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A THEORY OF SPATIALLY PERIODIC PHASE DISTRIBUTION (MODULATED STRUCTURES) PRODUCED IN THE DECOMPOSITION OF SOLID SOLUTIONS

A. G. KHACHATURYAN

Institute of Metallography and Metal Physics

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A system is considered in which there occurs a decomposition of a cubic solid solution into two cubic phases; the phases differ from one another only in the concentration of the components and hence in their specific volumes. The problem concerning the distribution of inclusions of the separating phases insuring a free energy minimum with allowance for the elastic stress energy is solved. The solution of the corresponding variational problem leads to the conclusion that three types of macroperiodic distributions of inclusions exist: one-dimensional and two-dimensional distributions, and two-dimensional structures with a secondary periodic modulation. Since the inclusions of the various phases differ from each other only in their composition, these distributions can be conceived of as macroperiodic composition modulations which are usually referred to as modulated structures. A common property of these structures is the fact that the basis vectors of their Bravais translations coincide with the directions of the cubic ⟨100⟩ axes of the matrix, and their corresponding "reciprocal lattices" have points which are located only along ⟨100⟩ type directions around the reciprocal lattice points of the matrix. On x-ray and electron diffraction patterns the "reciprocal lattice" of modulated structures appears in the form of satellites surrounding the Laue reflections of the matrix lattice.

ELECTRON-microscope and x-ray studies of the decomposition of a cubic solid solution into two cubic phases which differ from one another and from the matrix only in concentration and in their specific volume have led to the conclusion that the distribution of inclusions of the produced phases exhibits a clearly manifest periodicity.[1-4] In the literature these distributions are usually referred to as modulated structures. The periodicity is in various cases of a one, two-, or possibly three-dimensional nature. A common feature of the observed distributions is, first, the fact that their basic translation vectors are directed along the ⟨100⟩ type crystallographic axes of the matrix; secondly, the distributions are of a macroscopic nature and their periods amount to tens and hundreds of angstroms. The diffraction of x rays and electrons by such systems leads to the appearance of additional reflections—satellites located along the ⟨100⟩ type directions about the reciprocal lattice points of the matrix crystal. The distances between them are inversely proportional to the period of the modulation.

In the case in which the correlation length in the solid solution is of the same order of magnitude as the period of the distribution, the observed periodicity can be connected with metastable periodic modulations of the composition.[5] However, theory[5] cannot explain the existence of relatively stable periodic distributions if their period exceeds appreciably the correlation length (the characteristic thickness of the interphase boundaries). Under these conditions the periodic distributions of the type mentioned should according to theory[5] lose their stability. One can readily convince oneself of the latter if one takes into account the fact that small shifts of the interphase boundaries which conserve the total volumes of the phases do not lead to any change of the chemical free energy of the system since the latter depends only on the total volume of the phases and not on their mutual spatial distribution. Apparently, only the energy of the elastic stresses depends on the mutual spatial distribution of the inclusions. In this connection an attempt is made below to explain the mechanism of the production of modulated structures with a large period by means of the contribution of the energy of the elastic stresses to the energy balance of the phase transformation.

The elastic energy of a system of inclusions of arbitrary configuration can apparently only be written in its general form with the assumption that the elastic moduli of all the phases participating in the transformation are equal and that their coupling is coherent. Under this assumption the phases will differ from one another only in the values of the specific volume in the free state and in the concentration of the components. This assumption is not strict since for substitution systems in which the phase transition is not connected with a rearrangement of the crystal lattice but consists only in the redistribution of the atoms over the lattice sites, the relative difference in the elastic constants is of the order of 10^{-2}. The second assumption about the coherent coupling between inclusions is generally not a strong limitation. It is known that the violation of the coherence of the phases consists in the production of a system of epitaxial dislocations on the interphase boundaries. Epitaxial dislocations increase, on the one hand, the surface energy and decrease, on the other hand, the incompatibility of the coupling of the phases along the boundaries which reduces in effect to a decrease of the difference in the specific volumes of the adjoining phases. For this reason the presence of epitaxial dislocations should only affect the numerical values of the parameters entering in the theory.

In calculating the elastic energy of the system of inclusions it is convenient to introduce into the treatment a tensor $\epsilon_{ij}^{0}(\mathbf{r})$ which characterizes the deformation undergone by an elementary volume of the matrix (or by its unit cell) at the point $\mathbf{r}$ in a phase transformation taking place in the unstressed, free state. In the case considered, in which all phases are cubic and the phase transformation is only connected with a change in the specific volume which is in turn uniquely connected with the concentration of one of the components $c(\mathbf{r})$ (the concentration is reckoned from the average composition of the alloy):

$$\varepsilon_{ij}{}^{0}(\mathbf{r}) = \varepsilon_0(c(\mathbf{r}))\delta_{ij} = \tilde{\varepsilon}_0(\mathbf{r})\delta_{ij}. \tag{1}$$

The function $\tilde{\epsilon}_0(\mathbf{r})$ in essence completely describes the spatial distribution of the inclusions[1].

The problem of the elastic energy of an anisotropic inhomogeneous system satisfying the above formulated limitations was solved in[6]. Making use of $\epsilon_{ij}^{0}(\mathbf{r})$ in the form (1), one can rewrite the expression for the elastic energy of an inhomogeneous system with an arbitrary configuration from[6] in the form

$$E = \frac{1}{2}\int \frac{d^3\mathbf{k}}{(2\pi)^3} B(\mathbf{n})\,|\varepsilon_0(\mathbf{k})|^2, \tag{2}$$

where

$$B(\mathbf{n}) = 9K - 9K^2\Omega_{ii}(\mathbf{n}) > 0, \quad K = (c_{11} + 2c_{12})/3;$$

c_{11} and c_{12} are the elastic constants, $\epsilon_0(\mathbf{k}) = \int d^3r\,\epsilon_0(\mathbf{r})\exp(-i\mathbf{k}\cdot\mathbf{r})$, $\mathbf{k}$ is the wave vector—the Fourier transform parameter, $\Omega_{ij}(\mathbf{n}) = k^{-2}G_{ij}(\mathbf{k})$, $G_{ij}(\mathbf{k})$ is the Fourier component of the Green tensor of the elastic problem, $\mathbf{n} = \mathbf{k}/k$ is a unit vector. Summation over repeated indices is implied. Making use of the value of the Fourier components for the Green tensor from[7], we obtain

$$B(\mathbf{n}) = 9K - 9K^2\frac{1+2\Delta(n_x{}^2n_y{}^2 + n_x{}^2n_z{}^2 + n_y{}^2n_z{}^2) + 3\Delta^2n_x{}^2n_y{}^2n_z{}^2}{c_{11} + (c_{11}+c_{12})\Delta(n_x{}^2n_y{}^2 + n_z{}^2n_y{}^2 + n_x{}^2n_z{}^2) + \Delta^2(c_{11}+2c_{12}+c_{44})n_x{}^2n_y{}^2n_z{}^2}, \tag{3}$$

where c_{44} is the single-crystal elastic constant; n_x, n_y, and n_z are the components of the vector $\mathbf{n}$ along the axes of the cube, and $\Delta = (c_{11} - c_{12} - 2c_{44})/c_{44}$ is the elastic anisotropy parameter. If it is assumed that the alloy is a binary alloy and $\epsilon_0(\mathbf{r}) = \omega[c(\mathbf{r}) - \bar{c}]$ (Vegard's law is fulfilled, ω being the concentrational expansion coefficient and $\bar{c}$ the composition of the alloy), then expression (3) coincides in particular with the coefficient of the square of the amplitude of the concentration wave in the expression for the elastic energy of a system of concentration waves obtained in[8].

