Incommensurate phases in the statistical theory of the crystalline state

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The paper is devoted to the elaboration of a mathematical apparatus for studying second-order phase transitions, both commensurate and incommensurate, and the properties of emerging phases on the basis of the approach in equilibrium statistical mechanics proposed earlier by the author. It is shown that the preliminary symmetry analysis for a concrete crystal can be performed analogously with the one in the Landau phenomenological theory of phase transitions. The analysis enables one to deduce a set of transcendental equations that describe the emerging phases and corresponding phase transitions. The treatment of an incommensurate phase is substantially complicated because the symmetry of the phase cannot be described in terms of customary space groups. For this reason, a strategy of representing the incommensurate phase as the limit of a sequence of long-period commensurate phases whose period tends to infinity is worked out.

1. Introduction

Incommensurate phases in dielectric crystals were intensively investigated both theoretically and experimentally in the 1970–1980s (Blinc & Levanyuk, 1986). Interest in them persists nowadays as well. The incommensurate phases are a special state of solids that differs from ordinary crystals by the lack of periodicity in one or more directions whereas a long-range order exists unlike amorphous solids. Usually, the incommensurate phases attend some second-order phase transitions: an incommensurate phase can appear as an intermediate phase between a high-temperature parent phase and a low-temperature (commensurate) phase. The reasons for the appearance of the incommensurate phase and its properties are well described by the Landau theory of phase transitions. The Landau theory, however, is a phenomenological theory relying upon some general argumentation, the theory that is not designed to explain microscopic causes of the phenomenon, *i.e.* causes relevant to properties of molecules or atoms.

A strict microscopic theory is statistical mechanics inasmuch as it tries to explain phenomena by proceeding from a knowledge of the intermolecular potential and of other properties of the molecules and atoms. In the late 1990s, a new approach in equilibrium statistical mechanics was worked out which is not based upon the Gibbs ensembles (Golovko, 1996; see also Golovko, 2008a). The classical version of the approach used in the present paper (the approach was devised initially for quantum systems) leans upon the BBGKY hierarchy of equations for reduced distribution functions while the distinctive feature of the approach lies in constructing thermodynamics compatible with the hierarchy. Among other

things, the approach proved to be seminal in studies of the crystalline state (Golovko, 2001, 2004, 2007). In particular, Golovko (2004) has employed the approach for studies of second-order phase transitions and the results obtained are in full accord with the Landau phase-transition theory.

The main aim in the present paper is to apply the statistical approach to investigation of the incommensurate phases in dielectric crystals. Besides, the example of a second-order phase transition considered by Golovko (2004) is rather peculiar, in which the possibility of the transition is directly seen from the expressions for effective potentials deduced in that paper. Usually, an individual analysis is required to see the possibility of a phase transition in a concrete crystal. We shall show also how the analysis can be carried out in statistical theory. This can be done analogously with the Landau theory although some refinements are needed which are not obligatory in the Landau theory.

Many theoretical studies on incommensurate phases are based on the Landau free energy characteristic of ammonium fluorberyllate, $(NH_4)_2BeF_4$, whose high-temperature space group is D_{2h}^{16} (note that the high-temperature phase of many crystals that have an incommensurate phase pertains to the same orthorhombic space group). To be specific and for the purposes of comparison with the Landau theory we shall carry out our investigation using, as an example, the sequence of the phase transitions that occur in ammonium fluorberyllate. At the same time, the approach that will be employed is developed in detail only for systems containing particles of one kind with spherically symmetric interaction.[1] An equilibrium

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[1] An extension of the approach to systems that contain particles of several kinds can be found in Golovko (2008b).

crystal composed of such particles should be of cubic symmetry. Of course, the orthorhombic lattice may be obtained from the cubic one by applying appropriate external stresses. However, space group D_{2h}^{16} is not a subgroup of any other space group of a higher crystal class if no change in the number of particles in the unit cell is involved (Boyle & Lawrenson, 1972) and thereby it cannot be obtained from a cubic space group by continuous deformation. For this reason, a D_{2h}^{16} crystal composed of particles of one kind with spherically symmetric interaction can be in a metastable state alone, which may also entail other peculiarities irrelevant to our problem. Our main goal in this paper is to work out a mathematical apparatus for treating incommensurate phases in statistical theory, and the example of space group D_{2h}^{16} is sufficiently general and well suited for this. At the same time, it should be emphasized that the results obtained cannot be applied directly to ammonium fluorberyllate, whose molecules are by no means spherically symmetric.

As mentioned above, one of the aims in the present paper is to compare the approach used and the results obtained with its help with the ones that follow from the Landau phase-transition theory. To this end, in §2 we outline the Landau theory as applied to incommensurate phases and adduce its results needed in this paper. In §3, we formulate the basic equations of the statistical approach employed for consideration of the crystalline state and apply them in §4 to the D_{2h}^{16} parent phase from which the phase transitions studied commence. We show in §5 how the symmetry analysis concerning a commensurate phase transition can be carried out in statistical theory and how the theory describes the emerging phase. §6 is devoted to the incommensurate phases in statistical theory and to corresponding phase transitions.

