

Spontaneous strains in an incommensurate phase and their effect on the transition to a commensurate one

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Strains produced in an incommensurate phase by their interaction with the order parameter owing to the presence of the Lifshitz invariant are considered on the basis of a phenomenological theory. Exclusion of the strains from the thermodynamic potential produces in the latter a term whose form differs from that of those customarily employed. Minimization of the thermodynamic potential leads to a self-consistent system of equations for the order parameter in the incommensurate phase. Using as examples two cases for which the equations for the order parameter can be solved with mathematical rigor, it is shown that when the strains are taken into account the transition from the incommensurate to the commensurate phase is of first order. One of these cases explains the character of the spontaneous strains in the entire region where the incommensurate phase exists. It is also shown that in a “clamped” crystal the incommensurate—commensurate transition is of second order, but its singularities are other than those obtained if the local strains are neglected.

Clarification of the influence of spontaneous strains on the properties of an incommensurate phase is worthy of attention primarily in connection with the question of phase transitions from an incommensurate phase to a commensurate one, a question widely discussed in the literature. According to most theoretical papers, this transition should be continuous^{1–5}; experiment, however, shows it to be of first order (see Ref. 6 and the references therein). Account was taken in that reference of the connection between the order parameter and the strain, and the result was a first-order transition, but a different approach to treatment of this connection⁷ yielded a second-order transition as before.

This problem was considered in greatest detail in Ref. 8, but the conclusion arrived at there, that the connection between the order parameter and the strain leads to a first-order transition, cannot be regarded as convincing for a number of reasons. In Ref. 8, as in other cited papers, the “constant amplitude” approximation is used, but even if the strains are disregarded different methods of finding this amplitude can lead to a different order of the transition.⁹ In addition, this approximation is valid only in the limiting case of weak anisotropy in the space of the order-parameter components.¹⁰ We point out also that in Ref. 8 the symmetry of one part of the Hamiltonian does not correspond to the symmetry of another part, and the free energy is not bounded from below as $n \rightarrow \infty$, nor is it clear how these circumstances affect the final conclusion.

It is of interest to consider the question of the incommensurate-commensurate phase transition with allowance for strains in cases when there is a rigorous mathematical approach to the equations that describe the incommensurate phase.^{11,12} This is the subject of the present paper. We obtain first some general results concerning strains in the entire region of existence of the incommensurate phase, and their connections with the external stresses. These results are needed also because spontaneous strains are discussed in

Refs. 6–8 only near the point of transition into the commensurate phase, and furthermore the approach there is not general enough. We shall consider also the case of a “clamped” crystal, which has its own distinguishing properties.

STRAIN IN INCOMMENSURATE PHASE

We start with the thermodynamic potential Φ used in Refs. 11 and 12, adding to it several terms:

$$\Phi = \Phi_1 + \Phi_2 = \frac{1}{d} \int_0^d (\tilde{\Phi}_1 + \tilde{\Phi}_2) dx, \quad (1)$$

$$\tilde{\Phi}_1 = \frac{\alpha}{2} \rho^2 + \frac{\beta_1}{4} \rho^4 + \frac{\gamma}{6} \rho^6 + \frac{\beta_2}{4} \rho^4 \cos 4\varphi - \sigma \rho^2 \frac{d\varphi}{dx} + \frac{\delta}{2} \left[\left(\frac{d\rho}{dx} \right)^2 + \rho^2 \left(\frac{d\varphi}{dx} \right)^2 \right],$$

$$\tilde{\Phi}_2 = r_i u_i \rho^2 \frac{d\varphi}{dx} + \frac{1}{2} \lambda_{ij} u_i u_j - \sigma_i u_i + \frac{\delta_i'}{2} \rho^4 \left(\frac{d\varphi}{dx} \right)^2, \quad (2)$$

where d is the period of the functions $\tilde{\Phi}_1(x) + \tilde{\Phi}_2(x)$; $u_1 = u_{xx}$, $u_2 = u_{yy}$, $u_3 = u_{zz}$ are the components of the strain tensor, σ_i are the corresponding components of the stress tensor, and summation from 1 to 3 over the dummy indices is stipulated. The expression for $\tilde{\Phi}_1(x)$ is the same as in Ref. 11. The expression for $\tilde{\Phi}_2$ was written under the assumption that the crystal has orthorhombic symmetry in the high-temperature (symmetric) phase (suitable examples of such crystals are given in Ref. 11), when u_i are invariants and $\tilde{\Phi}_2$ contains products of u_i by the Lifshitz invariant $\rho^2 d\varphi/dx$. For other symmetries, terms in the thermodynamic potential are also possible, made up of products of Lifshitz invariants by invariant combinations of the components of the strain tensor. The quantities λ_{ij} are the elastic moduli in the symmetric phase. The last term of $\tilde{\Phi}_2$ was added to ensure that Φ is bounded from below, as will be shown later on.