Let us consider a certain fixed small region of the crystal Σ within which decomposition has occurred. Below we shall call this region a complex. We shall assume that for a fixed shape of the complex its internal fine structure will be determined from the condition of the minimum of the free elastic, chemical, and surface energy. It should, however, be borne in mind that in some cases the dimensions of the complex are not constant but increase as the decomposition process develops. The purely energetic approach just formulated will for this reason be correct only when the characteristic times of the relative change of the dimensions of the complex are appreciably longer than the characteristic relaxation times of the elements of its fine structure. The latter is correct under the conditions of inhibited growth when an increase of the dimensions of the complex is limited by crystal defects or by "collisions" with other analogous complexes growing from neighboring locations of the crystal. The thermodynamic approach may also be correct in the case of free growth of a complex since the diffusion relaxation of the fine-scale elements of the fine structure should for not too large supercooling occur much more rapidly than the relative change of the dimensions of the complex.

Combining the chemical free energy of a complex and its elastic energy (2), we obtain an expression for the elastic and chemical free energy

$$F = \int\limits_{(V_\Sigma)} d^3\mathbf{r}f_{\text{chem}}(c) + \frac{1}{2}\int \frac{d^3\mathbf{k}}{(2\pi)^3} B(\mathbf{n})\,|\varepsilon_0(\mathbf{k})|^2, \tag{4}$$

where V_Σ is the volume of the complex. Since $B(\mathbf{n}) > 0$, $F \geq F_0$ where

$$F_0 = \int\limits_{(V_\Sigma)} d^3\mathbf{r}f_{\text{chem}}(c) + \frac{1}{2}\min B(\mathbf{n})\int \frac{d^3\mathbf{k}}{(2\pi)^3}\,|\varepsilon_0(\mathbf{k})|^2 = \int\limits_{(V_\Sigma)} d^3\mathbf{r}f(c), \tag{5}$$

where $f(c) = f_{\text{chem}}(c) + \frac{1}{2}\min B(\mathbf{n})[\tilde{\epsilon}_0(c)]^2$ and $\min B(\mathbf{n})$ is the minimum value of $B(\mathbf{n})$. In (5) use has been made of the condition that $\tilde{\epsilon}_0[c(\mathbf{r})]$ differs from zero only inside the region Σ. The minimization of the free energy in the right-hand side of (5) is carried out in the standard way with the condition of the conservation of the number of particles. The decomposition of a homogeneous solid solution will occur when the curve $f(c)$ as a function of the concentration has a common tangent at two points c_1 and c_2. In this case the free energy takes on a minimum value if complete stratification occurs in the complex into two equilibrium phases whose concentrations are c_1 and c_2 and the ratio of whose volumes is $\gamma = c_2/(-c_1)$. Each of these phases will be characterized by a deformation $\tilde{\epsilon}_0(c_1) = (a_1 - a_0)/a_0$ and $\tilde{\epsilon}_0(c_2) = (a_2 - a_0)/a_0$ where a_1, a_2, and a_0 are the lattice parameters of the first and second phase and of the matrix respectively.

It follows from the above discussion that the minimum value of the free energy F_0 is the lower bound of the free energy of a complex ($F \geq F_0$). From a comparison of (4) and (5) it follows that $F \to F_0$ if $|\epsilon_0(\mathbf{k})|^2$ differs from zero only for those directions $\mathbf{n}_0$ of the vector $\mathbf{k}$ for which $\min B(\mathbf{n}) = B(\mathbf{n}_0)$. It follows from (3) that for $\Delta < 0$ (a case realized in practically all known decomposing alloys) $B(\mathbf{n})$ takes on the minimum value $9K - 9K^2/c_{11}$ for $\mathbf{n} = \mathbf{n}_0$ directed along one of the cubic $\langle 100\rangle$ axes. Thus, for the case $\Delta < 0$ the free energy F tends asymptotically to F_0 if $|\epsilon_0(\mathbf{k})|^2$ differs from zero in the region of $\mathbf{k}$ space representing one or several intersecting thin and long rods directed along the cubic $\langle 100\rangle$ axes. The situation when $|\epsilon_0(\mathbf{k})|^2$ differs from zero within the limits of one rod in $\mathbf{k}$ space in the [001] direction corresponds to a spatial distribution of deformation and composition inhomogeneities within the limits of a complex which is of a one-dimensional nature, i.e., depends

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[1] For simplicity we consider everywhere below a binary alloy, although the obtained results can also be directly generalized to the case of a multi-component alloy.

only on one z projection of the vector $\mathbf{r}$ on the [001] direction:

$$\tilde{\varepsilon}_0(\mathbf{r}) = \tilde{\varepsilon}_1^{[001]}(z). \tag{6}$$

The function $|\epsilon_0(\mathbf{k})|^2$ differs from zero in the region of $\mathbf{k}$ space representing two rods in the [100] and [010] directions if within the limits of the complex

$$\tilde{\varepsilon}_0(\mathbf{r}) = \tilde{\varepsilon}_2^{[100]}(x) + \tilde{\varepsilon}_2^{[010]}(y), \tag{7}$$

and three rods in the [100], [010], and [001] directions if

$$\tilde{\varepsilon}_0(\mathbf{r}) = \tilde{\varepsilon}_3^{[100]}(x) + \tilde{\varepsilon}_3^{[010]}(y) + \tilde{\varepsilon}_3^{[001]}(z). \tag{8}$$