2. Incommensurate phases in the Landau phase-transition theory

A typical density of the Landau free energy used for treatment of an incommensurate phase is of the form (Levanyuk & Sannikov, 1976a,b)

$$\tilde{F}(y) = \overline{F} + \frac{\alpha}{2}\left(\eta^2 + \xi^2\right) + \frac{\beta_1}{4}\left(\eta^2 + \xi^2\right)^2 + \frac{\beta_2}{4}\left[\left(\eta^2 - \xi^2\right)^2 - \left(2\eta\xi\right)^2\right]$$
$$+ \sigma\left(\xi\frac{d\eta}{dy} - \eta\frac{d\xi}{dy}\right) + \frac{\delta}{2}\left[\left(\frac{d\eta}{dy}\right)^2 + \left(\frac{d\xi}{dy}\right)^2\right]. \quad (1)$$

Here $\overline{F}$ is a term irrelevant to our problem, η and ξ are components of the order parameter. The term with the coefficient σ is the Lifshitz invariant (for convenience in the following we assume that the incommensurate modulation occurs along the y axis). The invariant can exist only if the order parameter has two components or more. In the case where the invariant is admitted by the irreducible representation that describes the phase transition in question, there inevitably appears an incommensurate phase. The invariants of fourth order in η and ξ with the coefficients β_1 and β_2 are written in a form convenient for further treatment. We assume that $\beta_1 > |\beta_2|$, otherwise invariants of sixth order in η and ξ

must be taken into account. If the length of the crystal in the y direction is L, the free energy per unit length is

$$F = \frac{1}{L}\int_0^L \tilde{F}(y)\,dy. \quad (2)$$

As is usual in the Landau theory, we presume that the coefficient α alone depends upon the temperature varying linearly with it.

Were the Lifshitz invariant lacking, the minimum of F would correspond to a uniform solution $\eta = $ constant and $\xi = $ constant because of the last term in equation (1), which is always present (we assume that $\delta > 0$). Minimizing the free energy in that event, one would, if $\alpha < 0$, arrive at two nontrivial solutions corresponding to two possible commensurate phases:

(i) $\eta \neq 0$, $\xi = 0$ or vice versa,

$$\eta^2 = -\frac{\alpha}{\beta_1 + \beta_2}, \quad F = \overline{F} - \frac{\alpha^2}{4(\beta_1 + \beta_2)}; \quad (3)$$

(ii)

$$\eta^2 = \xi^2 = -\frac{\alpha}{2(\beta_1 - \beta_2)}, \quad F = \overline{F} - \frac{\alpha^2}{4(\beta_1 - \beta_2)}. \quad (4)$$

The first solution is energetically preferable if $\beta_2 < 0$, the second one if $\beta_2 > 0$.

Before proceeding further it is instructive to discuss the problem from the viewpoint of the concept of a soft mode in the high-temperature parent phase. The soft mode in ammonium fluorberyllate occurs at the boundary of the Brillouin zone to which the wavevector $K = a_2/2$ corresponds, where $\mathbf{a}_2$ is the basic reciprocal-lattice vector oriented along the y axis in the present notation (Fig. 1, where the Brillouin-zone boundary is denoted as point B with the vertical line). If the Lifshitz invariant does not exist at $K = a_2/2$, the soft-mode branch has an extremum at $K = a_2/2$ as in Fig. 1(a). In the case where the extremum is a minimum (curve 1 in Fig. 1a), as the temperature lowers [the length of the segment AB in Fig. 1 is proportional to the coefficient α in equation (1)], it is the frequency ω at $K = a_2/2$ that vanishes. As a result, in the crystal an atom-displacement wave is frozen in and there occurs a phase transition at $\alpha = 0$ into a commensurate phase described by equation (3) or (4), whereas the crystal period along the y
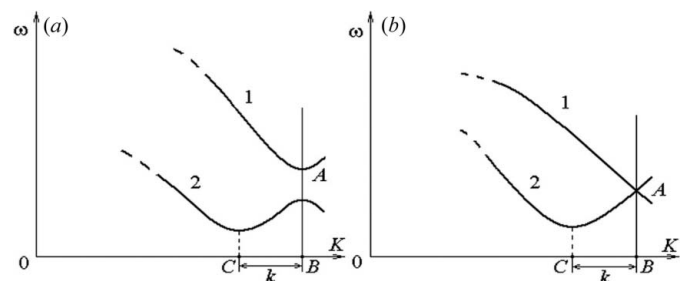

Figure 1
Dispersion curves (phonon branches) near the Brillouin-zone boundary (point B) in the parent phase: (a) the Lifshitz invariant is lacking, (b) the Lifshitz invariant exists.

axis doubles for the wavelength corresponding to $K = a_2/2$ is equal to $2d_2$ where d_2 is the period in the parent phase.

The existence of the Lifshitz invariant at $K = a_2/2$ signifies a nonzero slope of the phonon branch at point A (Fig. 1b). In actual fact, two phonon branches meet at point A in this instance as long as all dispersion curves can be transferred to the first Brillouin zone. The lower branch is necessarily a minimum inside the zone and, as the temperature lowers, it is the frequency at point C that vanishes first, although $\alpha > 0$. As a result, a superstructure with the wavevector $K = a_2/2 - k$ arises in the crystal whereas there is no reason for the ratio k/a_2 to be rational. The ratio being irrational, one will have two mutually incommensurable periods in the crystal, namely, the period d_2 of the underlying structure that remains and the period of the superstructure, that is to say, one will have an incommensurate phase without any periodicity along the y axis but with a definite long-range order.

Even if the Lifshitz invariant does not exist, the extremum at $K = a_2/2$ can be a maximum (curve 2 in Fig. 1a). As the temperature lowers, it is the frequency at point C that vanishes first and one will again have an incommensurate phase called type II (the incommensurate phase discussed previously is called type I). The emergence of the incommensurate phase of type II is due to peculiarities of intermolecular interactions that lead to a dispersion curve with a minimum inside the Brillouin zone while the inevitability of the type-I incommensurate phase can be forecast from symmetry considerations. Both of these types are observed experimentally in crystals (Blinc & Levanyuk, 1986).

