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# Theoretical Treatment of Incommensurate-Commensurate Phase Transitions

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Incommensurate-commensurate phase transition is theoretically treated near and far from the Lifshitz point on the phase diagram for a two-component order parameter. This transition is shown to be of the first order only. Analytical expressions valid in the whole range of stability of the incommensurate phase are given for the order parameter and for anomalies of thermodynamic quantaties.

Theoretical treatment of incommensurate (IC)-commensurate (C) phase transition involves considerable difficulties connected with necessity of solving nonlinear differential equations. Therefore one has often to use numerical calculations (see, for example, ref. 1). At the same time any analytical solution even for specific case is of particular interest allowing to obtain a more general information about this transition. This paper presents the analytical treatment of the IC-C phase transition for two cases. In the first case the anisotropy in the space of the order parameter components is small. In the second case the anisotropy has the largest possible value and the IC phase is close to the Lifshitz point which separates on the phase diagram the lines of phase transitions into IC and C phases. In both cases we obtained analytical expressions for the order parameter and for anomalies of thermodynamic quantaties valid in the whole region of stability of IC phase.

The free energy density $\phi(x)$ for a two-component order parameter $\eta$, $\xi$ is given by the power series in invariants (for polar coordinates $\varrho$ and $\varphi$; $n \geq 3$)

$$\eta=\varrho\cos\varphi,\ \xi=\varrho\sin\varphi;$$
$$\phi(x)=\alpha\varrho^2+\beta\varrho^4+\alpha'\varrho^n\cos n\varphi$$
$$-\sigma\varrho^2\frac{\partial\varphi}{\partial x}+\delta\left[\left(\frac{\partial\varrho}{\partial x}\right)^2+\varrho^2\left(\frac{\partial\varphi}{\partial x}\right)^2\right]. \tag{1}$$

The well known examples of crystals with IC phase transitions described by free energy (1) are ammonium fluoroberyllate ($n=4$) and potassium selenate ($n=6$) crystals. It is assumed that $\beta>0$, $\delta>0$ and $\alpha'>0$ (it is sufficient to consider only one sign of $\alpha'$). The parent (P)-IC phase transition is of the second order ($\beta>0$) and occurs at the point $\alpha=\alpha_0$. The IC-C phase transition is shown to be of the first order and occurs at the point $\alpha=\alpha_1$ where $\phi_{IC}=\phi_C$.

Let us consider first the case of a small anisotropy when the dimensionless parameter $\varepsilon_n$ is small:

$$\varepsilon_n=\frac{n}{4}\frac{\alpha^\circ}{\beta}\left(\frac{\alpha'}{\alpha^\circ}\right)^{2/(n-2)},\ \alpha^\circ=\frac{\pi^2}{8}\alpha_0,\ \alpha_0=\frac{\sigma^2}{4\delta};$$
$$\varepsilon_3=\frac{3}{4}\frac{\alpha'^2}{\beta\alpha^\circ},\ \varepsilon_4=\frac{\alpha'}{\beta},\ \varepsilon_6=\frac{3}{2}\frac{(\alpha'\alpha^\circ)^{1/2}}{\beta}. \tag{2}$$

If $\varepsilon_n \ll 1$, one can use the IC phase solution which was first obtained and investigated by Dzyaloshinskii[2)] in the constant amplitude approximation, $\partial\varrho/\partial x=0$. Corrections to this solution can be obtained and they prove to be small, hence the solution is valid for two regions I and II. Region I is in the vicinity of the P-IC phase transition, while region II is close to the IC-C phase transition. In region I the solution has the form

$$\varrho^2=\frac{\alpha_0-\alpha}{2\beta},\quad \varphi=q_0x,$$
$$\phi=-\frac{(\alpha_0-\alpha)^2}{4\beta},\quad q_0^2=\frac{\sigma^2}{4\delta^2}. \tag{3}$$