Note that, generally speaking, mixed invariants other than those in (2) are possible, containing the strain-tensor components and the order parameter, e.g., $u_{xy}\rho^2 \cos 2\varphi$. Such invariants, however, merely renormalize the thermodynamic-potential coefficients (see below) and therefore do not influence the type of the incommensurate-commensurate transition. The mixed invariants taken into account in (2) are of only one type, the most significant for the problem on hand (in particular, the invariants $u_i\rho^2$, whose role is the same in commensurate and incommensurate phases, have not been written out).

Since the strain tensor is expressed in terms of the strain vector \mathbf{U} , the independent variables should be taken to be the components of \mathbf{U} . In our case periodicity is possible only along the x axis, so that the most general form of the \mathbf{U} vector components is

$$U_x = f_1(x) + a_6 y + a_5 z, \quad U_y = f_2(x) + a_2 y + a_4 z,$$

$$U_z = f_3(x) + a_1' y + a_3 z,$$

where $a_i = \text{const}$. Determining from this the strain tensor¹³ and recognizing that $u_{xy} = u_{xz} = u_{yz} = 0$, since these components are not linked with the order parameter when (2) is used, we obtain $df_2/dx = -a_6$, $df_3/dx = -a_5$, $a_4 = -a_4'$. The constants a_4 , a_5 , and a_6 correspond to pure rotation of the crystal and play no role. In addition, we obtain $u_1 = df_1/dx$, $u_2 = a_2$, $u_3 = a_3$. Substituting this in (2) and minimizing Φ with respect to f_1 with allowance for the fact that σ_1 is a constant (this follows from the equilibrium equation $\partial\sigma_{ik}/\partial x_k = 0$, Ref. 13), we get

$$u_1 = \frac{df_1}{dx} = -\frac{r_1}{\lambda_{11}} \rho^2 \frac{d\varphi}{dx} + a_1. \quad (3)$$

The appearance in (3) of an arbitrary constant a_i that must be additionally defined is due to the specifics of the strains. Were we to minimize (2) with respect to u_i as with respect to ordinary normal coordinates, no arbitrary constant would appear and substitution of the results in (2) would lead to simple renormalization of the components. The fact that (3) contains two terms that are not determined simultaneously is due to the qualitative difference, in a solid, between the spatially inhomogeneous and homogeneous strains (cf., e.g., Ref. 14). We note that if the aforementioned invariant $u_{xy}\rho^2 \cos 2\varphi$ were added to (2), an arbitrary constant would likewise appear, but its determination by the method used below to determine a_i would show it to be zero. In this case the reason is that the point symmetry of the incommensurate phase is the same as that of the symmetric one,¹⁵ and the presence of a constant part in u_{xy} would mean a change of the point symmetry.

Upon substitution of (3), that part of Φ which contains u_i takes the form

$$\begin{aligned} \Phi_2 = & \frac{\delta_1}{2d} \int_0^d \rho^4 \left(\frac{d\varphi}{dx} \right)^2 dx \\ & + \left(-\frac{\lambda_{12}}{\lambda_{11}} r_1 a_2 - \frac{\lambda_{13}}{\lambda_{11}} r_1 a_3 + r_2 a_2 + r_3 a_3 + \frac{r_1}{\lambda_{11}} \sigma_1 \right) I \\ & + \frac{1}{2} \lambda_{ij} a_i a_j - \sigma_i a_i, \end{aligned} \quad (4)$$

$$I = \frac{1}{d} \int_0^d \rho^2 \frac{d\varphi}{dx} dx, \quad (5)$$

where $\delta_1 = \delta_1' - r_1^2/\lambda_{11}$. We determine the constants a_i by minimizing Φ with respect to them (this corresponds to minimization of Φ with respect to the averaged macroscopic strains \bar{u}_i), and obtain thus the equations

$$\begin{aligned} \lambda_{ij} a_j = A_i; \quad A_1 = \sigma_1, \quad A_2 = \left(\frac{\lambda_{12}}{\lambda_{11}} r_1 - r_2 \right) I + \sigma_2, \\ A_3 = \left(\frac{\lambda_{13}}{\lambda_{11}} r_1 - r_3 \right) I + \sigma_3. \end{aligned} \quad (6)$$

