New type of phase diagram with incommensurate phase

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The case is considered when an irreducible representation of the symmetry group of the initial phase of a crystal does not allow a Lifshitz invariant, but an invariant appears as a result of a phase transition into one of the commensurate phases. A phase diagram is obtained, on which an incommensurate phase appears between two commensurate ones that are not subgroup related. The incommensurate phase borders on the initial phase along a line of second-order phase transitions; this line is continued in both directions by lines of phase transitions, likewise of second order, between the initial and commensurate phases. The incommensurate phase borders on one of the commensurate phases along a line of continuous transitions, and on the other along a line of first-order phase transitions. The phase diagram has accordingly two different triple points.

It is known that if the symmetry-group irreducible representation, according to which the order parameter of an initial crystal phase is transformed, admits of a Lifshitz gauge invariant[1] that is linear in the spatial derivatives and quadratic in the order-parameter components, an incommensurate phase appears on the phase diagram of the crystal. Since the thermodynamic potential contains the Lifshitz invariant, the initial phase loses stability relative to a spatially inhomogeneous order parameter, so that a phase transition takes place from the initial into an incommensurate phase. Only later (when the temperature is lowered further), a transition takes place to one of the commensurate phases with a spatially homogeneous order parameter.[4,5] The Lifshitz invariant can exist only for a multicomponent order parameter, and in the simplest case of a two-component parameter $\eta=\rho\cos\varphi$, $\xi=\rho\sin\varphi$ this invariant is of the form

$$\eta\partial\xi/\partial z-\xi\partial\eta/\partial z=\rho^2\partial\varphi/\partial z.$$

Note that to realize the initial—incommensurate—commensurate phase transition sequence the coefficient of the invariant that is anisotropic in the component space of the order parameter (an invariant of the form $\rho^n\cos n\varphi$ for a two-component order parameter) must not be too large. Otherwise a first order transition takes place directly from the initial to the corresponding commensurate phase (see, e.g., Refs. 6–8). It is also important in what follows that corresponding to a multicomponent order parameter are several commensurate phases that are stable in different regions of the space of the thermodynamic-potential coefficients, and when an external parameter, such as temperature or pressure, on which these coefficients depend, is altered, transitions can occur between different commensurate phases. In the case of a two-component order parameter there exist three commensurate phases, and the transitions between them can be described on a unified basis, using the thermodynamic potential of the initial phase (see Ref. 9).

This leads to another possible appearance of an incommensurate phase on the phase diagram. Assume that the representation of the initial phase does not allow a Lifshitz invariant, but the representation of one of the commensurate phases (which are subgroups of the symmetry group of the initial phase) does. This invariant is formed from a gauge invariant that is linear in the derivatives; these must be of degree not higher than second in the order-parameter components, since definite combinations of the order-parameter components acquire spontaneous values in the commensurate phase. If the commensurate-phase symmetry-group representation that allows a Lifshitz invariant describes a phase transition to a neighboring commensurate phase, an incommensurate phase can appear between them. This is in fact the case considered in the present article.

Obviously, the simplest realization of our case is a three-component order parameter. For a two-component parameter, transitions between commensurate phases are described by one-dimensional representations of the symmetry groups of these phases, and no Lifshitz invariant can exist for them (see Ref. 9). Three-dimensional representations exist in crystal classes of cubic syngony. There are five such classes: O_h, O, T_d, T_h, T, and eleven representations. These representations can be divided into three categories. Out of the eleven, three (two of class O and one of class T) allow a Lifshitz invariant, as do also two-dimensional representations of the corresponding subgroups. These subgroups are C_3 and C_4 for the vector representation F_1 of class O; D_3 and D_3 (different) for the nonvector representation of class O, and C_3 and C_3 for the vector representation of class T. These are the most complicated cases because several different incommensurate phases exist on the phase diagram; we do not consider them here.

Five representations, three (F_{1u}, F_{1g}, F_{2g}) of class O_h and one (F_2) of class T_d, and one (F_g) of class T_h allow now Lifshitz invariant, nor do the two-dimensional representations of the subgroups corresponding to them. These cases will likewise not be considered here. Note that according to several papers (see, e.g., Refs. 10–13) an incommensurate phase can exist on the phase diagram.