The first order correction to solution (3) with respect to the small parameter $k^2 \ll 1$ is given by

$$\frac{\Delta\varrho}{\varrho}=-\frac{k_0^2}{4n}\frac{1}{1+A}\cos nq_0x,\ \Delta\varphi=\frac{k_0^2}{4n}\sin nq_0x,$$
$$k_0^2=\frac{2\alpha'}{\alpha_0}\varrho^{n-2},\ A=\frac{2}{n^2}\frac{\alpha_0-\alpha}{\alpha_0}. \tag{4}$$

Since an expansion in a power series in $k_0^2$ has a good convergence (numerical coefficient $1/4n$ is small) solution (3) is valid for almost all the values up to $k \simeq 1$.

In region II the solution has the form

$$\varrho^2 = \frac{-\alpha}{2\beta},\ \varphi = \frac{2}{n}\mathrm{am}\left(\frac{n}{2}qx, k\right),$$

$$\phi = -\beta\varrho^4 - \alpha'\varrho^n \frac{2-k^2}{k^2},$$

$$\frac{k^2}{E^2} = \frac{\alpha'}{\alpha^\circ}\varrho^{n-2},\ q^2 = \frac{2\alpha'}{\delta k^2}\varrho^{n-2} = \left(\frac{\pi}{2}\frac{q_0}{E}\right)^2. \quad (5)$$

Use is made of the Jacobian elliptic functions am, sn, cn, dn and of the complete elliptic integrals $K(k)$ and $E(k)$ of the first and second kind respectively with the modulus $k$. Solution (5) ceases to exist at $k=1$. The point $\alpha=\alpha_s$ corresponding to the value $k=1$, refered to as stop point, is defined by

$$\alpha_s = -2\beta\varrho_s^2 = -2\beta\left(\frac{\alpha^\circ}{\alpha'}\right)^{2/(n-2)}. \quad (6)$$

This point for solution (5) is at the same time the IC-C phase transition point: $\alpha_1 = \alpha_s$.

The first order correction to solution (5) is given by

$$\frac{\Delta\varrho}{\varrho} = \frac{\alpha^\circ}{\alpha}\left[\frac{n}{4}\frac{k^2}{E^2}(\mathrm{cn}^2 - \mathrm{sn}^2) + \frac{\mathrm{dn}^2}{E^2} - \frac{4}{\pi}\frac{\mathrm{dn}}{E}\right]. \quad (7)$$

The maximum absolute value of $2\Delta\varrho/\varrho$ (at $x=0$) is aproximatly equal to $\varepsilon_n'$,

$$\varepsilon_n' = \frac{n}{2}\frac{\alpha^\circ}{-\alpha}. \quad (8)$$

Thus solution (5) holds in the region of such values of $\alpha$ for which condition $\varepsilon_n' \ll 1$ is fulfilled. At the stop point we have $\varepsilon_n' = \varepsilon_n$ (2).

First order corrections $\Delta\phi/\phi \sim \varepsilon_n'^2$ and $\Delta k/k \sim \Delta q/q \sim \varepsilon_n'$ are too combersome to be given here. However if account is taken of these corrections it alters significantly the nature of the dependences $\phi(k)$, $\alpha(k)$ and $\phi(\alpha)$ in the region very close to the stop point. These dependences become nonmonotonic. In particular, function $\phi(\alpha)$ is not longer single valued in the range $\alpha_i < \alpha < \alpha_s$ with IC phase losing its stability at the point $\alpha = \alpha_i$, while solution (5), (7) proves to be unstable in the range $k_i < k < 1$, where $k_i$ is defined by the following expression

$$\ln^{-1}\frac{4}{k_\mathrm{i}'} = \varepsilon_n\left(\frac{n-2}{2} + \frac{8^2}{\pi^2}\frac{1}{2n}\right),\ k'^2 = 1 - k^2. \quad (9)$$

The IC-C phase transition point $\alpha = \alpha_1$ is defined by the same value (9), $k_1 = k_i$, with accuracy up to the corrections of higher order in $\varepsilon_n$. The values of $k_1'$ and $k_i'$ are exponentialy small and when considering anomalies of thermodynamic quantities it can be assumed that $k_1' = k_i' = 0$ and hence $\alpha_1 = \alpha_s$.