These equations are easily solved by introducing the elastic compliances χ_{ij} given by $\chi_{ij}\lambda_{jk} = \delta_{ik}$, so that we get $a_i = \chi_{ij} A_j$. If a free crystal is considered ($\sigma_i = 0$), by substituting the constants a_i in (4) and taking (1) into account we obtain

$$\Phi = \frac{1}{d} \int_0^d \left[\tilde{\Phi}_1 + \frac{\delta_1}{2} \rho^4 \left(\frac{d\varphi}{dx} \right)^2 \right] dx - \frac{b}{2} I^2, \quad (7)$$

$$b = \chi_{ij}' r_i r_j = \frac{1}{\chi_{11}'} \left\{ (\chi_{1i} r_i)^2 + \frac{2}{\lambda_{11}} \det[\chi_{ij}] (\lambda_{13} r_2 - \lambda_{12} r_3) \right\}, \quad (8)$$

where $\det[\chi_{ij}]$ is the determinant of the matrix $[\chi_{ij}]$, $\chi'_{11} = \chi_{11} - \lambda_{11}^{-1}$, and the remaining $\chi'_{ij} = \chi_{ij}$. Since the quadratic form $\lambda_{ij} u_i u_j$ is positive-definite, it follows that $\det[\chi_{ij}] > 0$ and $\chi'_{11} \geq 0$, with $\chi'_{11} = 0$ only if $\chi_{12} = \chi_{13} = 0$. Therefore $b \geq 0$ always. For the sake of clarity we consider anisotropic body and introduce in place of λ_{ij} the hydrostatic compression modulus K_{el} and the shear modulus μ_{el} .¹³ We then obtain from (8), putting $r_1 = r_2 = r_3$

$$b = 4\mu_{el} r_1^2 / (3K_{el} + 4\mu_{el}) K_{el}. \quad (9)$$

Thus, exclusion of the strains from the initial thermodynamic potential leads to expression (7) in which the last term differs substantially from the preceding ones. This term can be broken up into two factors and represented as a renormalization of the coefficient σ of the Lifshitz invariant ($\sigma \rightarrow \sigma + bI/2$). It can be seen here that the renormalization depends on the structure of the incommensurate because of the presence of I , i.e., it is nonlocal. Expression (9) shows that this effect results, as might be expected, from a characteristic property of the solid, viz., the presence of a shear modulus that gives rise to elastic long-range action. We note that the quantity b of (8) is zero not only in the isotropic case at $\mu_{el} = 0$. Thus, the conclusion of Ref. 7 that the incommensurate—commensurate phase transition remains of second order even when the strain is taken into account applies to the special case $r_2 = r_3 = \lambda_{12} = \lambda_{13} = 0$ (and then $\chi'_{11} = \chi_{12} = \chi_{13} = 0$), when $b = 0$, too. This was obtained because the connection between the order parameter and only one component $u_1 = u_{xx}$ was taken into account in Ref. 7.

Expression (7) contains two unknown functions, $\rho(x)$ and $\varphi(x)$, the equations for which we obtain by minimizing Φ with respect to them:

$$\begin{aligned} \delta\rho'' - \delta\rho(\varphi')^2 - 2\delta_1\rho^3(\varphi')^2 + 2\delta\rho\varphi' \\ - \alpha\rho - \beta_1\rho^3 - \gamma\rho^5 - \beta_2\rho^3 \cos 4\varphi = 0, \end{aligned} \quad (10)$$

$$\delta\rho\varphi'' + \delta_1\rho^3\varphi'' + 2\delta\rho'\varphi' + 4\delta_1\rho^2\rho'\varphi' - 2\delta\rho' + \beta_2\rho^3 \sin 4\varphi = 0, \quad (11)$$

where the prime denotes a derivative with respect to x and $\tilde{\sigma} = \sigma + bI$. These equations are of the usual form, but the last term of (7) introduced here an unknown constant I , a self-consistent equation for which is obtained after substituting the solutions of these equations in (5).