Finally three representations, viz., F_{2u} of class O_h, F_1 of class T_d, and F_u of class T_h do not allow a Lifshitz invariant, but two-dimensional representations of their subgroups do, namely the subgroup D_3 the representation F_{2u} of class O_h, and the subgroup C_3 for the representation F_1 of class T_d and for the representation F_u of class T_h. We consider below the first of these three cases. Note that it was already considered

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in the literature.[13,14] In Ref. 13, however, no account was taken in fact of the anisotropic invariant, which plays a major role, while the phase diagram was not considered in Ref. 14. In addition, the principal gauge invariant of third degree in the components of the order parameter and linear in the derivative was incorrectly written in Refs. 13 and 14 (the expression given there is not an invariant). We note also that arguments similar to those used here, with respect to the possible appearance of a Lifshitz invariant induced by a phase transition, have already been advanced in Ref. 15, but were applied to four-dimensional representations, and the phase diagram, which judging from the text was not calculated, differs in principle from the diagram of the present paper.

The three-dimensional representation F_{2u} of the crystal class O_h allows three independent invariants[16]:

$$I_2=u^2+v^2+w^2,\quad I_4=u^4+v^4+w^4,\quad I_6=u^2v^2w^2, \tag{1}$$

where the number superscript denotes here and elsewhere the degree of the corresponding invariant with respect to the components u, v, and w of the basis of the F_{2u} representation. These are components of a third-rank tensor (see, e.g., Ref. 17):

$$u\sim x(y^2-z^2),\quad v\sim y(z^2-x^2),\quad w\sim z(x^2-y^2).$$

The subgroups of the symmetry group O_h in the representation F_{2u} and the corresponding types of solutions for the order parameter u, v, w are (see, e.g., Ref. 17):

$$\begin{gathered}1)\ D_3\ (u=v=w),\ 2)\ D_{2d}\ (u=v=0),\\ 3)\ C_{2v}\ (u=v,\ w=0),\ 4)\ C_2(u=v),\\ 5)\ C_s(w=0),\ 6)\ C_1.\end{gathered} \tag{2}$$

We set up, for the F_{2u} representation, gauge invariants that are linear in the derivatives, and confine ourselves to the lowest—third—degree in the order-parameter components. There are two such invariants:

$$\begin{aligned}\tilde{I}_3&=u_x(v^2-w^2)+v_y(w^2-u^2)+w_z(u^2-v^2),\\ \tilde{I}_3'&=(v_z-w_y)vw+(w_x-u_z)wu+(u_y-v_x)uv,\end{aligned} \tag{3}$$

where the subscripts x, y, and z denote here and elsewhere the derivatives with respect to the corresponding coordinates. The second invariant, however, differs from the first by a total derivative

$$2\tilde{I}_3'-\tilde{I}_3=[u(w^2-v^2)]_x+[v(u^2-w^2)]_y+[w(v^2-u^2)]_z,$$

and we need therefore consider only one invariant $\tilde{I}_3$, which leads in the D_3 phase to a Lifshitz invariant.

The gauge invariants quadratic in the derivatives and in the order-parameter components are of the form[18]

$$\begin{aligned}\tilde{I}_2&=u_x^2+v_y^2+w_z^2-(u_xv_y+w_zu_x+v_yw_z),\\ \tilde{I}_2'&=(u_x+v_y+w_z)^2,\\ \tilde{I}_2'',{}'''&=(v_z\pm w_y)^2+(w_x\pm u_z)^2+(u_y\pm v_x)^2.\end{aligned} \tag{4}$$

They are linearly related by the total derivative:

$$\begin{aligned}&{}^1/_3(\tilde{I}_2-\tilde{I}_2')+{}^1/_4(\tilde{I}_2''-\tilde{I}_2''')\\ &=(wu_z-uv_y)_x+(uv_x-vw_z)_y+(vw_y-wu_x)_z\end{aligned}$$

and we need consider only three of them.

