THEORY OF MACROSCOPIC PERIODICITY FOR A PHASE TRANSITION IN THE SOLID STATE

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It is shown that in a phase transition from a cubic phase to a tetragonal one the minimum of elastic energy of the system is realized when the tetragonal inclusions with tetragonality axes situated along two cubic directions form a periodic system. These inclusions are plates which are closely adjacent to one another, tangent to the (110) plane and are located in a twinned position with respect to this plane. The unit cell of the periodic distribution consists of two plates with differing tetragonality axes, whereas the period is proportional to the square root of their extent. In turn, this system forms a "macroscopic" plate, which coherently related to the cubic matrix.

One of the fundamental peculiarities of a phase transition in the solid state consists in the fact that it is often accompanied by considerable elastic deformations of the crystal lattice. At the same time the phase transition occurs in such a manner that at each step the loss of free energy of the system due to the deformations turns out to be minimal. The minimization of the elastic energy is possible because of the optimal form and distribution of the inclusions of the new phase, which are coherently bound to the matrix, and also by means of the formation of epitaxial dislocations at the interphase boundaries (violation of coherence), if the possibilities of reduction of the stresses due to changes of orientations and form of the inclusions are limited.

The purpose of the present paper is an attempt to construct a theory by means of which one could find the optimal form and orientation of the inclusions of the new phase. For this purpose one must answer the question: what is the energy of a non-simply-connected domain of non-simply-connectedness? The problem in such a general formulation does not seem to have a solution in closed form. However, such a solution can be found if one assumes that the elasticity moduli of the domains of non-simply-connectedness are not essential.

Let a phase transition in a state free of stress \( \sigma_{ij} = 0 \), where \( \sigma_{ij} \) is the stress tensor, be accompanied by a homogeneous deformation of the transformed volume, \( \epsilon_{ij}^v(1) \). The deformation tensor \( \epsilon_{ij}^v(1) \) is related to the crystallographic axes of the matrix. The index \( v \) denotes the directions of the principal axes of the tensor \( \epsilon_{ij}^v \). Owing to the symmetry of the lattice of the matrix there exist several other crystallographically equivalent directions of the principal axes, described by the labels 2, 3, ..., \( p \), ....

Further, the orientation of the inclusions of one and the same phase in the matrix will be characterized by the indices \( p \).

If one refers the elastic energy to the undeformed state, it can be written in the form

\[
E = \frac{1}{2} \sum_{V (i)} (\sigma_{ij}^p(r) \delta_{ij}(r)) + \lambda_{ij} \delta_{ij}(r) \epsilon_{im}(r) dV.
\]

where \( \sigma_{ij}^p = \lambda_{ij} \epsilon_{im} \) is the tensor of elastic moduli, \( \delta_{ij}(r) \) is a function of the shape of the inclusion of type \( p \), function which is equal to one inside the inclusion and zero outside, \( V \) is the volume of the system, and the summation in (1) runs over all types of inclusions in the system, and over all repeated indices.

We note that the shape function \( \delta_{ij}(r) \) is in general multiply connected, i.e., it describes several inclusions of type \( p \). Effecting a local variation of (1) with respect to the deformations \( \epsilon_{ij}(r) \), we transform the usual manner (cf., e.g., (11)) to the equation of equilibrium of the medium

\[
\lambda_{ij} \frac{\partial \delta_{im}}{\partial r_j} = \sum_{(i)} \epsilon_{ij}^v(p) \frac{\partial}{\partial r_j} \delta_{ij}(r).
\]

Transforming (1) and (2) to the k-representation and substituting the solution (2) into (1), we obtain

\[
E = \frac{1}{2V} \sum_{p,q} (k, \delta_{ij}^v(p) \tilde{G}(k) \delta_{ij}^v(q) k) \Theta_p(k) \Theta_q^*(k).
\]

where \( \ldots, \ldots \) denotes the scalar product of the vectors, \( \delta_{ij}^v(p) \) and \( \tilde{G}(k) \) are operators, the matrix elements of which are the components of the tensors \( \delta_{ij}^v(p) \) and \( G_{ij}(k) \), where \( G_{ij}(k) \) is the Fourier component of the Green's tensor of the elastic problem, and

\[
\Theta_p(k) = \int d^3 \tilde{G}(k) \Theta_p(r) e^{-ikr}.
\]

The summation with respect to \( k \) is over all the points of the quasicontinuum.