We revert now to the Landau free energy. Substituting equation (1) into (2) and minimizing the functional F yields the following Euler–Lagrange equations:

$$\delta \frac{d^2\eta}{dy^2} + 2\sigma \frac{d\xi}{dy} - \alpha\eta - \beta_1\eta(\eta^2 + \xi^2) - \beta_2\eta(\eta^2 - 3\xi^2) = 0, \quad (5)$$

$$\delta \frac{d^2\xi}{dy^2} - 2\sigma \frac{d\eta}{dy} - \alpha\xi - \beta_1\xi(\eta^2 + \xi^2) - \beta_2\xi(\xi^2 - 3\eta^2) = 0. \quad (6)$$

Near the phase-transition point where η and ξ are small, one can neglect the nonlinear terms in equations (5) and (6). The resulting linear equations admit a solution

$$\eta = \rho \cos ky, \quad \xi = \rho \sin ky \quad (7)$$

with $\rho = $ constant and

$$k = \frac{1}{\delta}\left[\sigma \pm (\sigma^2 - \alpha\delta)^{1/2}\right]. \quad (8)$$

The last equation shows that the maximal value of α at which a real value of k exists is $\alpha = \alpha_0 \equiv \sigma^2/\delta$ while then $k = \sigma/\delta$. Therefore, at $\alpha = \alpha_0 > 0$ there occurs a phase transition into an incommensurate phase in accord with Fig. 1(b).

Equations (5) and (6) do not lend themselves to analytical solution in the general case. The equations were solved numerically (Ishibashi & Dvořák, 1978; Shiba & Ishibashi, 1978) and there exists a strict analytical solution valid for an especial relation between the coefficients in equation (1) (Golovko, 1984a,b); approximate methods were exploited as

well (Golovko, 1980a,b). The solutions obtained show that, as the temperature lowers, the value of k decreases and tends to zero. When k approaches zero, there occurs a phase transition to one of the commensurate phases described by equations (3) or (4). This phase transition, referred to as a lock-in transition, has specific features in comparison with an ordinary second-order transition (Blinc & Levanyuk, 1986, Vol. 1, ch. 2).

Near the lock-in transition, the incommensurate phase becomes domain-like. The structure of the incommensurate phase inside the domains factually coincides with that of the corresponding low-temperature commensurate phase, whereas distinctions take place only in the domain walls, called the discommensurations. If the lock-in transition is continuous, it happens when the distance between the discommensurations becomes infinite, in which case the crystal will contain only one or two domains with the commensurate phase.

Closing the section, it should be emphasized that the Landau phase-transition theory is strict only in the immediate vicinity of the phase-transition point [excluding the critical region (Ginzburg $et\ al.$, 1980)]. All modes in the crystal are coupled with one another, which gives rise to secondary order parameters that should be taken into account in the free energy and whose role augments as the temperature lowers. In the case of an incommensurate phase, higher derivatives of the order parameters and their powers can play a part if the temperature is not sufficiently close to the phase-transition temperature. Appreciably below this temperature, the Landau theory based upon a simplified free energy of the type of equation (1) should be regarded only as a model.

3. Basic equations of the statistical theory of the crystalline state

In the present paper, we assume the same form of the pair correlation function as in the paper by Golovko (2007) and utilize the same equations for the crystalline state. The first equation of the BBGKY hierarchy with that pair correlation function yields, for the singlet density distribution $\rho(\mathbf{r})$,

$$\rho(\mathbf{r}) = C \exp[-U(\mathbf{r})/\theta], \quad (9)$$

where θ is the temperature in units of energy. The constant C is to be found from the normalization condition

$$\int_V \rho(\mathbf{r})\,d\mathbf{r} = N, \quad (10)$$

where the integration is carried out over the volume V of the crystal that contains N particles.

Equation (9) relates the density $\rho(\mathbf{r})$ with the effective potential

$$U(\mathbf{r}) = \int K_g(|\mathbf{r} - \mathbf{r}'|)\,\rho(\mathbf{r}')\,d\mathbf{r}', \quad (11)$$

in which

$$K_g(r) = \int_\infty^r \frac{dK(r')}{dr'}\,g(r')\,dr'. \quad (12)$$

Here $g(r) \equiv g(|\mathbf{r}|)$ is the pair correlation function and we imply that the particles interact by means of a two-body potential $K(|\mathbf{r}_i - \mathbf{r}_j|)$.

Upon placing equation (11) in equation (9) we obtain a nonlinear integral equation for $\rho(\mathbf{r})$. Of course, we should know the pair correlation function $g(r)$ that figures in equation (12). Strictly speaking, the function has to be found from the second equation of the BBGKY hierarchy. In this paper we shall carry out our investigation without specifying the form of $g(r)$. Certainly, to apply results obtained in the paper to a concrete crystal a knowledge of $g(r)$ is required, which will be discussed in the concluding section. In the papers by Golovko (2001, 2004, 2007) it was demonstrated that many interesting results for a crystal can be obtained without specifying the form of $g(r)$. This is connected with the fact that the leading role for the crystal is played by the first BBGKY equation that is satisfied identically for a fluid where, for this reason, the leading role goes over to the second BBGKY equation for the pair correlation function, whereas this second equation is auxiliary for the crystal (Golovko, 2004, 2007).

The main idea in the papers by Golovko (2001, 2004, 2007) as to treating the integral equation for the density $\rho(\mathbf{r})$ is to expand $\rho(\mathbf{r})$ in a Fourier series:

$$\rho(\mathbf{r}) = \sum_{l,m,n=-\infty}^{\infty} a_{lmn} \exp(i\mathbf{A}\mathbf{r}), \qquad (13)$$

where $\mathbf{A} = l\mathbf{a}_1 + m\mathbf{a}_2 + n\mathbf{a}_3$ with the basic reciprocal-lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$. Upon substituting equation (13) into equation (11) one finds the expansion for $U(\mathbf{r})$,

$$U(\mathbf{r}) = \sum_{l,m,n} a_{lmn}\sigma(A) \exp(i\mathbf{A}\mathbf{r}), \qquad (14)$$

in which $A = |\mathbf{A}|$ and

$$\sigma(A) = \int K_g(|\mathbf{r}|) \exp(i\mathbf{A}\mathbf{r})\,\mathrm{d}\mathbf{r} = \frac{4\pi}{A} \int_0^\infty r K_g(r) \sin Ar\,\mathrm{d}r. \quad (15)$$