Thus it should be emphasized that solution (5) is not valid for very small values of $k'$, i.e. within a very narrow region near the stop point. Dimension of this region is determined in the order of magnitude by the same value of $k_i'$ (9).

It can be seen from eqs. (3)-(8) that if the anisotropy is small, i.e. $\varepsilon_n \ll 1$, regions I and II overlap. Hence the whole range of stability of IC phase can be described by a single solution with $\varrho$ from (3) and $\varphi$ from (5). However for anomalies of thermodynamic quantaties such unification can not be performed so uniquely and it is more reasonable to consider regions I and II separatly.

Now to describe the anomalies of specific heat $C = -T\partial^2\phi/\partial T^2$, of dielectric susceptibility $\chi = \mathrm{d}P/\mathrm{d}E$, of the soft mode frequence $\omega_\varrho$ corresponding to the homogeneous vibrations of the amplitude $\varrho$, one has to introduce additional invariants in free energy density $\phi(x)$ and in kinetic energy density $T(x)$:

$$\phi(x) = aP\varrho^{\frac{n}{2}}\sin\frac{n}{2}\varphi + \kappa P^2 - PE,$$

$$T(x) = \mu\left[\left(\frac{\partial\varrho}{\partial t}\right)^2 + \varrho^2\left(\frac{\partial\varphi}{\partial t}\right)^2\right], \quad (10)$$

where $n$ is even. It is also assumed that only one coefficient $\alpha$ is temperature-dependent: $\alpha = \alpha_T(T - \theta)$.

In region I we ovtain for solution (3)

$$C = \frac{T\alpha_T^2}{2\beta},\ \chi = \chi_\mathrm{P} + \frac{a^2}{16\kappa^2}\frac{2}{\alpha_0}\varrho^{n-2}\frac{1+2A}{1+A},$$

$$\omega_\varrho^2 = \frac{2(\alpha_0 - \alpha)}{\mu};\ \chi_\mathrm{P} = \frac{1}{2\kappa},\ \omega_{\varrho\mathrm{P}}^2 = \frac{\alpha}{\mu}. \quad (11)$$

In region II we obtain for solution (5)

$$C = \frac{T\alpha_T^2}{2\beta}\left\{1 + \frac{n-2}{4}\frac{\alpha^0}{-\alpha}\left[\frac{(n-2)E}{k'^2K^3} + \frac{n(1+k'^2)}{E^2} - \frac{3n-2}{EK}\right]\right\},$$

$$\chi = \chi_\mathrm{P} + \frac{a^2}{16\kappa^2}\frac{1}{\alpha'}\left(\frac{E}{k'^2K} - 1\right),$$

$$\omega_\varrho^2 = \frac{-2\alpha}{\mu} - \frac{n(n-1)}{2\mu}\left(\frac{1+k'^2}{E^2} - \frac{2}{EK}\right) \quad (12)$$

(note that $E \to 1$, $K \to \ln 4/k'$ if $k' \to 0$).

Expansion of expressions (5) into power series in small $k'$ leads to the following relation between $k'$ and $\alpha - \alpha_s$ near the stop point:

$$K'^2\left(\ln\frac{4}{k'} + \frac{1}{2}\right) = \frac{n-2}{2}\frac{\alpha-\alpha_s}{-\alpha_s} = \frac{n-2}{2}\frac{T-T_s}{\theta-T_s}. \quad (13)$$

Consequently in the vicinity of the IC-C phase transition point, the susceptibility $\chi$ defined by eq. (12) changes according to the Curie-Weiss law. The Curie constant is relatively large, being inversely proportional to the small value of $\alpha'$. The specific heat $C$ changes approximately in the same way but the corresponding "Curie" constant is relatively small since it is proportional to the small value of $\varepsilon_n/K^2$. In other words, a remarkable increase of $C$ can be observed only in a vary narrow neighbourhood of the transition point.