Since a Lifshitz invariant exists for a two-dimensional representation of the symmetry group D_3 of the commensurate phase 1, it is convenient to change from the variables u, v, w into new ones that transform respectively in accordance with the two-dimensional and one-dimensional representations of the group D_3, and replace similarly the variables x, y, z by X, Y, Z. The relations between the old and new variables are

$$\begin{gathered}\eta=-\frac{1}{\sqrt{6}}(u+v-2w),\quad \xi=\frac{1}{\sqrt{2}}(u-v),\quad \zeta=\frac{1}{\sqrt{3}}(u+v+w),\\ u=\frac{1}{\sqrt{6}}(-\eta+\sqrt{3}\,\xi+\sqrt{2}\,\zeta),\quad v=-\frac{1}{\sqrt{6}}(\eta+\sqrt{3}\,\xi-\sqrt{2}\,\zeta),\\ w=\frac{1}{\sqrt{3}}(\sqrt{2}\,\eta+\zeta),\\ X=-\frac{1}{\sqrt{6}}(x+y-2z),\quad Y=\frac{1}{\sqrt{2}}(x-y),\quad Z=\frac{1}{\sqrt{3}}(x+y+z),\\ x=\frac{1}{\sqrt{6}}(-X+\sqrt{3}\,Y+\sqrt{2}\,Z),\quad y=-\frac{1}{\sqrt{6}}(X+\sqrt{3}\,Y-\sqrt{2}\,Z),\\ z=\frac{1}{\sqrt{3}}(\sqrt{2}\,X+Z),\end{gathered} \tag{5}$$

meaning rotations of the coordinates in the corresponding spaces. It is convenient also to replace and by an amplitude and a phase

$$\eta=\rho\cos\varphi,\quad \xi=\rho\sin\varphi. \tag{6}$$

In the new variables, the invariants (1) become

$$I_2=\zeta^2+\rho^2,\quad 6I_4=2\zeta^4+12\zeta^2\rho^2+3\rho^4+4\sqrt{2}\zeta\rho^3\cos 3\varphi, \tag{7}$$

$$\begin{aligned}108I_6=&4\zeta^6-12\zeta^4\rho^2+9\zeta^2\rho^4+4\sqrt{2}\zeta^3\rho^3\cos 3\varphi\\ &-6\sqrt{2}\zeta\rho^5\cos 3\varphi+2\rho^6\cos^2 3\varphi.\end{aligned}$$

The invariant $\tilde{I}_3$ [Eq. (3)] takes the form

$$\begin{aligned}\sqrt{3}\tilde{I}_3=&2\zeta(\xi\eta_Z-\eta\xi_Z)+2\zeta(\xi\zeta_X-\eta\zeta_Y)-\sqrt{2}\,2\eta\xi\zeta_X\\ &-\sqrt{2}(\eta^2-\xi^2)\zeta_Y-2\eta\xi(\eta_X-\xi_Y),\end{aligned} \tag{8}$$

where we have discarded the total derivatives with respect to X, Y, and Z. We disregard hereafter terms with derivatives with respect to X and Y, since we are interested only in the term with the derivative with respect to Z, a term that takes in the commensurate phase 1, where $\zeta=\zeta_s$, the form of a Lifshitz invariant:

$$\tilde{I}_3=-2\zeta\rho^2\varphi_Z/\sqrt{3}.$$

The invariants (4) are then given by

$$\begin{gathered}2\tilde{I}_2=\eta_Z^2+\xi_Z^2=\rho_Z^2+\rho^2\varphi_Z^2,\quad \tilde{I}_2'=\zeta_Z^2,\\ 3\tilde{I}_2''=2\tilde{I}_2+4\tilde{I}_2',\quad \tilde{I}_2'''=2\tilde{I}_2,\end{gathered} \tag{9}$$

where the derivatives with respect to X and Y were also discarded.

We represent the thermodynamic potential of the initial phase O_h in the form

$$\begin{gathered}\Phi=\int\Phi(Z)\,dZ\Big/\int dZ,\\ \Phi(Z)=\alpha I_2+\beta I_2^2+3\beta' I_4+\sqrt{3}\sigma\tilde{I}_3/2+2\delta\tilde{I}_2+\delta'\tilde{I}_2'.\end{gathered} \tag{10}$$

To make this potential finite, we must assume coefficients

$\beta > 0, \beta + 3\beta' > 0, \delta > 0, \delta' > 0$. The minimum number of invariants was taken into account in (10). If homogeneous invariants of higher degrees are included, e.g., $\gamma I_2^3 + \gamma' I_2 I_4 + \gamma'' I_6 + \delta'' I_4^2$, the phase diagram can have besides the commensurate phases 1 and 2 also other commensurate phases, phase 3 (at $\gamma'' > 0$) and phase 5 (at $\delta'' > 0$, or more accurately at $\delta'' > \gamma'^2/4\beta$). These phases, however, will be stable only at relatively large values of $|\alpha|$, and the phase diagram does not change in the region of small values of $|\alpha|$.