If one inserts equations (13) and (14) into equation (9), one obtains a set of equations for a_{lmn} (Golovko, 2001):

$$
\begin{aligned}
a_{lmn} = \frac{\rho_0}{8\pi^3 G} \int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi} &\exp\left\{-\frac{1}{\theta}\sum_{l',m',n'=-\infty}^{\infty\prime} a_{l'm'n'}\sigma(A')\right.\\
&\times \exp[i(l'\xi_1 + m'\xi_2 + n'\xi_3)]\\
&\left. - i(l\xi_1 + m\xi_2 + n\xi_3)\right\}\,\mathrm{d}\xi_1\,\mathrm{d}\xi_2\,\mathrm{d}\xi_3
\end{aligned}
$$

$$(16)$$

with

$$
\begin{aligned}
G = \frac{1}{8\pi^3} \int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi} &\exp\left\{-\frac{1}{\theta}\sum_{l,m,n}{}' a_{lmn}\sigma(A)\right.\\
&\left.\times \exp[i(l\xi_1 + m\xi_2 + n\xi_3)]\right\}\,\mathrm{d}\xi_1\,\mathrm{d}\xi_2\,\mathrm{d}\xi_3, \qquad (17)
\end{aligned}
$$

where the prime over the summation signs denotes omission of the term with $l' = m' = n' = 0$ in equation (16) or with $l = m = $

$n = 0$ in (17), $A' = |\mathbf{A}'| = |l'\mathbf{a}_1 + m'\mathbf{a}_2 + n'\mathbf{a}_3|$, and $\rho_0 = a_{000} = N/V$ is the average number density. It will be noted that equations (16) and (17) are written down as in Golovko (2007) and differ slightly in form from those of Golovko (2001, 2004).

It is worthy of remark that all information in equations (16) and (17) about the intermolecular potential $K(r)$, the pair correlation function $g(r)$ and even about the crystal periods $\mathbf{d}_1$, $\mathbf{d}_2$ and $\mathbf{d}_3$ resides only in $\sigma(A)$. The quantity $\sigma(0)$ that plays an important role for fluids (Golovko, 2007) is not present in equations (16) and (17). It is not even necessary to know the full function $\sigma(k)$, for equations (16) and (17) contain the value of the function only at a discrete set of points in reciprocal space since $A = |l\mathbf{a}_1 + m\mathbf{a}_2 + n\mathbf{a}_3|$. Aside from $\sigma(A)$, only two external parameters ρ_0 and θ figure in (16) and (17). In this paper we shall neglect the dependence of $\sigma(A)$ upon the temperature θ because the dependence should be weak for crystals according to §4 of Golovko (2007) and does not impact on the principal results obtained in the present paper. If necessary, the dependence can be taken into account when dealing with a concrete situation.

For what follows we need also the Helmholtz free energy [equation (5.9) of Golovko (2007)],

$$F = F_f - N\theta\ln G - \frac{V}{2}\sum_{l,m,n}{}' |a_{lmn}|^2 \sigma(A), \qquad (18)$$

in which F_f is the free energy of the corresponding fluid that is not required for our purposes.

Golovko (2004) has demonstrated that the concrete form of the Fourier series of equation (13) is different for different space groups and, moreover, is characteristic of each space group (only cubic space groups were considered in that paper). The form of the Fourier series specifies a definite form of the system of equations for the Fourier coefficients a_{lmn}, which in its turn determines peculiarities of solutions to the system and eventually influences properties of the relevant crystal and phase transitions in it.

4. Parent phase

We proceed now to a study of the high-temperature parent phase with space group D_{2h}^{16} from which the phase transitions considered in the following sections originate. As long as we utilize Kovalev's (1986, 1993) tables in the next sections, we adopt the description of space groups given by Kovalev (1986, 1993), which implies an appropriate choice of the coordinate system. First of all, we should establish the form of the Fourier series if space group D_{2h}^{16} is involved.

Seeing that this space group pertains to the orthorhombic system, instead of the general form of equation (13) the Fourier series can be written in the form

$$\rho(\mathbf{r}) = \sum_{l,m,n=-\infty}^{\infty} a_{lmn} \exp[i(la_1 x + ma_2 y + na_3 z)]. \qquad (19)$$

In our case it is convenient to consider the effective potential $U(\mathbf{r})$ of equation (14) that has the same symmetry as $\rho(\mathbf{r})$ for $\sigma(A) = \sigma[(l^2 a_1^2 + m^2 a_2^2 + n^2 a_3^2)^{1/2}]$ does not change the

symmetry. An analysis akin to the one carried out in the appendix of the paper by Golovko (2004) shows that first terms in $U(\mathbf{r})$ for D_{2h}^{16} are of the form

$$
\begin{aligned}
U(\mathbf{r}) = \rho_0\sigma(0) &+ 4\alpha_1\sigma\big[(a_1^2 + a_3^2)^{1/2}\big]\cos a_1 x \sin a_3 z \\
&+ 4\alpha_2\sigma\big[(a_2^2 + a_3^2)^{1/2}\big]\sin a_2 y \cos a_3 z \\
&+ 8\alpha_3'\sigma\big[(a_1^2 + a_2^2 + a_3^2)^{1/2}\big]\cos a_1 x \cos a_2 y \cos a_3 z \\
&+ 2\alpha_4'\sigma(2a_1)\cos 2a_1 x + 2\alpha_4''\sigma(2a_2)\cos 2a_2 y \\
&+ 2\alpha_4'''\sigma(2a_3)\cos 2a_3 z + \ldots,
\end{aligned}
\tag{20}
$$

where

$$
\alpha_1 = ia_{101},\ \alpha_2 = ia_{011},\ \alpha_3' = a_{111},\ \alpha_4' = a_{200},\ \alpha_4'' = a_{020},
$$
$$
\alpha_4''' = a_{002}.
\tag{21}
$$

For simplicity's sake, we shall assume henceforward that $a_1 = a_2$ and $a_3 \simeq a_1$.