Let us also find the condition that separates from the solutions of Eqs. (10) and (11), with different values d of the period, a period such that Φ reaches an absolute minimum. This condition $\partial\Phi/\partial d = 0$, just as relation (9) of Ref. 11, is reduced by using (7) to the form

$$\frac{\delta}{2} [(\rho')^2 + \rho^2(\varphi')^2] + \frac{\delta_1}{2} \rho^4(\varphi')^2 - \frac{\alpha}{2} \rho^2 - \frac{\beta_1}{4} \rho^4 - \frac{\gamma}{6} \rho^6 - \frac{\beta_2}{4} \rho^4 \cos 4\varphi = -\Phi + \frac{b}{2} I^2. \quad (12)$$

To clarify some details, we consider the constant-amplitude approximation $\rho = \text{const}$. In this case (5) yields $I = \pi\rho^2/2d$ and, following the procedure used to derive Eq. (6) of Ref. 9, we get from (7)

$$\Phi = \Phi_c + \frac{\beta_2\rho^4}{2k^2K} [2E - (1-k^2)K] - \frac{\pi\sigma\rho^3}{2kK} \left(\frac{\beta_2}{\delta + \delta_1\rho^2} \right)^{1/2} - \frac{\pi^2 b\beta_2\rho^6}{8k^2K^2(\delta + \delta_1\rho^2)}. \quad (13)$$

Here and elsewhere K and E are complete elliptic integrals with modulus k , and Φ_c is the thermodynamic potential of the commensurate phase (we assume for the sake of argument that $\beta_2 > 0$).

We use (13) to cast light on the lower bound of Φ . At finite ρ the value of Φ increases without limit as $k \rightarrow 0$, with

$$\Phi \rightarrow \frac{\beta_2\rho^4}{2k^2(\delta + \delta_1\rho^2)} [\delta + (\delta_1 - b)\rho^2].$$

Therefore Φ is bounded from below at all ρ only if $\delta_1 > b$. This demonstrates the need for introducing in (2) the term containing δ'_1 , with $\delta'_1 > b + r_1^2/\lambda_{11}$.

Introducing the soliton density $n = 1/d$, we obtain from (13) as $k \rightarrow 1$

$$\Phi = \Phi_c + n\rho^2 \left\{ \rho [\beta_2(\delta + \delta_1\rho^2)]^{1/2} \times \left[1 + 4 \exp \left(- \frac{2\rho\beta_2^{1/2}}{n(\delta + \delta_1\rho^2)^{1/2}} \right) \right] - \frac{\pi}{2} \sigma \right\} - \frac{\pi^2}{8} b\rho^4 n^2. \quad (14)$$

The sign of the last term indicates attraction between the solitons, and this leads to a first-order incommensurate-commensurate phase transition in accord with Refs. 6 and 8. We see that the introduction of δ_1 , which makes correct the behavior of Φ as $k \rightarrow 0$ (i.e., as $n \rightarrow \infty$), does not change the behavior (14) of Φ as $n \rightarrow 0$, something not obvious beforehand.

Consider now an incommensurate phase near the point $\alpha = \alpha_0$ of the transition from a symmetric phase. As $\rho \rightarrow 0$ Eqs. (10) and (11) have the solutions $\rho = \text{const}$ and $\varphi' = Q = \text{const}$, with $I = \rho^2 Q$, so that (cf. Ref. 16)

$$\rho^2 = \frac{\alpha_0 - \alpha}{\beta_1 + 2(\delta_1 - b)q_0^2}, \quad Q = \frac{q_0}{1 + (\delta_1 - b)\rho^2/\delta},$$

$$\Phi = - \frac{(\alpha_0 - \alpha)^2}{4[\beta_1 + 2(\delta_1 - b)q_0^2]};$$

$$\alpha_0 = \frac{\sigma^2}{\delta}, \quad q_0 = \frac{\sigma}{\delta}.$$

Since $\delta_1 > b$, the denominator in ρ^2 and Φ remains positive (at $\beta_1 > 0$), and therefore the spontaneous deformations do not alter the order of the transition from the symmetric to the incommensurate phase.

CASE OF EXACT SOLUTION

An exact solution of the equations for an incommensurate phase was obtained in Ref. 11 at definite values of the constant. This solution turns out to be convenient also when the strains are taken into account. To apply directly the results of Ref. 11 we must put $\delta_1 = 0$. Since we need $\delta_1 > b$ for Φ to have a lower bound, we must see to it that the Φ minimum corresponding to the incommensurate-phase equilibrium state not land in the region of "unphysical" parameters where $\Phi \rightarrow -\infty$.