If one refers the energy to the stress-free state \( \sigma_{ij} = 0 \), one obtains

\[
E = \frac{1}{2} \sum_{p,q} (\sigma_{ij}^p(p) \sigma_{ij}^q(q) - (k, \delta_{ij}^v(p) \tilde{G}(k) \delta_{ij}^v(q) k)) \Theta_p(k) \Theta_q^*(k).
\]

We consider a simply connected domain \( s \) inside the matrix which includes all the inclusions. We introduce the shape-function \( \Theta_p(r) \) of this domain. Then \( \Theta_p(r) \) may
be represented in the form of a sum of its averages over the domain and of the fluctuating part \( \Delta \Theta_\lambda(p) \):

\[
\Theta_\lambda(t) = \langle \Theta_\lambda(t) \rangle + \Delta \Theta_\lambda(t) = \frac{V_\lambda}{V} \Theta_\lambda(t) + \Delta \Theta_\lambda(t),
\]

where \( V_\lambda \) is the total volume of inclusions of the type \( p \), \( V_S \) is the volume of the region \( s \). We have for the Fourier component

\[
\Theta_\lambda(k) = \frac{V_\lambda}{V} \Theta_\lambda(k) + \Delta \Theta_\lambda(k).
\]  

(6)

The function \( \Theta_\lambda(k) \) is nonvanishing in a small region of \( k \)-space, near \( k = 0 \): \( \Delta k^2 \sim (2\pi)^2/V_\lambda \). On the contrary, the function \( \Delta \Theta_\lambda(k) \) vanishes in this region and is different from zero at distances \( \sim 2\pi/L_p \), where \( L_p \) is a characteristic dimension of a simply connected inclusion of type \( p \). Since the characteristic dimensions of the inclusions are much smaller than the characteristic dimensions of the region surrounding them, the product \( \Theta_\lambda(k) \Delta \Theta_\lambda(k) = 0 \). Then we obtain, substituting (6) into (4)

\[
\varphi = \frac{1}{2} \sum_{\lambda, \mu} \sum_{p, q} \left[ (\Theta_\lambda(k) \Theta_\mu(k) - (\Theta_\lambda(p) \Theta_\mu(q)) \right]_{\lambda} \left[ (\Theta_\lambda(p) \Theta_\mu(q)) \right]_{\lambda} \Delta \Theta_\lambda(k) \Delta \Theta_\mu(k),
\]

where \( \Theta_\lambda(k) \) is the average of the stresses over the region \( s \).

The first term in (7) characterizes essentially the energy of one large inclusion—"the average crystal," having volume \( V_S \) and subjected to the average strain

\[
\varepsilon = \sum_{\lambda} \frac{V_\lambda}{V} \tilde{\varepsilon}^\lambda(p) \tag{8}
\]

in a phase-transition in the free state\(^{[2]} \)

\((\tilde{G}_{ij} = \hat{A}_{ij} |_{m \neq m})\). The second term describes the fluctuation part of the elastic energy, related to local deviations of the stresses \( \tilde{\varepsilon}^\lambda(p) \) from their average values, \( \tilde{\varepsilon} \).

It was shown in\(^{[2]} \) that the formation of a single inclusion in the new phase in an infinite anisotropic continuum is accompanied by a minimum value of the elastic energy if the inclusion has the form of a thin extended plate, the normal unit vector \( n_0 \) of which is determined by the condition of maximum for the quantity \( \Lambda(n) = k \cdot (\hat{G}(k) \cdot \hat{\kappa}(k)) \), where \( n = k/k \). The energy of such an inclusion equals

\[
E_1 = \frac{1}{2} \left[ (\tilde{G}_{ij} n_0^i n_0^j - \Theta_\lambda(n_0)) V_\lambda (1 + o(D_1/L_1)) \right],
\]

where \( D_1 \) is the thickness of the plate and \( L_1 \) is its length.