In the following we shall use the Kirkwood approximation for a crystal (Kirkwood & Monroe, 1941; Golovko, 2004). The approximation consists in putting $\sigma(A) = 0$ if $A > A_0$ in the effective potential $U(\mathbf{r})$ of equation (14) and in other formulae. In the paper by Golovko (2007) it is demonstrated using the Lennard-Jones potential as an example that the Kirkwood approximation is rather good for the crystal. It should be underlined that, although one retains only several Fourier harmonics in $U(\mathbf{r})$, the density $\rho(\mathbf{r})$ contains all harmonics because the approximation does not concern a_{lmn}.

Implying the Kirkwood approximation we suppose that $\sigma(\zeta a_i) = 0$ if $\zeta > 2^{1/2}$, in which case equation (20) becomes

$$
U(\mathbf{r}) = \rho_0\sigma(0) + 4\alpha_1\sigma_1 \cos a_1 x \sin a_3 z + 4\alpha_2\sigma_1 \sin a_2 y \cos a_3 z,
\tag{22}
$$

where $\sigma_1 = \sigma\big[(a_1^2 + a_3^2)^{1/2}\big] = \sigma\big[(a_2^2 + a_3^2)^{1/2}\big]$.

We see from equation (22) that with the approximation used it is sufficient to deduce equations for α_1 and α_2 alone. This can be performed with the help of equations (16) and (21). When reducing equation (16) it is necessary to prove that some integrals vanish, which can be done by appropriate replacement of the variables of integration. As a result, we shall obtain the following set of transcendental equations:

$$
\frac{\alpha_1}{\rho_0} = \frac{I_1^{(1)}(\beta_1, \beta_2)}{I_0^{(1)}(\beta_1, \beta_2)}, \qquad \frac{\alpha_2}{\rho_0} = \frac{I_2^{(1)}(\beta_1, \beta_2)}{I_0^{(1)}(\beta_1, \beta_2)},
\tag{23}
$$

where

$$
\begin{aligned}
I_0^{(1)}(\beta_1, \beta_2) = \frac{1}{8\pi^3}\int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi} &\exp[-4(\beta_1\cos\xi_1\sin\xi_3 \\
&+ \beta_2\sin\xi_2\cos\xi_3)]\,d\xi_1\,d\xi_2\,d\xi_3,
\end{aligned}
\tag{24}
$$

$$
\begin{aligned}
I_1^{(1)}(\beta_1, \beta_2) = \frac{1}{8\pi^3}\int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi} &\cos\xi_1\sin\xi_3 \exp[-4(\beta_1\cos\xi_1\sin\xi_3 \\
&+ \beta_2\sin\xi_2\cos\xi_3)]\,d\xi_1\,d\xi_2\,d\xi_3,
\end{aligned}
\tag{25}
$$

$$
\begin{aligned}
I_2^{(1)}(\beta_1, \beta_2) = \frac{1}{8\pi^3}\int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi} &\sin\xi_2\cos\xi_3 \exp[-4(\beta_1\cos\xi_1\sin\xi_3 \\
&+ \beta_2\sin\xi_2\cos\xi_3)]\,d\xi_1\,d\xi_2\,d\xi_3,
\end{aligned}
\tag{26}
$$

$$
\beta_1 = \frac{\alpha_1\sigma_1}{\theta}, \qquad \beta_2 = \frac{\alpha_2\sigma_1}{\theta}.
\tag{27}
$$

It can be readily shown that

$$
I_1^{(1)}(\beta_1, \beta_2) = -\frac{1}{4}\frac{\partial I_0^{(1)}(\beta_1, \beta_2)}{\partial\beta_1}, \quad I_2^{(1)}(\beta_1, \beta_2) = -\frac{1}{4}\frac{\partial I_0^{(1)}(\beta_1, \beta_2)}{\partial\beta_2},
$$
$$
I_1^{(1)}(\beta_1, \beta_2) = I_2^{(1)}(\beta_2, \beta_1).
\tag{28}
$$

Consequently it is sufficient to investigate the integral $I_0^{(1)}$ alone. The simplest method for calculating $I_0^{(1)}$ is to expand the exponential of equation (24) in a series with the result (cf. Golovko, 2004)

$$
\begin{aligned}
I_0^{(1)}(\beta_1, \beta_2) = I_0^{(1)}(\beta_2, \beta_1) = \sum_{n=0}^{\infty}\frac{1}{n!}\sum_{m=0}^{n}&\frac{(2n - 2m)!(2m)!}{(n - m)!^3(m)!^3} \\
&\times \beta_1^{2m}\beta_2^{2n-2m}.
\end{aligned}
\tag{29}
$$

With use made of equation (23), the equations of (27) can be rewritten as

$$
\frac{\theta}{\rho_0\sigma_1} = \frac{I_1^{(1)}(\beta_1, \beta_2)}{\beta_1 I_0^{(1)}(\beta_1, \beta_2)}, \qquad \frac{\beta_2 I_1^{(1)}(\beta_1, \beta_2)}{\beta_1 I_2^{(1)}(\beta_1, \beta_2)} = 1.
\tag{30}
$$

In actual fact, equations (23) and (30) directly yield the temperature dependence of α_1 and α_2 in a parametric form, β_1 and β_2 being the parameters. At a given temperature θ, from equation (30) we find β_1 and β_2 which give the corresponding values of α_1 and α_2 when substituted into equation (23). According to equations (24), (29) and (28), always $I_0^{(1)} > 0$ whereas $I_1^{(1)}$ is opposite in sign to β_1. Therefore the right-hand side of the first equation of (30) is always negative and in consequence the solution exists only if $\sigma_1 < 0$ (cf. Golovko, 2004).