At $\delta_1 = 0$ Eqs. (10) and (11) agree fully with Eqs. (1.3) and (1.4) [the number 1 preceding a decimal point labels an equation from Ref. 11]. Their solution is therefore given by Eqs. (1.5)–(1.7) with σ replaced by σ . These equations must be supplemented by an equation for I , which is obtained by substituting (1.5) in (5):

$$I = \frac{8\alpha_0 q_0 c (\beta_1 + \beta_2 c)^2}{(3\beta_2 c - \beta_1)^3 (2 - k^2 + k^2 c) (1 - c) K} \times \left\{ 2K - (2 - k^2 + k^2 c) \Pi \left(\frac{k^2}{2} (c - 1), k \right) \right\} \times \left(1 + \frac{b}{\sigma} I \right)^3, \quad (15)$$

where $\alpha_0 = \sigma^2/\delta$, $q_0 = \sigma/\delta$. In place of (1.10) and (1.11) we obtain from (12) and (7)

$$\Phi - \frac{b}{2} I^2 = - \frac{8k^2 c (\beta_1 - \beta_2 c) (\beta_1 + \beta_2 c)^2 (\sigma + bI)^4}{\delta^2 (2 - k^2 + k^2 c) (\beta_1 - 3\beta_2 c)^4} = - \frac{1}{d} \int_0^d \left(\frac{\beta_1}{4} \rho^4 + \frac{\gamma}{3} \rho^6 + \frac{\beta_2}{4} \rho^4 \cos 4\varphi \right) dx. \quad (16)$$

It follows therefore that relation (1.12) remains unchanged.

At the specified values of the other parameters, Eq. (15) yields for I three roots. The root chosen must tend to zero as $k \rightarrow 0$ and $k \rightarrow 1$, as follows from (5) (the two other roots tend to infinity in these cases).

Since the expression for $\Phi - bI^2/2$ coincides according to (16) with the expression for Φ [Eq. (1.10) with the substitution $\sigma \rightarrow \tilde{\sigma}$], we obtain as $k \rightarrow 1$, according to (1.21)

$$\Phi = \Phi_c - \frac{16\alpha_0^2 c (\beta_1 + \beta_2 c)^2 (2\beta_2 c^2 + \beta_2 c - \beta_1)}{(1+c)^3 (\beta_1 - 3\beta_2 c)^4} (1 - k^2) + \frac{b}{2} I^2. \quad (17)$$

As $k \rightarrow 1$ we can neglect $1 - k^2$ compared with $I^2 \sim K^{-2} \sim \ln^{-2}(1 - k^2)$ [this follows from (15)], and we get

$\Phi > \Phi_c$. The incommensurate phase is therefore unstable at $k \approx 1$; the transition to the commensurate phase occurs before k reaches unity, and is of first order. We note that the sign of the last term in (13) differs from that in (17), since there was no minimization with respect to the period d in (13).

The solution considered sheds light on the behavior of the spontaneous strains in the entire region where the incommensurate phase exists. Consider for simplicity the case $\gamma = 0$, when $c = 1$ (Ref. 11). Equation (15) takes then the form

$$I = \frac{4\alpha_0 q_0 (\beta_1 + \beta_2)^2}{(3\beta_2 - \beta_1)^3 K} [E - (1 - k^2)K] \left(1 + \frac{b}{\sigma} I\right)^3.$$

This equation must be solved jointly with (1.15), with replacement $\sigma \rightarrow \bar{\sigma}$ in the latter. Numerical calculation shows that a finite real value of I exists at all k only when $b < 0.07 \beta_1 / q_0^2$. An influential fact at $b > 0.07 \beta_1 / q_0^2$ is that we assume $\delta_1 = 0$, and some of the results may be unrealistic. We shall therefore not consider the case $\beta_1 \rightarrow 0$, which was analyzed in Ref. 11. We note that this restriction on b is not stringent since the superstructure wave vector q_0 is small at $\alpha = \alpha_0$.

Figure 1 shows a curve at whose points the solution considered is in equilibrium (cf. the figure in Ref. 11). It shows also the variations of the superstructure wave vector $Q = \pi/2d$ (i.e., the wave vector corresponding to the order parameters η and ξ , Ref. 11) and the integral I vary on this curve. The integral I determines the averaged spontaneous strains \bar{u}_i , so that at $\sigma_1 = 0$ we have from (3) and (6) $\bar{u}_i = -\chi_{ij} r_j I$. We note that Q does not vary greatly over the entire region of existence of the incommensurate phase, as is frequently observed in experiment (see, e.g., Refs. 17 and 18).