The variables x, y, and z in (6)–(8) are the coordinates of the vector $\mathbf{r}$ along the cubic [100], [010], and [001] directions. Formula (7) describes a two-dimensional modulation which is a superposition of two one-dimensional modulations, and formula (8) describes a three-dimensional modulation which is a superposition of three one-dimensional ones. If the characteristic dimensions of the complex in a direction perpendicular to $\mathbf{n}_0$ are of the order of L_Σ and the characteristic scale of the inhomogeneity $\tilde{\epsilon}_0(\mathbf{r})$ in the direction of the modulation is of the order of d, then the length of the corresponding rod in k space within which $|\epsilon_0(\mathbf{k})|^2 \neq 0$ is of the order of $2\pi/d$ and the thickness is of the order of $2\pi/L_\Sigma$. It follows hence that the requirement formulated above that the rod be sufficiently narrow and long reduces to the inequality $d/L_\Sigma \ll 1$. Taking into account the properties of $|\epsilon_0(\mathbf{k})|^2$ for $d/L_\Sigma \ll 1$ one can take out the quantity $B(\mathbf{n}) = B(\mathbf{n}_0) = \min B(\mathbf{n})$ from under the integral sign in the right-hand side of (4) and go over from F to F_0. The accuracy of this procedure is of the order of d/L_Σ:

$$F = F_0 + \Delta E, \quad \Delta E = \int \Delta B(\mathbf{n}) |\varepsilon_0(\mathbf{k})|^2 \frac{d^3\mathbf{k}}{(2\pi)^3}, \tag{9}$$

where ΔE is a quantity of the order of d/L_Σ, and $\Delta B(\mathbf{n}) = B(\mathbf{n}) - \min B(\mathbf{n}) > 0$.

Since $\Delta E > 0$, the free energy of the complex will be the lower, the smaller the ratio d/L_Σ. The latter means that from the point of view of the elastic and chemical free energy it is convenient for the complex to subdivide into infinitely thin structural elements. This process stops because in the course of the subdivision of the complex the number of separating surfaces between the constituent phases increases and consequently the contribution of the surface energy of the interphase boundaries increases. In those instances in which the surface energy is sufficiently small (the criteria for the smallness of the surface energy will be cited below) the ratio $d/L_\Sigma \ll 1$. Thus, under the condition that d/L_Σ is small one can neglect the second term in (9) and obtain the ratio of the volumes of the separating phases and their equilibrium concentrations, minimizing the free energy F_0. As was shown above, F_0 takes on minimum values when the matrix in the complex decomposes into two phases with equilibrium concentrations c_1 and c_2, the ratio of whose volumes is $\gamma = c_2/(-c_1)$.

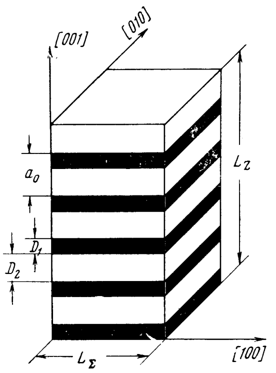

FIG. 1. A one-dimensional periodic structure. The dark and light regions illustrate the inclusions of equilibrium phases.

The realization of this two-phase state is only possible in the case of the one-dimensional distribution (6) since the two-dimensional distribution (7) describes as a minimum the coexistence of three phases and the three-dimensional distribution (8)—the coexistence of four phases. Thus, a complex consisting of successive thin plates of both phases with the surfaces of these plates normal to the modulation direction [001] and a ratio of the volumes of the equilibrium phases γ has the minimum free energy. Since the volume part of the free energy F in (9) depends solely on the ratio of the volumes of the phases, one must, in order to determine the mutual distribution of inclusions, investigate the minimum of the small contribution to F_0—the quantity ΔE. Calculations carried out in the Appendix show that the minimum of the quantity ΔE determined with the additional conditions of the constancy of the ratio of the volumes of the phases γ and the constancy of the volume of the complex and of the given number of plate-like inclusions (fixed surface energy), is assured by a one-dimensional periodic distribution. In it all the inclusions of the first phase are in the form of equal parallel plates equidistant from one another. The intervals between the inclusions of the first phase are filled with the second phase (Fig. 1). At the same time

$$\Delta E = B(\varepsilon_1^0 - \varepsilon_2^0)^2 \alpha(\gamma) a_0 S_\Sigma, \tag{10}$$

where a_0 is the period of distribution determined by the dimension of the complex in the [001] direction and by the number of inclusions; $\alpha(\gamma)$ is a constant determined in (A.9); S_Σ is the external surface of the complex passing along the perimeter of the plate-like inclusions parallel to the [001] direction; $B = 9K^2 c_{11}^{-2} |\Delta| (c_{11} - c_{12})$. From the definitions (5) and (10) it follows that the quantity F_0 has the meaning of the volume free energy of the complex and the quantity ΔE—of the surface energy, elastic in origin, of the complex, The appearance of elastic energy proportional to the external area of the complex is connected with the contribution of elastic stresses localized near the ends of the plate-like inclusions constituting the complex.

The last parameter to be determined is the number of inclusions or the period a_0 uniquely related to it. In order to determine the period a_0, one must add to the free energy (9) the surface energy of the interphase boundaries which is

$$E_s = 2\sigma_{(001)} V_\Sigma / a_0, \tag{11}$$

where $\sigma_{(001)}$ is the coefficient of surface tension at the interphase boundaries along the (001) planes along which the plate-like inclusions make contact, and V_Σ is the volume of the complex. Minimizing the sum of (10) and (11) with respect to a_0 (the free energy F_0 does not depend on a_0), we obtain

$$a_0 = (r_0 L_\Sigma)^{1/2}, \tag{12}$$

where $r_0 = 2\sigma_{(001)}[B(\epsilon_1^0 - \epsilon_2^0)^2\alpha(\gamma)]^{-1}$ is a quantity having the dimensions of length, $L_\Sigma = S_{(001)}/P_{(001)}$ is the characteristic dimension of the complex in a direction normal to the [001], $S_{(001)}$ is the area of the section of the complex by the (001) plane, and $P_{(001)}$ is the perimeter of this cross section. Making use of (12), one can reduce the requirement $d/L_\Sigma \ll 1$, within the framework of which the calculation of ΔE is carried out, to the condition

$$d/L_\Sigma = (r_0 L_\Sigma^{-1})^{1/2} \ll 1, \tag{13}$$

which is fulfilled for the typical values of the parameters $r_0 \sim 1$ Å and $L_\Sigma \sim 10^3$ Å.

Let us consider the possibility of the existence of the two-dimensional distribution (7). Let us assume for simplicity that there is a linear relationship between the deformation $\tilde{\varepsilon}_0(\mathbf{r})$ and the local concentration $c(\mathbf{r})$ at the point $\mathbf{r}$ reckoned from the average composition of the alloy (Vegard's law is valid):

$$\tilde{\varepsilon}_0(\mathbf{r}) = \omega c(\mathbf{r}), \tag{14}$$

where ω is the linear coefficient in the concentration dependence of the lattice parameter of the alloy. The two-dimensional distribution (7) consists of a minimum of three phases differing from one another in composition. Here the functions $\tilde{\varepsilon}_2^{[100]}(x)$ and $\tilde{\varepsilon}_2^{[010]}(y)$ should have a step-like form and take on only two values.