It was shown in\(^{[2]} \) that the elastic energy of such an inclusion vanishes, up to asymptotically small terms of the order \( D_1/L_1 \), if

\[
\varepsilon^\lambda = \frac{1}{2} \varepsilon^\lambda (n_1^i + n_2^i),
\]

(10)

where \( n \) is a unit vector normal to the plate and \( L \) is an arbitrary unit vector. The deformation (10) is plane. The part of the elastic energy related to a correction of order \( D_1/L_1 \) coincides with the energy of a dislocation loop\(^{[2]} \) situated on the perimeter of the plate.

Thus, selecting the volume of the inclusions such that the average deformation (8) is plane we can in many cases make the first term in (7) vanish, up to terms of order \( D_1/L_1 \). Since the tensor \( \tilde{G}_{ij}(k) \) is positive definite, the second term in (7) is also positive. Consequently, the minimal value which it can take on is zero. Then the optimal distribution of inclusions, from the point of view of elastic energy, will be a distribution when both terms (7) tend asymptotically to zero. If this is not possible, the problem of determination of the minimum of the elastic energy becomes essentially more complicated. However, for a large class of phase transitions the vanishing of both terms in (7) may occur.

We consider as an example the transformation of the cubic phase into a tetragonal one. Here there are three types of inclusions with the deformations:

\[
\tilde{\varepsilon}^1 = \begin{pmatrix} e_1 & 0 & 0 \\ 0 & -e_1 & 0 \\ 0 & 0 & -e_1 \end{pmatrix},
\tilde{\varepsilon}^2 = \begin{pmatrix} e_1 & 0 & 0 \\ 0 & e_1 & 0 \\ 0 & 0 & e_1 \end{pmatrix},
\tilde{\varepsilon}^3 = \begin{pmatrix} 0 & -e_2 & 0 \\ -e_2 & 0 & 0 \\ 0 & 0 & e_2 \end{pmatrix},
\]

(11)

where \( e_1 > 0 \) and \( e_2 > 0 \) (or \( e_1 < 0 \), \( e_2 < 0 \)). Substituting (11) into (8), one can convince oneself that there is a degeneracy, in other words that the plane deformation (1) (the asymptotic vanishing of the first term in (7)) can be obtained in several ways. This degeneracy is lifted due to the fact that the asymptotic vanishing of the second term in (7) is possible only in the case when one of the three types of inclusion is absent. Let, e.g. \( V_3 = 0 \). Then the procedure for determining a plane deformation becomes unique and the tensor

\[
\tilde{\varepsilon} = \tilde{\varepsilon}_1 V_1 + \tilde{\varepsilon}_2 V_2 + \tilde{\varepsilon}_3 V_3
\]

(12)

describes such a deformation if

\[
V_1/V_2 = e_1/e_2.
\]

Then the first term in (7) vanishes up to the energy of a dislocation loop which encircles the average crystal along its perimeter.

In order to make the second term vanish asymptotically it is, first of all, necessary to bring it to the same form as the first term, and this, in turn, is possible only if\(^{[1]} \):

\[
\Delta \Theta_1(k) + \Delta \Theta_2(k) = 0,
\Delta \Theta_3(k) = 0.
\]

(13)

It is just the necessity of the identity \( \Delta \Theta_3 = 0 \) which leads to the condition \( V_3 = 0 \). The first identity in (13) is equivalent to the condition that the inclusions of the first and second type completely fill the volume \( V_S \), i.e., \( V_1 + V_2 = V_S \). Substituting (13) into the first term in (7) we obtain:

\[
E_2 = \frac{1}{2} \sum_{k} \left[ \left( \Delta \Theta_1(k) + \Delta \Theta_2(k) - (k \cdot \hat{G}(k) \cdot \hat{\kappa}(k)) \right) \Delta \Theta_3(k) \right]^2
\]

where \( \Delta \Theta_3 = \hat{\varepsilon}_3^0 (1) - \hat{\varepsilon}_3^0 (2) \), \( \Delta \Theta_3^0 = \hat{\varepsilon}_3^0 (1) - \hat{\varepsilon}_3^0 (2) \). It follows from the definition (11) that \( \Delta \hat{\varepsilon} \) represents a plane deformation and is a symmetrized dyadic formed by the vectors \( m = 2 \hat{\varepsilon}_3^0 [110] \) and \( l = 2 \hat{\varepsilon}_3^0 [110] \): \( \Delta \hat{\varepsilon} = (\varepsilon_1 - \varepsilon_2)/3 \times 1 \). The vanishing of (14) is possible only when the function \( \Delta \Theta_3(k) \) is different from zero, either