CASE OF SMALL COEFFICIENT β_2

Consider now another case, when a rigorous mathematical approach to the solution of Eqs. (10) and (11) is possible. This occurs in the case of weak anisotropy in the space of the order parameter, i.e., at small β_2/β_1 (Ref. 12), thus supplementing the foregoing analysis that is valid when β_2 is close to or exceeds β_1 (see Fig. 1). Since the term with the coefficient γ does not play a substantial role in the incommensurate-commensurate phase transition, we put for simplicity $\gamma = 0$. We shall now, however take into account, however, the terms with the coefficient δ_1 , since they can play a noticeable role, as was shown above. Allowance for these terms requires that the details of the solution be modified somewhat compared with Ref. 12.

We introduce the dimensionless parameters κ , β , μ , ζ and the functions r , ψ , and f :

$$\alpha = -\frac{\bar{\alpha}_0 \kappa}{\beta^{1/2}}, \quad \beta = \frac{\beta_2}{\beta_1},$$

$$\Phi - \frac{b}{2} I^2 = -\frac{\alpha^2}{4(\beta_1 - \beta_2)} - \frac{\bar{\alpha}_0^2 \beta_2 \mu}{4\beta_1^2}, \quad \zeta = \frac{\delta_1 \bar{q}_0^2}{\beta_1}, \quad (18)$$

$$\bar{\alpha}_0 = \bar{\sigma}^2 / \delta, \quad \bar{q}_0 = \bar{\sigma} / \delta; \quad \rho^2 = \bar{\alpha}_0 \kappa r^2 (\beta_1 \beta_2)^{-1/2}, \quad \psi = \varphi - \pi/4, \quad \bar{q}_0 f = d\psi/dx.$$

The function ψ was chosen for convenience, to have in the commensurate phase $2\psi = 0$ if β_2 is assumed.

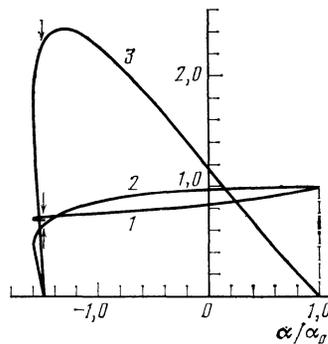


FIG. 1. Relation between α/α_0 and β_2/β_1 at which the employed solution corresponds to an equilibrium state of the incommensurate phase (curve 1); the wave vector of incommensurate superstructure Q (curve 2, which shows Q/q_0) and the integral I (curve 3, which shows $\beta_1 I / \alpha_0 q_0$) as a function of α/α_0 . The arrows mark the point of transition to the commensurate phase. The curves were plotted at $bq_0^2/\beta_1 = 0.02$, and the point indicated corresponds to $\alpha = -1.51\alpha_0$ ($k = 0.994$).

We proceed next as in Ref. 12. In the region where $\sin 2\psi$ is not small, which corresponds to a domain wall (soliton), we use Eqs. (10) and (11), the solution of which we seek, after making the substitution (18), in the form

$$r = \sum_{n=0}^{\infty} \beta^{n/2} R_n, \quad f = \sum_{n=1}^{\infty} \beta^{n/2} f_n. \quad (19)$$

For the first terms we obtain

$$R_0 = 1, \quad R_1 = 0, \quad R_2 = \frac{1}{2} + \frac{|\sin 2\psi|}{\kappa \zeta^{1/2}} - 2 \sin^2 2\psi;$$

$$f_1 = \frac{|\sin 2\psi|}{\zeta^{1/2}}, \quad f_2 = -\frac{|\sin 2\psi|}{2\kappa \zeta^{3/2}}.$$

Since the succeeding terms contain $\sin 2\psi$ in the denominator [$R_n \sim (\sin 2\psi)^{3-n}$, $f_n \sim (\sin 2\psi)^{2-n}$], the series (19) converge asymptotically, e.g., in the interval $0 \leq \psi \leq \pi/4$, if $O(\psi) \gg \beta^{1/2}$.