As was shown above, the two-dimensional distribution (7) is described in the main by the volume free energy F_0. The correction ΔE in (9), as well as for the one-dimensional distribution (6), characterizes the surface energy of the complex connected with elastic strains and is of the order of $d/L_\Sigma \ll 1$. For this reason the equilibrium composition and the volumes of the structural components of the complex should be determined from the condition of F_0 being a minimum. A necessary requirement for the minimum of F_0, when the number of particles is conserved, is the requirement

$$\partial f/\partial c = \mu, \tag{15}$$

where f is determined in (5) and μ is an undetermined Lagrange multiplier fulfilling the role of the chemical potential. Equation (15) determines the equilibrium concentrations of the phases into which the complex decomposes and has in the general case three solutions (see Fig. 2): $c_1(\mu)$, $c_2(\mu)$, and $c_3(\mu)$.

It follows from (14) that a two-dimensional distribution of the deformation (7) corresponds to a two-dimensional distribution of concentrations:

$$c(\mathbf{r}) = c_2^{[100]}(x) + c_2^{[010]}(y). \tag{16}$$

This distribution will take on three values only in the case when each of the functions $c_2^{[100]}(x)$ and $c_2^{[010]}(y)$ takes on only two values: $c_1(\mu)/2$ and $c_2(\mu)/2$. The two values of $c(\mathbf{r})$ are $c_1(\mu)$ and $c_2(\mu)$, and the third value is $\frac{1}{2}[c_1(\mu) + c_2(\mu)]$. The equality $\frac{1}{2}[c_1(\mu) + c_2(\mu)] = c_3(\mu)$ where $c_3(\mu)$ is the third solution of (15) is the equation for determining μ. We shall use γ_1 to denote the fraction of the volume of the complex V_Σ within which $c_2^{[100]}(x)$ takes on the value $c_1/2$ and γ_2—the fraction of the volume V_Σ within which $c_2^{[010]}(y)$ takes on the value $c_2/2$. Then the volume of the phase with concentration c_1 is $\gamma_1\gamma_2 V_\Sigma$, with a concentration c_2 it is $(1 - \gamma_1)(1 - \gamma_2)V_\Sigma$, and with a concentration $\frac{1}{2}(c_1 + c_2)$ it is $(\gamma_1 + \gamma_2 - 2\gamma_1\gamma_2)V_\Sigma$. Since all the concentrations are reckoned from the average concentration of the alloy, the condition for the conservation of the number of particles is of the form

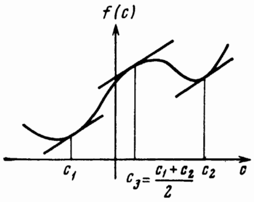

FIG. 2. The solution of Eq. (15).

$$c_1\gamma_1\gamma_2 + c_2(1 - \gamma_1)(1 - \gamma_2) + \tfrac{1}{2}(c_1 + c_2)(\gamma_1 + \gamma_2 - 2\gamma_1\gamma_2) = 0 \tag{17a}$$

or

$$\gamma_1 + \gamma_2 = 2c_2/(c_2 - c_1), \tag{17b}$$

and the free energy

$$F_0 = V_\Sigma\Big[f(c_1)\gamma_1\gamma_2 + f(c_2)(1 - \gamma_1)(1 - \gamma_2) + f\Big(\frac{c_1 + c_2}{2}\Big)(\gamma_1 + \gamma_2 - 2\gamma_1\gamma_2)\Big]. \tag{18}$$

Minimizing (18) with respect to γ_1 and γ_2 with account of (17b), we obtain

$$\gamma_1 = \gamma_2 = c_2/(c_2 - c_1) < 1. \tag{19}$$

It should be noted that the limitations on the form of the function $c_2^{[100]}(x)$ and $c_2^{[010]}(y)$ just obtained do not as yet fully determine the form of $c(\mathbf{r})$: there is an infinite set of functions of the type (16) which satisfy the obtained limitations with respect to which the minimum value of the free energy F_0 is degenerate. For this reason a full clarification of the form of the function $c(\mathbf{r})$ requires, as in the one-dimensional case, a minimization of additional terms not accounted for previously in the free energy: the elastic energy ΔE proportional to the external area of the complex, and the surface energy of the interphase boundaries E_S.

It follows from (7) and (2) that the quantity ΔE for the two-dimensional distribution separates into a sum of two quantities:

$$\Delta E = \Delta E_{[100]} + \Delta E_{[010]}, \tag{20}$$

characterizing the corresponding one-dimensional distributions in the [100] and [010] directions. For this reason the minimization problem of the quantity ΔE for a two-dimensional distribution for a given volume V_Σ and a given number of interphase boundaries (number of inclusions) reduces to the problem of minimizing ΔE for a one dimensional distribution, considered in the Appendix. We can, thus, state that the minimum of ΔE is realized if $c_2^{[100]}(x)$ and $c_2^{[010]}(y)$ are periodic functions of the same form as in the one-dimensional case. The corresponding values of $\Delta E_{[100]}$ and $\Delta E_{[010]}$ are determined by equations of the type of (10):

$$\Delta E_{[100]} = \tfrac{1}{4}B\omega^2(c_1 - c_2)^2\alpha(\gamma_1)S_{[100]}a_{[100]}, \tag{20a}$$

$$\Delta E_{[010]} = \tfrac{1}{4}B\omega^2(c_1 - c_2)^2\alpha(\gamma_2)S_{[010]}a_{[010]}, \tag{20b}$$

where $S_{[100]}$, $S_{[010]}$, $a_{[100]}$, and $a_{[010]}$ are the external area of the complexes and the periods of the one-dimensional distributions parallel to the directions

[100] and [010]. In (20a) and (20b) we have taken into account the definitions following from (14):

$$\varepsilon_1{}^0 = \omega c_1/2, \quad \varepsilon_2{}^0 = \omega c_2/2, \quad \varepsilon_1{}^0 - \varepsilon_2{}^0 = {}^1/_2\omega(c_1 - c_2).$$