Below are given the expressions for the C phase obtained in the same approximation as for expressions (5) and (12):

$$\varrho^2 = \frac{-\alpha}{2\beta}, \quad \cos n\varphi = -1, \quad \phi = -\frac{\alpha^2}{4\beta}\left(1 + \frac{4}{n}\varepsilon_n''\right),$$

$$C = \frac{T\alpha_T^2}{2\beta}\left(1 + \frac{n-2}{2}\varepsilon_n''\right), \quad \chi = \chi_P + \frac{a^2}{16\kappa^2}\frac{n\,\varepsilon_n''}{2\,\alpha'},$$

$$\omega_\varrho^2 = \frac{-2\alpha}{\mu}\left(1 - \frac{n-1}{2}\varepsilon_n''\right), \quad \varepsilon_n'' = \frac{n}{2}\frac{\alpha'}{-\alpha}\varrho^{n-2} \quad (14)$$

(note that at the stop point $\varepsilon_n'' = \varepsilon_n' = \varepsilon_n$). Solution (14) is valid and is of interest in a small anisotropy aproximation in the region near the IC-C phase transition point. Comparison of (5), (12) with (14) shows that in the given approximation ($k_1' = 0$, i.e. $\alpha_1 = \alpha_s$) the quantaties $\varrho^2$, $\Phi$, $\omega_\varrho^2$ do not exhibit any discontinuities at the transition point.

Let us consider briefly the second case of the largest anisotropy. The Lifshitz point is determined by

$$\alpha = \alpha_0, \quad \alpha' = \alpha_n'; \quad \alpha_3' = 2(\beta\alpha_0)^{\frac{1}{2}},$$
$$\alpha_4' = \beta + 2(\gamma\alpha_0)^{\frac{1}{2}}, \quad (15)$$

where the values of $\alpha_n'$ for $n=3, n=4$ are given; $\gamma$ is a coefficient in front of $\varrho^6$ in (1). At the Lifshitz point (15) the three phase transition lines are converged: $\alpha = \alpha_0$—being the line of the second order P-IC phase transition, $\alpha = \alpha_1$—being the line of the first order IC-C phase transition, $\alpha = \alpha_2$—being the line of the first order P-C phase transition:

$$\alpha_2 = \frac{\alpha'^2}{4\beta}\ (n=3), \quad \alpha_2 = \frac{(\alpha'-\beta)^2}{4\gamma}\ (n=4). \quad (16)$$

The lines $\alpha = \alpha_1$ and $\alpha = \alpha_2$ have a common tangent at the Lifshitz point.

In the vicinity of the Lifshitz point satisfying the condition $(\alpha_0 - \alpha)/\alpha_0 \ll 1$ solution (3) with correction (4) is valid for IC phase in the entire range of its stability, $\alpha_1 < \alpha < \alpha_0$ (where $A$ is assumed to be zero). The IC-C phase transition occurs at the point $\alpha = \alpha_1$:

$$\alpha_1 = \alpha_0\left(\frac{\alpha'}{(\beta\alpha_0)^{\frac{1}{2}}} - 1\right)\ (n=3),$$

$$\alpha_1 = \alpha_0\left(\frac{\alpha'-\beta}{(\gamma\alpha_0)^{\frac{1}{2}}} - 1\right)\ (n=4) \quad (17)$$

and is obviously of the first order. Calculation of the stability losing point $\alpha = \alpha_i$ for solution (3), (4) yields values (different for various $n$) which fall outside the validity of this solution and therefore are not worth being cited. As to the solution of C phase and hence to anomalies of thermodynamic quantities they should be considered separately for each value of $n$ (for $n = 4$ see ref. 3).

## References

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