The phase diagram corresponding to the thermodynamic potential (10) is shown in the figure.

Substituting expressions (7)–(9) in (10), we get

$$\Phi(Z) = \alpha\zeta^2 + \alpha\rho^2 + (\beta+\beta')\zeta^4 + 2(\beta+3\beta')\zeta^2\rho^2 + (\beta + {}^3/_2\beta')\rho^4 + 2\sqrt{2}\beta'\zeta\rho^3\cos 3\varphi - \sigma\zeta\rho^2\varphi_z + \delta\rho^2\varphi_z{}^2 + \delta\rho_z{}^2 + \delta'\zeta_z{}^2. \quad (11)$$

Varying the thermodynamic potential Φ (10) with $\Phi(z)$ (11) with respect to the variables ζ, ρ, and φ we get a system of three nonlinear equations for ζ, ρ, and φ:

$$\alpha\zeta + 2(\beta+\beta')\zeta^3 + 2(\beta+3\beta')\zeta\rho^2 + \sqrt{2}\beta'\rho^3\cos 3\varphi - {}^1/_2\sigma\rho^2\varphi_z - \delta'\zeta_{zz} = 0,$$
$$\alpha\rho + 2(\beta+3\beta')\zeta^2\rho + (2\beta+3\beta')\rho^3 + 3\sqrt{2}\beta'\zeta\rho^2\cos 3\varphi - \sigma\zeta\rho\varphi_z + \delta\rho\varphi_z{}^2 - \delta\rho_{zz} = 0,$$
$$3\sqrt{2}\beta'\zeta\rho^3\sin 3\varphi - {}^1/_2\sigma\rho^2\zeta_z - \sigma\zeta\rho\rho_z + 2\delta\rho\rho_z\varphi_z + \delta\rho^2\varphi_{zz} = 0. \quad (12)$$

The initial phase corresponds to a trivial solution of Eqs. (12): $\zeta = \rho = 0$ or $u = v = w = 0$. Corresponding to the commensurate phases 1 and 2 are respectively the solutions:

$$1)\ \zeta^2 = \frac{-\alpha}{2(\beta+\beta')}, \quad \rho^2 = 0, \quad \Phi = -\frac{\alpha^2}{4(\beta+\beta')},$$
$$2)\ 2\zeta^2 = \rho^2 = \frac{-\alpha}{3(\beta+3\beta')}, \quad \cos 3\varphi = 1, \quad \Phi = -\frac{\alpha^2}{4(\beta+3\beta')}. \quad (13)$$

The solution in phase 1 is for two out of the eight possible domains that correspond to the diagonals of the cube made up of u, v, and w [see Eq. (2)]. We consider hereafter only one domain, assuming $\zeta > 0$. In phase 2 there are six domains corresponding to the edges of the cube [see (2)]. In the incommensurate phase there will be only 24 domains if the domains are understood here in the same sense as in the commensurate phases. If, however, a distinction is made only between regions with different direction (but not sign) of the wave vector of the incommensurate superstructure, there will be four such regions (corresponding to the four diagonals of the cube).

For the incommensurate phase, we seek the solution of the system (12) in an approximation with constant ζ and ρ, when only the phase φ varies with Z: $\zeta_z = 0, \rho_z = 0$ (cf. Refs. 3, 19, and 20). We shall determine the conditions for the validity of this approximation below.

The third equation of (12) is then reduced to the equation of a mathematical pendulum:

$$\delta\rho^2\varphi_{zz} + 3\sqrt{2}\beta'\zeta\rho^3\sin 3\varphi = 0, \quad (14)$$

where the role of the time is played by the coordinate Z. The first integral of this equation is the sum of the "kinetic" and "potential" energies [see (11)]:

$$\delta\rho^2\varphi_z{}^2 - 2\sqrt{2}\beta'\zeta\rho^3\cos 3\varphi = c. \quad (15)$$