The surface energy of the distribution can also be represented in the form of a sum of surface energies of two-one-dimensional distributions:

$$E_s = \frac{2\sigma V_\Sigma}{a_{[100]}} + \frac{2\sigma V_\Sigma}{a_{[010]}}, \tag{21}$$

where σ is the average surface energy of a two-dimensional distribution over surfaces of separation of the type (100). It follows from (20) that the quantities $a_{[100]}$ and $a_{[010]}$ can be determined independently from one another by minimizing the sum of (19) and (21) with respect to $a_{[100]}$ and $a_{[010]}$. A procedure completely analogous to that presented for the one-dimensional case yields

$$a_{[100]} = \sqrt{r_1 L_{[100]}}, \quad a_{[010]} = \sqrt{r_1 L_{[010]}}, \tag{22}$$

where $L_{[100]} = S_{(100)}/P_{(100)}$ and $L_{[010]} = S_{(010)}/P_{(010)}$ are the characteristic linear dimensions of the complex; $r_1 = 2\sigma[{}^1/_4 B\omega^2(c_1 - c_2)^2\alpha(\gamma_1)]^{-1}$; $S_{(100)}$ and $S_{(010)}$, and $P_{(100)}$ and $P_{(010)}$ are the areas and perimeters of the sections of the complex by the (100) and (010) planes. Since from the point of view of the symmetry of the system the (100) and (010) planes are equivalent in all respects, one can in the majority of cases expect that $L_{[100]} \approx L_{[010]}$. The latter will attest to the fact that $a_{[100]} \approx a_{[010]} = a_0$. The complex will thus constitute a two-dimensional square periodic structure in the (001) plane of the crystal whose lattice points will be rods with square cross sections of two phases with compositions c_1 and c_2, close to the equilibrium composition, and rods with square cross sections and average composition close to the composition of the homogeneous solid solution ${}^1/_2(c_1 + c_2)$. All the rods are elongated along the [001] direction perpendicular to the plane of the square lattice (Fig. 3).

The free-energy minimum of the two-dimensional distribution found for the class of functions (16) corresponds to a three-phase composition of the complex and does not, therefore, insure an absolute minimum of the free energy: one of the structural components of the complex has the composition ${}^1/_2(c_1 + c_2)$ close to the composition of the undecomposed matrix. The absolute minimum corresponds, as has been shown at the beginning of the article, to a one-dimensional two-phase distribution. The distribution shown in Fig. 3 can for this reason only be metastable, i.e., stable with respect to small variations of the fine structure. In order to be convinced about the metastable nature of the obtained optimum two-dimensional distribution, one must investigate the change of the free energy of this distribution for variations of the concentration which remove the function c(r) from the class of functions (16). At the same time it is sufficient to analyze only the most "dangerous" variations which are, on the one hand, coupled with a minimum loss in the elastic and surface energy, and, on the other hand, with a maximum gain in the volume free energy. Since the minimum loss of elastic energy is connected with the formation of thin platelets along the cube faces, and the maximum gain in the volume free energy is connected with the decomposition of the rods which have the average composition ${}^1/_2(c_1 + c_2)$, close or identical to the composition of the initial matrix, then the most "dangerous" change in the fine structure of a two-dimensional complex will be the splitting of the rods with the composition ${}^1/_2(c_1 + c_2)$ into platelets of segregations. The composition of these platelets is close to the equilibrium composition and their planes are normal to the [001] axis of the rod (Fig. 4).

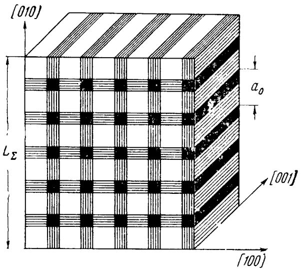

FIG. 3

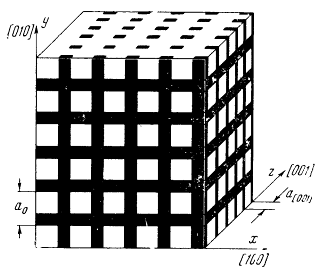

FIG. 4

FIG. 3. A two-dimensional structure. The dark and light regions illustrate the phases with compositions c_1 and c_2. The shaded regions have a composition $(c_1 + c_2)/2$.

FIG. 4. A two-dimensional structure after secondary decomposition. The dark and light regions have a composition c_1 and c_2 respectively.

The formation of one such platelet, for example with a concentration c_1, leads to an elastic-energy loss $\Delta E_{pl} = B(\epsilon_1 - \epsilon_2)^2\alpha d_1 v_1/l_1$ calculated in accordance with formula (9) for ΔE, in analogy with the calculation of ΔE in the Appendix [here $\epsilon_1 = \omega c_1$, $\epsilon_2 = \omega(c_1 + c_2)/2$, α is a numerical factor of the order of unity, d_1 and $l_1 = a_0(1 - \gamma_1)\gamma_1$ is the thickness and width of the platelet and v_1 is its volume], and to a loss in the surface-tension energy $E_s^{pl} = 2\sigma_{(001)}v_1/d_1$. Minimizing the sum of ΔE_{pl} and E_s^{pl} with respect to d_1 for a given volume v_1, we obtain $\Delta F_{pl} = 4\sigma_{(001)}v_1/\sqrt{r_1 l_1}$ or, using expression (22), $\Delta F_{pl} = 4\sigma_{(001)}v_1 r_1{}^{-3/4}L_{[100]}^{-1/4}$. At the same time, the gain in the volume free energy in the segregation of the platelet is $\Delta F_0 = [f(c_1) - f({}^1/_2(c_1 + c_2))]v_1 < 0$. Thus a complex which has the fine structure illustrated in Fig. 3 is metastable if the loss in the elastic and surface energy ΔF_{pl} in the formation of one platelet becomes larger than the gain in the volume free energy ΔF_0. This condition is valid when

$$4\sigma_{[001]}\left|f(c_1) - f\left(\frac{c_1 + c_2}{2}\right)\right|^{-1} r_1{}^{-3/4}L_{[100]}^{-1/4} > 1. \tag{23}$$

Condition (23) is valid for small supercooling when the specific free energy of the separating phases is close to the free energy of the matrix, as well as for short decomposition times when the dimensions of the complex $L_{[100]}$ are sufficiently small. In the opposite case the two-dimensional distribution becomes unstable against secondary decomposition which takes place in the rods with the average composition ${}^1/_2(c_1 + c_2)$. The secondary decomposition reduces to a transformation of the rods into packets of successive platelets of both phases normal to the rod direction [001] having phase compositions c_1 and c_2. Secondary decomposition can thus lead to a transition of the system from the three-phase to the two-phase state which ensures, as has been shown at the beginning of the article, a minimum of the volume free energy F_0.