\(^{[1]} \) All the results are of course independent of permutation of the indices that characterize the inclusion type.
for the direction l, or for the direction m. We are then led to the conclusion that the function \( \Delta \Theta_i(r) \) describes a set of parallel plates situated in the planes (110) (normal to l or m) such that the characteristic length of these plates, \( L_i \), is much larger than their characteristic thickness. In this case the function \( \Delta \Theta_i(k) \) is different from zero in a region of k-space having the form of a bar, as illustrated in Fig. 1. If one neglects the deviation of the vector \( k \) in (14) (the error committed in doing this is \( \sim d_i / L_i \ll 1 \)), the expression (14) can be rewritten in the form

\[
E_2 = \frac{1}{2} \{ \Delta \sigma_i \Delta \varepsilon_i + (\varepsilon_m \Delta \Theta_i (k m) \Delta \Theta_i (k m)) \} \frac{1}{V} \sum_k |\Delta \Theta_i (k)|^2 + o \left( \frac{d_i}{L_i} \right). \tag{15}
\]

Since \( \Delta \Theta^0 \) is related to a plane deformation, the expression in the square bracket vanishes (cf. the Appendix). Consequently, up to terms of the order \( d_i / L_i \), so does the second term in (7). This result does not depend on the ratio of the volumes \( V_1 \) and \( V_2 \), the selection of which has allowed us to set the first term in (7) equal to zero. These are the circumstances allowing us to minimize independently both terms in (7).

The analysis carried out above shows that the plates of the new phase situate themselves parallel to one another, in such a manner that the inclusions of different types alternate and are conjugate with respect to the planes (110). In order to determine the period of such a distribution one must use (14) in order to investigate the correction to \( E_2 = 0 \), which is of the order of \( d_i / L_i \). For this purpose we consider an arbitrary periodic distribution of parallel plates, which are densely adjacent to each other, and the total volume of which are in the ratio \( V_1 / V_2 = \varepsilon_1 / \varepsilon_2 \). The last assumption does not limit the generality of the problem, since a nonperiodic distribution is a limiting case of a periodic one, with the period tending to infinity. In this case the period a starts playing the role of a cyclic length.

For a periodic distribution of the plates the quantity \( \Delta \Theta_i (k) \) is nonzero at the vertices of the corresponding one-dimensional reciprocal lattice: \( \mathbf{k}_0 = 2 \pi h / a \), where \( h = \pm 1, \pm 2, \ldots \) and \( h \neq 0 \). The vector \( \mathbf{k}_0 \) of the reciprocal lattice has the length \( 2 \pi / a \) and is situated in plane which goes through the vectors \( m \) and \( l \), perpendicular to \( l \). Each of the vertices of the reciprocal lattice represents a plane disc of length of the order of \( 2 \pi / D_k \) and transverse dimension \( 2 \pi / L_k \). These vertices can be obtained as a result of sectioning the bar in Fig. 1 by means of a system of equidistant parallel planes, perpendicular to the direction of translation \( a \), and separated from one another by a distance \( 2 \pi / a \) (cf. Fig. 2b). It can be seen from Fig. 2b that the characteristic angle of deviation of the vector \( k \) from the direction \( m \) is of the order \( a / L_1 \). Since for \( k \parallel m \), the expression (14) takes on its minimal value equal to zero, the correction will be positive, and will be of the order \( a / L_0 \), the order of the angle between the vectors \( k \) and \( m \). Thus

\[
E_1 = B \frac{a}{L_1} > 0, \tag{16}
\]