At small ψ , which corresponds to the inner region of the domain, where the structure is practically commensurate ($\sin 2\psi \approx 0$), we substitute (18) in (10) and (11) and seek the solution of the latter in the form

$$r = \sum_{n=0}^{\infty} \beta^{n/2} r_n, \quad \psi = \sum_{n=1}^{\infty} \beta^{n/2} \psi_n, \quad p = \sum_{n=1}^{\infty} \beta^{n/2} p_n, \quad (20)$$

where p is an auxiliary parameter.¹² The first terms are

$$r_0 = 1, \quad r_1 = 0, \quad r_2 = \frac{1}{2}, \quad r_3 = \frac{2a}{\kappa \zeta^{1/2}} \operatorname{ch} y,$$

$$r_4 = \frac{3}{8} - \frac{a}{\kappa^2 \zeta^{3/2}} \operatorname{ch} y - 4a^2 \operatorname{ch} 2y;$$

$$\psi_1 = a \operatorname{sh} y, \quad \psi_2 = 0, \quad \psi_3 = -\frac{a^2}{12} \operatorname{sh} 3y;$$

$$p_1 = \frac{2}{\zeta^{1/2}}, \quad p_2 = -\frac{1}{\kappa \zeta^{3/2}},$$

$$p_3 = \frac{3 + 8\zeta + 8\zeta^2 \kappa^2 a^2}{4\kappa^2 \zeta^{5/2}},$$

where $y = p\bar{q}_0 x$, and the constant a is connected with μ by

a relation that takes in first-order approximation the form $a^2 = \mu/8\kappa^2$. The series (20) are asymptotic if x is not too large, and in this case $O(\psi) < 1$. The convergence regions of the series (19) and (20) overlap and can be joined, e.g., at $\psi \sim \beta^{1/4}$ and at an appropriate value of x obtainable from (20).

To supplement the procedure of Ref. 12 we must calculate I . This can be done by substituting the series (19) and (20) in (5). The thermodynamic potential is obtained from (18), and in the upshot we get

$$\Phi = \Phi_c - \frac{\tilde{\alpha}_0^2 \beta_2 \mu}{4\beta_1^2} + \frac{\pi^2 \tilde{\alpha}_0^2 b \kappa^2}{2\beta_1 \delta_1 \ln^2(\beta \mu / 32 \kappa^2)}. \quad (21)$$

It is clear hence that $\Phi \rightarrow \Phi_c$ as $\mu \rightarrow 0$, the last term predominates over the penultimate one, and $\Phi > \Phi_c$. The spontaneous strains cause therefore the incommensurate-commensurate transition to be in this case of first order. Note that in this case (small β_2), as can be seen from (21), we cannot put $\delta_1 = 0$.

The results can be compared with those of Ref. 19, where it was shown that for ordinary (commensurate) transitions, if the heat capacity of the solid becomes infinite at the transition point when no account is taken of the strains, interaction of the mode corresponding to the order parameter with acoustic phonons leads to a first-order transition. The heat capacity of the incommensurate phase diverges as the point of transition to the commensurate phase is approached, if the strains are not taken into account.^{11,12} We have shown in the present paper that allowance for the spontaneous strains also leads to a first-order transition, and deduced this on the basis of the Landau theory of the thermodynamic potential. If the crystal with the incommensurate phase is regarded as isotropic, allowance for the strains, just as in the isotropic model considered in Ref. 19, does not change the order of the transition if the shear modulus is zero, inasmuch as in this case $b = 0$ according to (9).

"CLAMPED" CRYSTAL

We consider now a clamped crystal, i.e., a crystal in which there are no macroscopic strains averaged over space ($\bar{u}_i = 0$). Local strains cannot be eliminated by homogeneous stresses, so that one cannot assume $u_i = 0$. At $\bar{u}_i = 0$ we have from (3)

$$a_i = r_i I / \lambda_{11}, \quad a_2 = 0, \quad a_3 = 0. \quad (22)$$

Substituting this in (6) we get $\sigma_i = r_i I$, thus determining the stresses needed to clamp the crystal. Substituting next all these relations in (4) and taking (1) into account we get

$$\Phi = \frac{1}{d} \int_0^a \left[\bar{\Phi}_1 + \frac{\delta_1}{2} \rho^4 \left(\frac{d\bar{\Phi}}{dx} \right)^2 \right] dx + \frac{b_0}{2} I^2, \quad b_0 = \frac{r_1^2}{\lambda_{11}}, \quad (23)$$

where $b_0 \geq 0$, since $\lambda_{11} > 0$ always.

In expression (23) for Φ , the sign preceding the last term turns it different from that in (7), leading to reversal of the signs of the last terms in (17) and (21). In these cases we obtain there $\Phi < \Phi_c$. The incommensurate-commensurate phase transition in a clamped crystal is thus of second order irrespective of the presence of local strains determined by the

stresses (3) and (22).