In order to describe a system undergoing secondary decomposition one must add to the two-dimensional distribution (16) the function $c^{[001]}(x, y, z)$ which differs from zero only in the rods of average composition $\frac{1}{2}(c_1 + c_2)$, and which modulates the composition only in the [001] direction of the z axis. Then,

$$c(\mathbf{r}) = [c_2^{[100]}(x) + c_2^{[010]}(y)] + c^{[001]}(x, y, z). \tag{24}$$

The system will be a two-phase system if $c_2^{[100]}(x)$ and $c_2^{[010]}(y)$ will, as before, take on the values $c_1/2$ and $c_2/2$ and $c^{[001]}(x, y, z)$ as a function of z will take on the values $\frac{1}{2}(c_1 - c_2)$ and $-\frac{1}{2}(c_1 - c_2)$. If the characteristic length of the d modulation described by the functions $c_2^{[100]}(x)$ and $c_2^{[010]}(y)$ is much smaller than the characteristic dimension of the complex in a direction perpendicular to the direction of modulation ($d/L_\Sigma \ll 1$), and the characteristic length d_1 of the modulation in the [001] direction described by the function $c^{[001]}(x, y, z)$ is much smaller than the characteristic transverse dimension d of the rod within which this modulation takes place ($d_1/d \ll 1$), then the correction to the volume free energy separates into the sum of corrections connected with three types of one-dimensional distributions:

$$F - F_0 = \Delta E_{[100]} + \Delta E_{[010]} + \Delta E_{[001]}. \tag{25}$$

The corrections $\Delta E_{[100]}$ and $\Delta E_{[010]}$ have been determined previously [see (20a) and (20b)]. They correspond to two one-dimensional periodic distributions in the [100] and [010] directions. The elastic energy $\Delta E_{[001]}$ represents the sum of the energies corresponding to one-dimensional periodic distributions—stacks of alternating platelets of two phases whose number is the same as that of the rods of average composition which have undergone secondary decomposition. The elastic energy of one stack is proportional to its lateral surface parallel to the [001] and is given by expression (10):

$$B\omega^2(c_1 - c_2)^2\alpha(\gamma_3)a_{[001]}\cdot 2(a^{[100]} + a^{[010]})L_z,$$

where L_Z is the dimension of the complex along the [001] axis, $2[a^{[100]} + a^{[010]}]L_Z$ is the area of the lateral surface of a single stack, and γ_3 is the ratio of the volume occupied by the phase with the composition c_1 to the volume of the entire stack. The value of $\Delta E_{[001]}$ can be obtained if one multiplies the energy corresponding to one stack by the number of such stacks equal to $S_{(001)}/a_{[100]}a_{[010]}$. We thus have

$$\Delta E_{[001]} = B\omega^2(c_1 - c_2)^2\alpha(\gamma_3)a_{[001]}\left(\frac{1}{a_{[100]}} + \frac{1}{a_{[010]}}\right)V_\Sigma. \tag{26}$$

It should be noted that in obtaining formula (26) we have taken no account of the contribution of the energy of elastic interaction of the stacks with one another, since this contribution is of a higher order of smallness in the parameter:

$$d_1/d \sim a_{[001]}/a_{[100]} \ll 1.$$

In order to determine the periods of the distributions $a_{[100]}$, $a_{[010]}$, and $a_{[001]}$, one must take into account the contribution of the surface tension at the interphase boundaries to the free energy. The homogeneous distributions $c_2^{[100]}(x)$ and $c_2^{[010]}(y)$ lead to a total surface-tension energy

$$E_s^{[100]} + E_s^{[010]} = 2\sigma V_\Sigma\left(\frac{1}{a_{[100]}} + \frac{1}{a_{[010]}}\right), \tag{27}$$

and the distribution $c^{[001]}(x, y, z)$ leads to a surface-tension energy

$$E_s^{[001]} = \frac{2\sigma_{(001)}(\gamma_1 + \gamma_2 - 2\gamma_1\gamma_2)V_\Sigma}{a_{[001]}}. \tag{28}$$

Minimizing the sum of (20a), (20b), and (26)–(28) with respect to $a_{[100]}$, $a_{[010]}$, and $a_{[001]}$, as well as with respect to γ_1, γ_2, and γ_3, with the condition that the dimensions of the complex in the [100] and [010] directions coincide and the ratio of the volumes of the phases is given and equal to

$$\gamma = \frac{\gamma_1\gamma_2 + (\gamma_1 + \gamma_2 - 2\gamma_1\gamma_2)\gamma_3}{(1 - \gamma_1)(1 - \gamma_2) + (\gamma_1 + \gamma_2 - 2\gamma_1\gamma_2)(1 - \gamma_3)}$$

we find $\gamma_1 = \gamma_2$

$$a_{[100]} = a_{[010]} = a_0 = \sqrt{(a_1 + r_1)L_\Sigma}, \tag{29a}$$

$$a_{[001]} = \sqrt{r_2 a_0}, \tag{29b}$$

where

$$L_\Sigma = S_{(001)}/P_{(001)}, \quad r_2 = 2\sigma_{(001)}(\gamma_1 + \gamma_2 - 2\gamma_1\gamma_2)[B\omega^2(c_1 - c_2)^2\alpha(\gamma_3)]^{-1}.$$

A simultaneous solution of Eqs. (29a) and (29b) gives

$$a_0 \approx \left(\frac{r_2}{r_1}\right)^{1/3}(r_1 L_\Sigma^2)^{1/3}\left[1 + O\left(\left(\frac{r_1}{L_\Sigma}\right)^{1/3}\right)\right], \tag{30}$$

where $O(r_1/L_\Sigma)^{1/3}$ is the order of the correction ($r_2 \sim r_1$). The expression for the quantities γ_1 and γ_3 is not presented since they must be determined from a very cumbersome transcendental equation that follows from the condition of the minimum of the free energy.

The condition of applicability of the present theory which leads to the fine structure shown in Fig. 4 is, as has already been indicated, of the form $d_1/d \sim a_{[001]}/a_0 \ll 1$; bearing in mind (29a), (29b), and (30), this reduces to the condition

$$(r_1/L_\Sigma)^{1/3} \ll 1. \tag{31}$$

Since the condition for the realization of the two-dimensional fine structure shown in Fig. 3, $(r_1/L_\Sigma)^{1/2} \ll 1$, is of a higher order of smallness than (31), condition (31) is stricter and is fulfilled for larger dimensions L_Σ (at later stages of the decomposition). Finally, we note that a three-dimensional distribution of the type (8) cannot in general insure a minimum of the total free energy. The reason for this consists in the fact that the minimum number of phases for such a distribution is four, whereas the necessary condition for the coexistence of phases in equilibrium (15) admits the coexistence of only three phases. It does not, however, follow from this that as a result of peculiarities of the kinetics under conditions when the contribution of the elastic energy of the system is sufficiently large a transitory existence of an unstable three-dimensional distribution is impossible.