where \( B \sim \lambda (\varepsilon_1 - \varepsilon_2) V_0 \) and \( \lambda \) is the characteristic elastic modulus. It is clear from (16) that \( E_2 = 0 \) for \( a \rightarrow 0 \). The latter means that the "fluctuational" elastic energy becomes minimal when the period \( a \) of the distribution of the plates tends to zero, i.e., when the "average crystal" begins to fragment into infinitely thin elements. This process stops owing to the fact that in the fragmentation of the "average crystal" the number of interfaces between the inclusions increases and at the same time the surface energy increases. The latter is proportional to the number of plates for fixed total volume of the same and increases as \( \gamma L_1 L_0 / a \sim \gamma V_0 / a \), where \( \gamma \) is the coefficient of surface tension on the boundary between inclusions of different types. The period a is determined from the condition of minimum for the sum of the elastic energy (17) and the surface energy:

\[
a \sim \left( \frac{\gamma}{\lambda (\varepsilon_1 - \varepsilon_2)} \right)^{1/2} \frac{V_0}{\gamma} \sim \left( \frac{\gamma}{\lambda} \right)^{1/2} \frac{V_0}{\varepsilon_1 - \varepsilon_2}. \tag{17}
\]

This result shows that the period in the distribution of the plates is related to the thickness of the "average crystal" according to a square-root law, which in principle is subject to experimental verification.

We now must clarify the problem whether the elementary cell consists of two or several plates of different type. We assume that the initial elementary cell consists of several plates of different types (cf. Fig. 3a). We further assume that the surface energy related to
The boundary between the inclusions is constant. This means that the number (but not the size) of the inclusions which form the "average crystal" is constant. In this situation a decrease of the period a, necessary for a decrease of the elastic energy is possible only on account of a reorganization of the initial elementary cell, when the number of inclusions in this cell does not change, but the thicknesses of the inclusions of each type become equal among themselves, whereas the ratio of the thicknesses of inclusions of different types is \( \frac{d_1}{d_2} = \frac{\varepsilon_1}{\varepsilon_2} \).

The above consideration is applicable to a whole class of systems in which the phase transition is not accompanied by a redistribution of the concentration. These are ordered substitutional and interstitial solid solutions (some ferroelectric materials, cases of polymorphism, etc.), if in all these systems there occurs the formation of a tetragonal phase in a cubic matrix.

For the enumerated systems the elasticity moduli change in the phase transition, as a rule by not more than 10%, which in itself makes it possible to apply the results of this theory to the class of systems under discussion. However, there exists another more profound reason for the possibility of using the computational data for the investigation of heterophase systems with different elastic moduli. This reason is related to the fact that the elastic energy of the optimal distribution of the inclusions is asymptotically zero, which speaks of the absence of elastic deformation (with the exception of boundary effects of the order of \( D_s/L_s \ll 1 \), and \( d_i/L_i \ll 1 \), occurring due to the deformations of the matrix only). Since the elastic deformation inside the inclusions is absent, the magnitude of their moduli does not affect the elastic energy of the system.

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**APPENDIX**

We prove that the term in the square brackets in (15) vanishes if \( \Delta \varepsilon = (\varepsilon_1 - \varepsilon_2) \text{m} \times 1 \). Since \( G(km) = k^2 G(m) \), we have

\[
B = (m_\varepsilon, \Delta \varepsilon^2 G(km) \Delta \varepsilon^2 km) = (m_\varepsilon, \Delta \varepsilon^2 G(km) \Delta \varepsilon^2 km) = m_\varepsilon \Delta \varepsilon m_\varepsilon = m_\varepsilon \Delta \varepsilon m_\varepsilon = (e_1 - e_2) m_\varepsilon \Delta \varepsilon m_\varepsilon.
\]

Since by definition \( G_{pqrs} = G_p^{-1} \) we obtain, using the trivial relation \( G_{jp} G_{ps}^{-1} = \delta_{j8} \),
\[ B = (e_1 - e_2) \frac{m_1 \Delta \sigma_i^0}{b} = \frac{\Delta \sigma_i^0}{b} (e_1 - e_2) m_j = \frac{\Delta \sigma_i^0}{b} \Delta s_i. \]

which implies the result.

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