An analysis shows that there exist three nontrivial solutions:

$$
\text{(i)}\ \alpha_1 \neq 0,\ \alpha_2 = 0, \quad \text{(ii)}\ \alpha_1 = 0,\ \alpha_2 \neq 0, \quad \text{(iii)}\ \alpha_1 = \alpha_2.
\tag{31}
$$

The solutions make their appearance when β_1 and β_2 are small, and the condition for this can be found upon placing the expansion of equation (29) in equation (23). All three solutions exist if $\theta \leq -\rho_0\sigma_1$. At $\theta = -\rho_0\sigma_1 = \rho_0|\sigma_1|$ there occurs a phase transition from the liquid to a D_{2h}^{16} crystal.

Now, by equation (18), we can calculate the difference $F - F_f$ of the Helmholtz free energies for the crystal and liquid. With the same assumption for $\sigma(A)$ as in equation (22), in dimensionless units we have

$$
F_c \equiv \frac{F - F_f}{\rho_0|\sigma_1|N} = 2\frac{\alpha_1^2 + \alpha_2^2}{\rho_0^2} - \tilde{\theta}\ln I_0^{(1)},
\tag{32}
$$

where $\tilde{\theta} = \theta/\rho_0|\sigma_1|$ is a dimensionless temperature.

The result of numerical calculations for the temperature dependence of F_c is presented in Fig. 2. The figure shows that the liquid–crystal phase transition should be second order in

the present case. An argument was adduced by Golovko (2004) that the second-order phase transition between a fluid and crystal is in fact impossible. This is of no importance for the present investigation inasmuch as we are interested in the D_{2h}^{16} crystal itself and not in the question as to how it can be obtained. It is to be added that we have set $a_1 = a_2$ above (if $a_1 \neq a_2$, Fig. 2 would be more complicated) and have used the simplified form of $U(\mathbf{r})$ of equation (22) instead of equation (20) in order to have the simplest variant of the D_{2h}^{16} phase because the phase plays an auxiliary role for the studies in this paper.

Let us point out nevertheless some curious results that follow from Fig. 2. Curve 1 corresponds to solutions (i) or (ii) of equation (31), curve 2 to solution (iii) of equation (31). Factually, solutions (i) and (ii) lead to two-dimensional crystals, which is seen from equation (22). Therefore, Fig. 2 indicates that, in the case under consideration, the two-dimensional crystals are energetically more preferable than the three-dimensional one relevant to solution (iii). This is due to the fact that we used the simplified form of $U(\mathbf{r})$ of equation (22) instead of equation (20). Besides, as noted in §1 a D_{2h}^{16} crystal composed of particles of one kind with spherically symmetric interaction can be in a metastable state alone. In the following sections, we shall study phase transitions implying that the parent phase corresponds to solution (iii) of equation (31) although the phase is metastable.

5. Commensurate phase transition

Seeing that our studies are based upon the sequence of phase transitions that occur in ammonium fluorberyllate, let us recall the relevant phase transitions (Iizumi & Gesi, 1977; Onodera & Shiozaki, 1977). The high-temperature D_{2h}^{16} phase exists at $T > 183$ K, between 183 and 177 K an incommensurate phase is observed, and below $T = 177$ K there emerges a polar commensurate phase with space group C_{2v}^9 in which the polarization is directed along the z axis and the period along the y axis doubles (we choose the coordinate system as in §4).

As is done in the Landau theory, we should first consider the transition from a D_{2h}^{16} phase to a C_{2v}^9 phase. When analysing
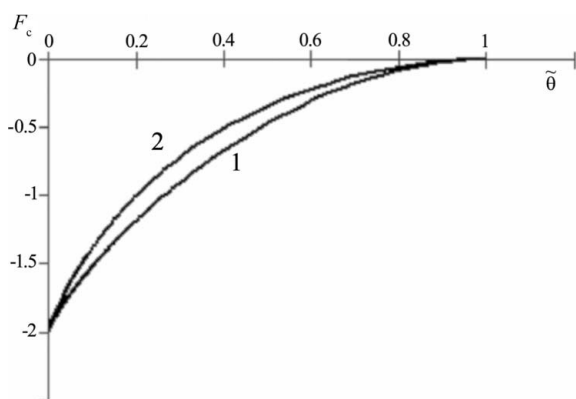

Figure 2
Temperature dependence of F_c defined in equation (32) for space group D_{2h}^{16}.

the transition in the Landau theory one finds that there exists a Lifshitz invariant and therefore a direct transition from the D_{2h}^{16} phase to the C_{2v}^9 phase is impossible (see §2). In the present section, we shall ignore the existence of the Lifshitz invariant and, using this example, show how a commensurate phase transition can be treated in statistical theory. This procedure corresponds to obtaining the solutions of equations (3) or (4).

First of all, it is necessary to establish the form of the Fourier series for space group C_{2v}^9. The group pertains to the same orthorhombic system and we have again equation (19). We must take a coordinate system compatible with the one chosen in the previous section for space group D_{2h}^{16}. To this end, the x and y axes adopted by Kovalev (1986, 1993) for space group C_{2v}^9 are to be interchanged. Now, analogously with equation (20), for this space group we have

$$
\begin{aligned}
U(\mathbf{r}) &= \rho_0 \sigma(0) + 4\alpha_2' \sigma\big[(a_1^2 + a_3^2)^{1/2}\big] \cos a_1 x \cos a_3 z \\
&\quad + 4\alpha_2'' \sigma\big[(a_1^2 + a_3^2)^{1/2}\big] \cos a_1 x \sin a_3 z \\
&\quad + 4\alpha_2''' \sigma\big[(a_1^2 + a_2^2)^{1/2}\big] \sin a_1 x \sin a_2 y \\
&\quad + 8\alpha_3' \sigma\big[(a_1^2 + a_2^2 + a_3^2)^{1/2}\big] \sin a_1 x \cos a_2 y \sin a_3 z \\
&\quad + 8\alpha_3'' \sigma\big[(a_1^2 + a_2^2 + a_3^2)^{1/2}\big] \sin a_1 x \cos a_2 y \cos a_3 z \\
&\quad + 2\alpha_4' \sigma(2a_1) \cos 2a_1 x + 2\alpha_4'' \sigma(2a_2) \cos 2a_2 y \\
&\quad + 2\alpha_4''' \sigma(2a_3) \cos 2a_3 z + 2\alpha_4'''' \sigma(2a_3) \sin 2a_3 z + \ldots,
\end{aligned}
$$