It follows from (13) and (31) that the present theory is valid under conditions when the inequality

$$r_0/L_\Sigma \ll 1 \tag{32}$$

($r_1 \sim r_2 \sim r_0$) is fulfilled. The breakdown of inequality (32) attests to the fact that the surface tension at the interphase boundaries which stimulates the formation of equilibrium inclusions begins to play a role com-

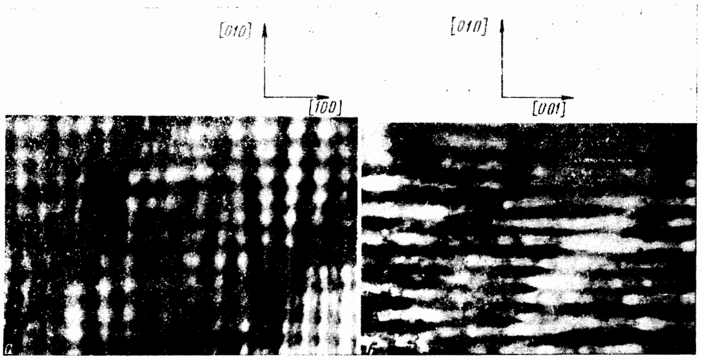

FIG. 5. Electron-microscope image: a – (001) section of a two-dimensional structure; b – (100) section of a two-dimensional structure.[9]

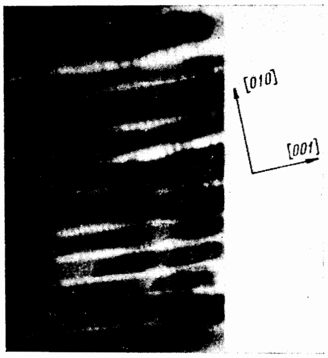

FIG. 6. Electron-microscope image of a (100) section of a two-dimensional structure with secondary decomposition.[9]

mensurate with the role of the elastic energy which "rolls" the inclusions into thin and extended platelets. The latter leads to the circumstance that the mechanism of the production of periodic distributions detailed above ceases to operate. Thus, making use of the inequality (32) one can make a number of predictions concerning the systems and conditions for which one can expect a macroscopic structure with a clearly pronounced periodicity. The periodic macroscopic distributions will be the more perfect, the better inequality (32) is fulfilled, i.e., the smaller the value of the characteristic length r_0 [see Eq. (13)]. The latter gives the following conditions for the existence of periodic distributions: 1) the separating phases should have crystal lattice parameters which differ strongly from one another [a large value of $(\epsilon_1^0 - \epsilon_2^0)^2$]; 2) the solid solution should have a large elastic anisotropy (a large value of $|\Delta|$); 3) the surface tension at the interphase boundaries should be sufficiently small. The best conditions in this sense are realized near the spinodal where $\sigma = 0$. An infringement of any of these conditions $(\sigma \to \infty, \Delta \to 0, \epsilon_1^0 - \epsilon_2^0 \to 0)$ leads to a destruction of the periodicity. It should also be noted that in some cases in which at the initial stage of the decomposition the characteristic dimension of the inclusion is sufficiently small $(r_0/L_\Sigma \sim 1)$, a random distribution of inclusions is formed which rearranges itself into a periodic distribution with the growth of the inclusions [with the increase of L_Σ and the corresponding transition to the inequality (32)].

Available experimental results are, apparently, in good agreement with the conclusions of the present theory. It has been shown in[4,9] by the methods of electron microscopy and electron microdiffraction that a two-dimensional periodic distribution of a form coinciding with that obtained in this article (compare Figs. 3 and 5) is formed during the decomposition of an alloy of the Ticonal type. In Fig. 5 we present two micrographs of a complex representing its mutually perpendicular sections by the (001) and (100) planes. As one can readily verify they have a form that coincides with the corresponding sections in the diagram of Fig. 3. At a later stage of the decomposition the rods of the experimentally observed distribution undergo secondary decomposition[9] and the configurations shown on the micrograph (Fig. 6) are formed in the (100) plane of the foil.

A comparison of the micrograph of Fig. 6 with the corresponding section of the complex in Fig. 4 by the (100) plane of the lattice of the matrix shows excellent agreement. The sequence of the fine-structure changes observed in[4,9] is also in agreement with the theory since it was shown above that the distribution (24) with a secondary fine structure has a lower free energy than a metastable two-dimensional distribution of the type (16) and should therefore occur at a later stage of the decomposition. The fact that all translation vectors of the obtained redistributions are directed solely along the ⟨100⟩ type cubic axes is also in agreement with experiment. Finally, attention should be drawn to the fact that the superpositions of one-dimensional distributions along ⟨100⟩ type directions, considered in the article, should lead to the formation of satellites in the cube directions near the reciprocal lattice points of the matrix. As has been shown, the formation of satellites in other directions will lead to an increase in the elastic energy of the system. This conclusion is in full agreement with the results of x-ray diffraction experiments (see, for example,[1]).

The author expresses his deep gratitude to I. M. Lifshitz for a discussion of the article which facilitated an appreciable improvement of it, and to E. G. Knizhnik for the possibility of using the results of her experiments.[4,9]

APPENDIX

Let us consider a complex in the form of a cylinder whose axis is along the [001] axis of the crystal with the sections by the (001) planes having an arbitrary shape. Let the volume of the complex be completely filled with plate-like inclusions of the two separating phases whose surfaces are parallel to one another and perpendicular to the [001] axis of the cylinder. We assume that the number of inclusions and the ratio of the volumes of the phases γ is given. All the plate-like inclusions are bounded by the cylindrical lateral surfaces of the complex and the surfaces of all inclusions have therefore the same shape. For this reason the Fourier components of the function of the form $\tilde{\Theta}_p(\mathbf{r})$[2)] can be represented in the form of the product

$$\Theta_p(\mathbf{k}) = S(\tau)\varphi_p(k_z), \tag{A.1}$$

where $\mathbf{k} = \{\tau, k_z\}$, τ is the component of the vector $\mathbf{k}$ in the (001) plane, and k_z is the component of the vector $\mathbf{k}$ in the [001] direction;

$$S(\tau) = \int\int_{-\infty}^{\infty} \tilde{S}(\rho)\exp(i\tau\rho)\,d^2\rho;$$

$$\varphi_p(k_z) = \int_{-\infty}^{\infty} \tilde{\varphi}_p(z)\exp(ik_z z)\,dz,$$

ρ is the component of the radius vector $\mathbf{r}$ in the (001) plane; $S(\rho)$ is a function of the shape of the section of the complex by the (001) plane equal to unity if the vector ρ lies in the plane of the cross section and zero otherwise; z is the component of the radius vector $\mathbf{r}$ in the [001] direction, $\tilde{\varphi}_p(z)$ is a function of the shape equal to unity when the z coordinate corresponds to a point located inside the inclusion of the p-th phase and zero otherwise.