The solution oof (15), and hence also of (14), is

$$\varphi(Z) = \frac{2}{3}\,\mathrm{am}\left(\frac{3}{2}pZ, k\right) + \varphi_0, \quad \cos 3\varphi_0 = \frac{\beta'}{|\beta'|},$$
$$k^2 = \frac{4\sqrt{2}|\beta'|\zeta\rho^3}{2\sqrt{2}|\beta'|\zeta\rho^3 + c}, \quad p^2 = \frac{4\sqrt{2}|\beta'|\zeta\rho}{\delta k^2}, \quad (16)$$

where am (z, k) is an elliptic Jacobi function with modulus k $(0 \leqslant k \leqslant 1)$. Since the origin Z_0 of the coordinate Z is arbitrary, the second integration constant Z_0 (the first is c or k) can be set equal to zero.

Substituting the solution (16) in the thermodynamic potential (11) and integrating with respect to Z, we obtain

$$\Phi = \alpha\zeta^2 + \alpha\rho^2 + (\beta+\beta')\zeta^4 + 2(\beta+3\beta')\zeta^2\rho^2 + \left(\beta + \frac{3}{2}\beta'\right)\rho^4 - 2\sqrt{2}|\beta'|\zeta\rho^3 - 4\sqrt{2}|\beta'|\zeta\rho^3\frac{1}{k^2K}\left[k'^2K - 2E + \left(\frac{4\sqrt{2}\beta^0}{|\beta'|}\frac{\zeta}{\rho}k^2\right)^{1/2}\right], \quad (17)$$

where K and E are complete elliptic integrals of the first and second kind, with modulus k, $k'^2 = 1 - k^2$, and we introduce for brevity the notation

$$\beta_0 = \sigma^2/16\delta, \quad \beta^0 = \pi^2\beta_0/8. \quad (18)$$

Varying (17) with respect to k we get

$$k^2/E^2 = (|\beta'|/\sqrt{2}\beta^0)\rho/\zeta. \quad (19)$$

Since the period of the functions η (Z) and ξ (Z), as follows from (16), is $l = 4K/p$, the wave number of the incommensurate superstructure is

$$q = 2\pi/l = {}^1/_2\pi p/K. \quad (20)$$

The constants ζ and ρ can be determined, just as, from the condition that the thermodynamic potential (17) be an extremum: $\partial\Phi/\partial\zeta = 0, \partial\Phi/\partial\rho = 0$. As a result, using (19), we get the expressions

$$\zeta^2 = \frac{-\alpha}{2\beta}\left[1 + \frac{\beta'}{\beta} + \left(1 + 3\frac{\beta'}{\beta}\right)\left(\frac{\beta^0}{\beta'}\right)^2\frac{2k^4}{E^4} - \frac{\beta^0}{\beta}\left(\frac{\beta^0}{\beta'}\right)^2\frac{2k^4}{E^6}\left(1 + k'^2 + \frac{2E}{K}\right)\right]^{-1},$$
$$\rho^2 = \frac{-\alpha}{2\beta}\left[1 + \frac{3}{2}\frac{\beta'}{\beta} + \left(1 + 3\frac{\beta'}{\beta}\right)\left(\frac{\beta'}{\beta^0}\right)^2\frac{E^4}{2k^4} - \frac{\beta'}{\beta}\frac{\beta'}{\beta^0}\frac{3E^2}{2k^4}\left(1 + k'^2 - \frac{2E}{3K}\right)\right]^{-1}. \quad (21)$$

Eliminating ζ and ρ from (19) and (21), we obtain an equation that relates the modulus of the elliptic functions k with the coefficients of the thermodynamic potential (10):

$$\left(\frac{\beta'}{\beta^0}\right)^3 - \frac{3}{2E^2}\left(1 + k'^2 - \frac{2E}{3K}\right)\left(\frac{\beta'}{\beta^0}\right)^2 - \frac{3k^4}{2E^4}\frac{\beta'}{\beta^0} + \frac{k^4}{E^6}\left(1 + k'^2 + \frac{2E}{K}\right) = 0. \quad (22)$$

Analysis of (22) shows that the function $k(\beta')$ has two branches. One exists in the β' interval from $2\beta^0$ to $\beta^0/2$, and at k values from 1 to 1 [*sic*!] and goes through a minimum $k^2 \approx 0.94$ at $\beta' \approx 1.03\beta^0$. This branch does not correspond to a minimum of the thermodynamic potential (10), and will therefore not be considered. The other branch exists in the β' intervals from β_0 to $-\beta^0$ and for k from 0 to 1, respectively. The values of for this branch first increase from 0 at $\beta' = \beta_0$, reach a maximum $k^2 \approx 0.61$ at $\beta' \approx 0.82\beta_0$, decrease again to 0 at $\beta' = 0$, and then increase to 1 at $\beta' = \beta^0$. This branch of the function $k(\beta')$ corresponds to an incommensurate phase, i.e., to the minimum of the thermodynamic potential (10).