(33)

where

$$
\begin{aligned}
&\alpha_2' - i\alpha_2'' = a_{101}, \quad \alpha_2''' = -a_{110}, \quad \alpha_2' + i\alpha_2'' = -a_{111}, \quad \alpha_4' = a_{200}, \\
&\alpha_4'' = a_{020}, \quad \alpha_4''' - i\alpha_4'''' = a_{002}.
\end{aligned}
$$

(34)

Proceeding in line with the Landau theory we should now identify the irreducible representation of space group D_{2h}^{16} responsible for the D_{2h}^{16}–C_{2v}^9 transition. Seeing that the period in the C_{2v}^9 phase doubles along the y axis, the representation must correspond to the point $K = a_2/2$ of the Brillouin zone (see also §2). According to Kovalev's (1986, 1993) tables there are two irreducible representations T_1 and T_2 under number $T70$ relevant to this point. A standard analysis (Landau & Lifshitz, 1980; Lyubarskii, 1957, 1960) shows that only T_2 leads to a C_{2v}^9 phase.

In the Landau theory, it remains only to determine the number of different invariants composed of the basis functions of the representation $\varphi_1(\mathbf{r})$ and $\varphi_2(\mathbf{r})$ (replaced further by η and ξ); in particular, one will see that there is a Lifshitz invariant in this case. Thereupon one can at once write down the free energy of equation (1), as the form of the invariants may be readily established, while the explicit form of $\varphi_1(\mathbf{r})$ and $\varphi_2(\mathbf{r})$ is not required.

In the statistical approach it is necessary to know the basis functions $\varphi_1(\mathbf{r})$ and $\varphi_2(\mathbf{r})$. It is not difficult to surmise a possible form of the functions, namely, $\varphi_1 = \sin a_1 x \exp(-ia_2 y/2)$ and $\varphi_2 = \sin a_1 x \exp(ia_2 y/2)$, and to verify that they transform according to the representation T_2. For our purposes we take linear combinations of these functions that are real-valued:

$$\varphi_1' = \sin a_1 x \sin \frac{a_2 y}{2}, \qquad \varphi_2' = \sin a_1 x \cos \frac{a_2 y}{2}. \qquad (35)$$

The C_{2v}^9 phase emerges when a wave corresponding to one of the functions is frozen-in in the crystal (cf. §2). It should be remarked that both the functions lead to the same C_{2v}^9 symmetry because they go over into each other if the coordinate origin is shifted along the y axis. If the coordinate system is chosen as in equation (33), we should use φ_1' of equation (35). Thus below the phase-transition point the potential $U(\mathbf{r})$ acquires the form

$$U(\mathbf{r}) = U_0(\mathbf{r}) + C_1 \sin a_1 x \sin \frac{a_2 y}{2}, \qquad (36)$$

where $U_0(\mathbf{r})$ is of D_{2h}^{16} symmetry. We take $U(\mathbf{r})$ of equation (22) for $U_0(\mathbf{r})$, which yields the potential that will enable us to study the phase transition and properties of the emerging C_{2v}^9 phase:

$$U(\mathbf{r}) = \rho_0 \sigma(0) + 4\alpha_1 \sigma_1 \cos a_1 x \sin a_3 z + 4\alpha_2 \sigma_1 \sin 2a_2' y \cos a_3 z$$
$$+ 4\alpha_3 \sigma_3 \sin a_1 x \sin a_2' y, \qquad (37)$$

where $a_2' = a_2/2$ and $\sigma_3 = \sigma[(a_1^2 + a_2'^2)^{1/2}] = \sigma[(a_1^2 + a_2^2/4)^{1/2}]$.

If one compares equation (37) with equation (33), one sees that equation (37) is a special case of equation (33). The terms of equation (37) with $\cos a_1 x \sin a_3 z$ and $\sin a_1 x \sin a_2' y$ are present in equation (33) [the comparison yields the unknown coefficient C_1 of equation (36)]. Although the term of equation (37) with $\sin 2 a_2' y \cos a_3 z$ is not written down in equation (33), it is admitted by the C_{2v}^9 symmetry. Only the term with $\cos a_1 x \cos a_3 z$ which figures in the general series of equation (33) and which is admitted by the Kirkwood approximation used for equation (22) is missing from equation (37). Strictly speaking, the Kirkwood approximation allows one more term, namely, the term with $\cos 2a_2' y$ from equation (33). For simplicity's sake we discard this term, implying that $\sigma(2a_2') = \sigma(a_2) \sim 0$.

We should next deduce equations for the parameters α_1, α_2 and α_3 that enter into equation (37), which can be done with use made of equation (16) as in §4. In place of equations (21) and (34) we have now $\alpha_1 = ia_{101}$, $\alpha_2 = ia_{021}$, $\alpha_3 = -a_{110}$. As a result, analogously to equations (23)–(26) we shall obtain that

$$\frac{\alpha_1}{\rho_0} = \frac{I_1^{(2)}(\beta_1, \beta_2, \beta_3)}{I_0^{(2)}(\beta_1, \beta_2, \beta_3)}, \frac{\alpha_2}{\rho_0} = \frac{I_2^{(2)}(\beta_1, \beta_2, \beta_3)}{I_0^{(2)}(\beta_1, \beta_2, \beta_3)}, \frac{\alpha_3}{\rho_0} = \frac{I_3^{(2)}(\beta_1, \beta_2, \beta_3)}{I_0^{(2)}(\beta_1, \beta_2, \beta_3)}, \qquad (38)$$