Let the plate-like inclusions in the complex form a one-dimensional periodic distribution. The elementary unit cell of such a distribution consists, in the general case, of an arbitrary number of inclusions of the two phases and of the matrix parallel to one another, each inclusion having an arbitrary thickness and an arbitrary position along the z axis. The latter assumptions do not limit the generality of setting the problem since a nonperiodic distribution is a special case of a periodic distribution if the period of the latter tends to infinity. Since the inclusions are distributed periodically along the [001] axis with a period a, the function $|\epsilon_0(\mathbf{k})|^2 = |\epsilon_1^0\Theta_1(\mathbf{k}) + \epsilon_2^0\Theta_2(\mathbf{k})|^2$ is nonzero only at "reciprocal lattice" points: $k_z = 2\pi m/a$ ($m = 0, \pm 1, \pm 2, \pm \ldots$). The integration for ΔE over k_z in expression (9) can for this reason be replaced by a summation of the expression

$$\Delta B\left(\frac{\tau}{\sqrt{(2\pi m/a)^2+\tau^2}}, \frac{2\pi m/a}{\sqrt{(2\pi m/a)^2+\tau^2}}\right)\frac{N}{a}\left|\varepsilon_1^0\varphi_1^0\left(\frac{2\pi m}{a}\right) + \varepsilon_2^0\varphi_2^0\left(\frac{2\pi m}{a}\right)\right|^2 |S(\tau)|^2,$$

over the "reciprocal lattice" points; here N is the number of unit cells in the complex, and $\varphi_p^0(2\pi m/a) = N^{-1}\varphi_p(2\pi m/a)$ is the Fourier component of the shape function of the inclusions of the p-th phase inside one unit cell of the distribution. The expression for ΔE in (9) can be rewritten in the form

$$\Delta E = \frac{NP_{(001)}}{2}\sum_{m=-\infty}^{\infty}{}' A(m)\left|\varepsilon_1^0\varphi_1^0\left(\frac{2\pi m}{a}\right) + \varepsilon_2^0\varphi_2^0\left(\frac{2\pi m}{a}\right)\right|^2, \tag{A.2}$$

$$A(m) = \int\int \Delta B\left(\frac{\tau}{\sqrt{(2\pi m/a)^2+\tau^2}}, \frac{2\pi m/a}{\sqrt{(2\pi m/a)^2+\tau^2}}\right)\frac{|S(\tau)|^2}{P_{(001)}a}\frac{d^2\tau}{(2\pi)^2}, \tag{A.2a}$$

where $P_{(001)}$ is the perimeter of the section of the complex by the (001) plane. The term corresponding to m = 0 is absent in formula (A.2). This is related to the fact that for a linear dependence $\epsilon_0(c) = \omega c$ the expression between the absolute value signs in (A.2) for m = 0 vanishes in accordance with the definition of the functions $\varphi_1^0(k_z)$ and $\varphi_2^0(k_z)$. Since the function $|S(\tau)|^2$ is localized in τ in the interval $\tau \sim 2\pi/L_\Sigma$ and $k_z \geq 2\pi/a$, then $\tau/k_z \sim a/L_z \ll 1$. For this reason we can with an accuracy to higher orders in a/L_Σ represent $\Delta B(\mathbf{k}/k)$ in the form of the first nonvanishing term of the expansion in the deviation of the vector $\mathbf{k}$ from the [001] direction:

$$\Delta B(\mathbf{n}) \approx B\frac{\tau^2}{k_z^2+\tau^2}, \tag{A.3}$$

where $B = -9K^2\Delta(c_{11} - c_{12})/c_{11}^2$ is a positive constant proportional to the elastic anisotropy constant Δ.

Expression (A.2a) for A(m) calculated with the aid of (A.3) is in the first nonvanishing approximation with respect to a/L_Σ of the form

$$A(m) = \frac{B}{4\pi}\frac{1}{|m|}. \tag{A.4}$$

Substituting (A.4) in (A.2), we obtain

$$\Delta E = \frac{1}{2}NP_{(001)}\frac{B}{4\pi}\sum_{m=-\infty}^{\infty}{}'\frac{1}{|m|}\left|\varepsilon_1^0\varphi_1^0\left(\frac{2\pi m}{a}\right) + \varepsilon_2^0\varphi_2^0\left(\frac{2\pi m}{a}\right)\right|^2. \tag{A.5}$$

From the definitions of the functions $\varphi_p^0(k_z)$ as the Fourier components of the one-dimensional shape function of the p-th phase of one unit cell it follows that

$$\varphi_p^0\left(\frac{2\pi m}{a}\right) = a\sum_{j=1}^{\nu_p}\frac{\sin(\pi d_j^{(p)}m/a)}{\pi m}\exp\left(i\frac{2\pi}{a}b_j^{(p)}m\right), \tag{A.6}$$

where ν_p^0 is the number of inclusions of the p-th phase in one elementary unit cell, and $b_i^{(p)}$ and $d_j^{(p)}$ are the coordinate and thickness of the j-th inclusion of the p-th phase.

In order to find the optimum distribution of plate-like inclusions in the unit cell, one must investigate the minimum of expression (A.6) under the additional condition of the conservation of the volumes of the first and second phase. As a result we find that the number of inclusions of both separating phases is equal to one another ($\nu_1 = \nu_2 = \nu$), and

$$b_j^{(1)} = \frac{a}{\nu}j,\ b_j^{(2)} = \frac{a}{\nu}j + \frac{a}{2\nu},\quad a_0 = \frac{a}{\nu}, \tag{A.7}$$

where $j = 0, 1, 2, \ldots, \nu - 1$. It follows from (A.7) that the quantity ΔE takes on a minimum value when the plate-like inclusions of the first phase have the same thickness and are located at equal distances from one another, the spaces between them being filled up with the second phase (see Fig. 1). Since the number of inclusions of each phase is given and equal to N, the period of the obtained one-dimensional distribution a_0 is determined by $a_0 = L_z/N$ where L_z is the dimension of the complex in the [001] direction. For such a distribution we have in expression (6) $\nu_p = 1$, $d^{(1)} = a_0\gamma$, $d^{(2)} = a_0(1 - \gamma)$, $b^{(1)} = 0$, and $b^{(2)} = a_0/2$. Making use of these relations in (A.5), we obtain

$$\Delta E = \frac{B}{(2\pi)^3}(\varepsilon_1^0 + \varepsilon_2^0)^2\alpha(\gamma)a_0S_\Sigma, \tag{A.8}$$

[2)] The shape function of the inclusion of the p-th phase (p = 1,2) $\Theta_p(\mathbf{r})$ is equal to unity if the radius vector is inside the inclusion of the p-th phase and zero otherwise.

where $S_\Sigma = P_{(001)}L_Z$ is the lateral area of the complex passing through the perimeter of its (001) section and parallel to the [001] direction,

$$\alpha(\gamma) = \sum_{m=-\infty}^{\infty}{}' \frac{\sin^2 \pi\gamma m}{|m|^3}.$$

Utilizing Poisson's summation method, one can obtain for $\alpha(\gamma)$ the integral representation

$$\alpha(\gamma) = 4\pi\gamma^2 \int_0^1 (-\ln 2|\sin \pi\gamma\xi|)(1-\xi)\,d\xi. \qquad \text{(A.9)}$$

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