In the region $\beta' = \beta_0$, expanding (17) and (19)–(21) in powers of the small dimensionless quantities $(\beta_0 - \beta')/\beta_0$ and k^2 and retaining only the leading terms, we get

$$\varphi = qZ, \quad \zeta^2 = \frac{-\alpha}{2(\beta+\beta_0)}, \quad \rho^2 = \frac{1}{2} k^4 \zeta^2,$$

$$\Phi = -\frac{\alpha^2}{4(\beta+\beta_0)}, \quad q = p = \zeta \frac{|\sigma|}{2\delta}, \quad k^4 = \frac{16(\beta_0-\beta')}{\beta_0}. \tag{23}$$

The solution (23) goes over continuously at $\beta' = \beta_0$ into the solution (13) for the commensurate phase 1, so that the phase transition from the commensurate phase 1 to an incommensurate phase behaves, in the approximation considered, as a second-order transition. However, analysis of the exact equations (12) and of the thermodynamic potential (11) shows that this transition is of first order. Thus, the approximation used here, with constant ζ and ρ, does not permit a correct identification of the order of the transition from the commensurate phase 1 to an incommensurate phase. We shall not dwell further on this problem, since its consistent solution calls for taking invariants of higher degrees into account in the thermodynamic potential (10).

In the region $\beta' = 0$, expanding expressions (17) and (19)–(21) in powers of the small dimensionless quantities β'/β_0 and k^2 and retaining only the leading terms, we obtain

$$\varphi = qZ, \quad \zeta^2 = \rho^2 = \frac{-\alpha}{4(\beta-\beta_0)}, \quad \Phi = -\frac{\alpha^2}{4(\beta-\beta_0)},$$

$$q = p = \zeta \frac{|\sigma|}{2\delta}, \quad k^2 = \frac{\sqrt{2}|\beta'|}{\beta_0}. \tag{24}$$

Solutions (23) and (24) can be called single-harmonic, since

$$\eta = \rho_0 \cos q_0 Z, \quad \xi = \rho_0 \sin q_0 Z, \quad \zeta = \zeta_0, \tag{25}$$

where ζ_0, ρ_0 and q_0 are determined from (23) or (24), and the forms of the solutions for u, v, and w in terms of the variables x, y, and z can be deduced from Eq. (5).

To estimate the region of values of β' at which the single-harmonic solution (24) is valid, we obtain for this solution, using the exact equations (12), corrections in the form of higher harmonics:

$$\frac{\Delta\zeta}{\zeta_0} = -\frac{\Delta\rho}{\rho_0} = \frac{1}{16}\frac{\beta'}{\beta_0}\left(1 + \frac{12\sqrt{2}}{13+9\delta'/\delta}\cos 3q_0 Z\right),$$

$$\Delta\varphi = \frac{1}{16}\frac{\beta'}{\beta_0}\left(q_0 Z + \frac{4\sqrt{2}}{3}\frac{16+9\delta'/\delta}{13+9\delta'/\delta}\sin 3q_0 Z\right). \tag{26}$$

For brevity we have neglected here β'/β compared with β'/β_0.

It follows from (16) that the relative corrections to the solution (24) are small if

$$\beta' \ll \beta_0. \tag{27}$$

It must also be taken into account that the numerical coefficient of the ratio β'/β_0 is small [see (26)]. The single-harmonic solution (14) is therefore valid in fact up to values of k that are close to its maximum limit $k = 1$, which corresponds to the limit of the existence of the solution (16), and hence of an incommensurate phase.

