role of long-range order parameters, which must be determined from dynamical considerations. Any other superstructure not described by a density of the form (6) does not correspond to a phase in the usual sense: its period changes under a small change of T, p, and μ. Thus, for example, the Ni_2Cr phase, which is assumed to be described by the density [5]

$$\rho(\mathbf{r}) = c + ae^{i\frac{2\pi}{3}(x+y)}, \tag{7}$$

* Everywhere below, when we speak of the dependence of the wave vector (period) of a superstructure on thermodynamic parameters, we mean not the usual expansion of the lattice, which leaves the crystallographic symmetry unchanged, but the change of the period of the superstructure in units of the elementary cell and of the wave vector in units of the reciprocal lattice of the disordered alloy.

must have a period that depends on the thermodynamic parameters. At present this effect has not been observed. It could apparently be detected from the mutual displacement of the superstructure and structural maxima of elastic scattering when the parameters T, p, and μ are varied.

In an entirely analogous manner one can carry out a study of the ordering of a spin system in a crystal magnet. In this case, those cases in which all $\mathbf{k}_{0j}$ in the spin density satisfy the symmetry criterion formulated above correspond to the ordinary antiferromagnetic state. If, however, the minimum of the free energy is provided by vectors $\mathbf{k}_{0j}$ of general form, then magnetic structures of the helical type must be realized. The pitch of the helix of such structures,

as is well known, depends on temperature and pressure. It should be noted that in Ref. ([3]) a rigorous proof of the Lifshitz criterion for second-order phase transitions was proposed. In doing so, it was shown, in essence, that a second-order phase transition is in principle possible not only for structures allowed by the Lifshitz criterion, but also for structures with an arbitrary vector $\mathbf{k}_0$. The latter occurs if the second-order invariant in the expansion of the free energy that depends on the wave vector $\mathbf{k}$, at the phase-transition temperature for $\mathbf{k} = \mathbf{k}_0$, vanishes and is minimal ($a(\mathbf{k}_0, T_0) = 0$, $\nabla_{\mathbf{k}} a(\mathbf{k}, T_0)|_{\mathbf{k}=\mathbf{k}_0} = 0$). It follows from this that the Lifshitz criterion is not a necessary criterion for all second-order phase transitions. However, the consideration carried out in the present article shows that this criterion is indeed a necessary condition for a second-order phase transition in the case when, on both sides of the transition point, ordinary phases with constant symmetry occur. On the other hand, the Lifshitz criterion is not a necessary condition for a second-order phase transition if, as a result of the phase transition, a structure of the helical type is formed.

Finally, it should be noted that the theory developed above is applicable irrespective of what kind of phase transition has led to the formation of the ordered phase.

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