The transition will have, however, a character different from that obtained by simply putting $u_i = 0$. Consider this with Eq. (14) as the example. If we assume $u_i = 0$, i.e., put $b = 0$ in (14), we find as the transition point is approached ($\rho \rightarrow \rho_c$) that $n \sim |\ln(\rho_c - \rho)|^{-1}$, and this determines the distinguishing features of such a transition.¹⁻⁶ If, however, (23) is taken into account, replacing b in (14) by $-b_0$, the exponential can be neglected and, leaving out δ_1 for simplicity, we get from (14) as $\rho \rightarrow \rho_c$:

$$\Phi = \Phi_c + n \rho_c^2 (\beta_2 \delta)^{1/2} (\rho - \rho_c) + \frac{\pi^2}{8} b_0 \rho_c^4 n^2,$$

$$\rho_c = \frac{\pi \sigma}{2(\beta_2 \delta)^{1/2}} = \frac{\pi q_0}{2} \left(\frac{\delta}{\beta_2} \right)^{1/2}.$$

This is the expression for the usual thermodynamic potential of the Landau parameter, with an order parameter $n^{1/2}$, so that the incommensurate-commensurate transition in a clamped crystal will be a second-order phase transition. The equilibrium of the soliton density is then given by

$$n = \frac{16\beta_2^{1/2}}{\pi^4 b_0 q_0^2 \delta^{1/2}} (\rho_c - \rho) = \frac{16\beta_2^2 (\alpha - \alpha_c)}{\pi^5 b_0 \delta q_0^3 (\beta_1 - \beta_2)}, \quad (24)$$

where $\rho^2 = -\alpha/(\beta_1 - \beta_2)$, and α_c is the value of α at the transition point. A similar result was obtained in Ref. 20 for a monolayer of atoms on an organic substrate (the condition $\bar{u}_1 + \bar{u}_2 = 0$ was used).

An incommensurate-commensurate phase transition in a clamped crystal has nonetheless certain peculiarities. If α is regarded as an ordinary linear function of temperature, the soliton density decreases abruptly as $\alpha \rightarrow \alpha_c$ because of the presence of the small term q_0 in the denominator of (24). Let us find the heat-capacity discontinuity in this transition:

$$\Delta C \sim -\frac{d^2 \Phi}{d\alpha^2} = \frac{4\beta_2^2}{\pi^4 b_0 q_0^2 (\beta_1 - \beta_2)^2}. \quad (25)$$

Here, too, q_0 is in the denominator and the jump will be large. We note that Eqs. (24) and (25) are, strictly speaking, valid only for small β_2 , when the constant amplitude approximation¹⁰ is valid, and must be regarded as approximations if the β_2 are not small.

We consider in conclusion the incommensurate phase at arbitrary stresses. In this case, using (6), we obtain in lieu of (7)

$$\Phi = \frac{1}{d} \int_0^a \left[\bar{\Phi}_1 + \frac{\delta_1}{2} \rho^4 \left(\frac{d\bar{\Phi}}{dx} \right)^2 \right] dx + \frac{r_1^2}{2\lambda_{11}} I^2 - \frac{1}{2} \chi_{ij} (\sigma_i - r_i I) (\sigma_j - r_j I). \quad (26)$$

The increment to the integral is zero if

$$\chi_{ij} (\sigma_i - r_i I) (\sigma_j - r_j I) = r_i^2 I^2 / \lambda_{11}. \quad (27)$$

If the stresses satisfy this equation, the incommensurate phase behaves as if no account were taken of the stresses, although the latter are present and are given by (3) and (6). In the isotropic case and under uniform hydrostatic stresses ($\sigma_1 = \sigma_2 = \sigma_3$) we obtain from (2) (σ_P is the Poisson coefficient¹³)

$$\sigma_1 = \left\{ 1 \pm \left[\frac{1 + \sigma_p}{3(1 - \sigma_p)} \right]^{1/2} \right\} r_1 l. \quad (28)$$

At stresses intermediate between the two values of (28), the crystal behavior relative to the incommensurate-commensurate phase transition is that of a clamped one; an analogous stress range is obtained also from (27). Note that the term "clamped crystal" was used above in a somewhat arbitrary sense, since not all the terms responsible for the thermal expansion were taken into account in the thermodynamic potential (cf. Ref. 21). The arguments just advanced show that the results deduced from (23) hold also in a stress range wider than that in which the crystal is clamped in the arbitrary sense indicated above.

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