Putting $k = 1$, we get $\beta' = \beta_0$ from (17), (19) and (21) and the same values for ζ, ρ, and Φ as in the commensurate phase 2 at $\beta' = -\beta^0$ [see (13)]. Nonetheless, the transition from the incommensurate phase to the commensurate 2 is not of second order in the approximation considered, but a very weak first-order transition. If the constants ζ and ρ are determined not from the condition that the thermodynamic potential be a minimum, as was done above, but are chosen to be the same as in the commensurate phase 2 [Eq. (13)], the transition from the incommensurate into the commensurate phase 2 will be continuous. This means that the terms which determine the first-order transition are outside the scope of the considered approximation.

The situation here is apparently the same as in the usual case, i.e., when a Lifshitz invariant is present in the thermodynamic potential of the initial phase (see Refs. 3, 19, and 20). In Refs. 21 and 22 were obtained, for particular cases, exact solutions for the distribution of the order parameter in an incommensurate phase near the transition into a commensurate phase, and the phase transition described by these solutions turned out to be continuous.

Note that the transition considered differs from the usual in the Landau theory of second-order transitions. It is therefore called here a continuous rather than a second-order transition. The specific features of the continuous phase transitions are illustrated, for example, by the anomalies of the heat capacity $C = T\partial^2\Phi/\partial T^2$ in an incommensurate phase near the transition. If it is assumed that only one coefficient β' has a linear dependence on the temperature, $\beta' = \beta'_T(T-\theta)$, we obtain approximately from (17) and (19), taking ζ and ρ in the incommensurate phase to be the same as in the commensurate phase 2 [Eq. (13)] (cf. Ref. 23)

$$C = \frac{8}{9}\frac{\alpha^2}{\beta}\frac{\beta_T'}{\beta}\frac{T_2}{T-T_2}\ln^{-2}\left[\frac{T-T_2}{8(\theta-T_2)}\right], \tag{28}$$

where T_2 is obviously determined from the relation $\beta^0 = \beta'_T(\theta - T_2)$. It follows from (28) that C increases abruptly, almost in inverse proportion to $(T - T_2)$, when the continuous-transition point $T = T_2$ is approached. In the commensurate phase 2 the value of C is small compared with (28) and can be assumed to be zero. We note also that the single-harmonic approximation is not valid in the vicinity of the continuous phase transition and the solution for the spatial distribution of the order parameter in the incommensurate phase is determined by an aggregate of harmonics of any order.

In the vicinity of the continuous transition, the condition for validity of the approximation of constant ζ and ρ (variation of only the phase φ with change of Z) can be shown to be, using the set of equations (12), the inequality

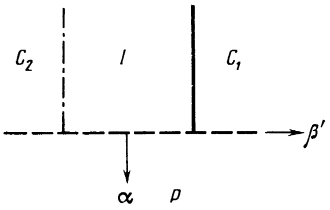

FIG. 1. Phase diagram on the plane of the thermodynamic-potential coefficients α and β'. Notation: $C_{1,2}$—commensurate phases, I—incommensurate phase, P—initial (progenitor) phase. The dashed lines correspond to second-order phase transitions, the solid line to a first-order transition, and the dash-dot line to a continuous transition.

$$\beta_0 \ll \beta. \tag{29}$$

This inequality suffices for the approximation of constant ζ and ρ to be valid also in the entire region of existence of the incommensurate phase (provided, of course, that ζ and ρ are relatively small, i.e., that $|\alpha|$ is not too large).

We emphasize that on the phase diagram shown in the figure there are three triple points,[24] of which the left-hand one differs by being the junction of two second-order transition lines and one continuous-transition line.

We emphasize also that the commensurate–incommensurate–commensurate sequence of phase transitions considered here is unusual because the commensurate phases are not connected by subgroup relations. Such a sequence of transitions through an incommensurate phase can be described within the framework of a phenomenological approach only by using the concept of a "progenitor" of the initial phase (cf. Ref. 9—for phase transitions via an intermediate commensurate phase).

An incommensurate phase is usually observed between two commensurate phases whose symmetry groups are subgroups of one another (see, e.g., Ref. 25). This, so to speak, is a classical situation corresponding, in particular, to the presence of a Lifshitz invariant in the thermodynamic potential.[4,5] An incommensurate phase, however, was observed also between two not-subgroup-related commensurate phases (see, e.g., Refs. 25–27). It is still to early to identify these cases with those considered above, in view of the lack of sufficient experimental data. The present paper does reveal the characteristic properties of incommensurate phase transitions of the considered type and facilitates by the same token an experimental search for such transitions.

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