where

$$I_0^{(2)}(\beta_1, \beta_2, \beta_3)$$
$$= \frac{1}{8\pi^3} \int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi} \exp[-4(\beta_1 \cos \xi_1 \sin \xi_3$$
$$+ \beta_2 \sin 2\xi_2 \cos \xi_3 + \beta_3 \sin \xi_1 \sin \xi_2)] \, d\xi_1 \, d\xi_2 \, d\xi_3, \qquad (39)$$

$$I_1^{(2)}(\beta_1, \beta_2, \beta_3) = \frac{1}{8\pi^3} \int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi} \cos \xi_1 \sin \xi_3$$
$$\times \exp[-4(\beta_1 \cos \xi_1 \sin \xi_3 + \beta_2 \sin 2\xi_2 \cos \xi_3$$
$$+ \beta_3 \sin \xi_1 \sin \xi_2)] \, d\xi_1 \, d\xi_2 \, d\xi_3, \qquad (40)$$

$$I_2^{(2)}(\beta_1, \beta_2, \beta_3) = \frac{1}{8\pi^3} \int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi} \sin 2\xi_2 \cos \xi_3$$
$$\times \exp[-4(\beta_1 \cos \xi_1 \sin \xi_3 + \beta_2 \sin 2\xi_2 \cos \xi_3$$
$$+ \beta_3 \sin \xi_1 \sin \xi_2)] \, d\xi_1 \, d\xi_2 \, d\xi_3, \qquad (41)$$

$$I_3^{(2)}(\beta_1, \beta_2, \beta_3) = \frac{1}{8\pi^3} \int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi} \sin \xi_1 \sin \xi_2$$
$$\times \exp[-4(\beta_1 \cos \xi_1 \sin \xi_3 + \beta_2 \sin 2\xi_2 \cos \xi_3$$
$$+ \beta_3 \sin \xi_1 \sin \xi_2)] \, d\xi_1 \, d\xi_2 \, d\xi_3, \qquad (42)$$

$$\beta_1 = \frac{\alpha_1 \sigma_1}{\theta}, \qquad \beta_2 = \frac{\alpha_2 \sigma_1}{\theta}, \qquad \beta_3 = \frac{\alpha_3 \sigma_3}{\theta}. \qquad (43)$$

From these formulae it follows that

$$I_1^{(2)} = -\frac{1}{4}\frac{\partial I_0^{(2)}}{\partial \beta_1}, \quad I_2^{(2)} = -\frac{1}{4}\frac{\partial I_0^{(2)}}{\partial \beta_2}, \quad I_3^{(2)} = -\frac{1}{4}\frac{\partial I_0^{(2)}}{\partial \beta_3}. \quad (44)$$

The integral $I_0^{(2)}$ can be calculated with the help of the series

$$I_0^{(2)}(\beta_1, \beta_2, \beta_3) = \sum_{n=0}^{\infty} \sum_{m=0}^{n} \frac{\beta_3^{2m}}{m!(n-m)!}$$
$$\times \sum_{l=0}^{n-m} \frac{(2n-2l)!(2n-2m-2l)!(2l)!\beta_1^{2l}\beta_2^{2n-2m-2l}}{(l!)^2(n-m-l)!^2(n-l)!(m+l)!(2n-m-2l)!}. \qquad (45)$$

With use made of equation (38) the equations of (43) can be recast as

$$\frac{\theta}{\rho_0 \sigma_1} = \frac{I_1^{(2)}(\beta_1, \beta_2, \beta_3)}{\beta_1 I_0^{(2)}(\beta_1, \beta_2, \beta_3)}, \quad \frac{\beta_2 I_1^{(2)}(\beta_1, \beta_2, \beta_3)}{\beta_1 I_2^{(2)}(\beta_1, \beta_2, \beta_3)} = 1,$$
$$\frac{\beta_3 I_1^{(2)}(\beta_1, \beta_2, \beta_3)}{\beta_1 I_3^{(2)}(\beta_1, \beta_2, \beta_3)} = \frac{\sigma_3}{\sigma_1}. \qquad (46)$$

These equations together with equation (38) yield the temperature dependence of α_1, α_2 and α_3 with β_1, β_2, β_3 as parameters. On the basis of equation (18), by analogy with equation (32), we calculate the Helmholtz free energy F_c relevant to the crystal,

$$F_c \equiv \frac{F - F_f}{\rho_0 |\sigma_1| N} = 2\frac{\alpha_1^2 + \alpha_2^2 + \sigma_3 \alpha_3^2 / \sigma_1}{\rho_0^2} - \tilde{\theta} \ln I_0^{(2)}, \qquad (47)$$

with the same dimensionless temperature $\tilde{\theta} = \theta/\rho_0 |\sigma_1|$.

If $\beta_3 = 0$, one can see that $I_0^{(2)} = I_0^{(1)}$, $I_1^{(2)} = I_1^{(1)}$, $I_2^{(2)} = I_2^{(1)}$ and $I_3^{(2)} = 0$, so that one has the parent phase of §4. If $\beta_3 \neq 0$, one has the C_{2v}^9 phase. Passing to the limit as $\beta_3 \rightarrow 0$ with $\beta_1 = \beta_2$ in the last equation of (46) one arrives at the condition for formation of the C_{2v}^9 phase:

$$\frac{\sigma_3}{\sigma_1} = -\frac{I_1^{(1)}(\beta_1, \beta_1)}{4\beta_1 I_{31}^{(2)}(\beta_1)}, \tag{48}$$

where

$$I_{31}^{(2)}(\beta_1) = \frac{1}{8\pi^3} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \sin^2 \xi_1 \sin^2 \xi_2$$

$$\times \exp[-4\beta_1(\cos \xi_1 \sin \xi_3 + \sin 2\xi_2 \cos \xi_3)]\, d\xi_1\, d\xi_2\, d\xi_3$$

$$= \frac{1}{16\pi^3} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \sin^2 \xi_1$$

$$\times \exp[-4\beta_1(\cos \xi_1 \sin \xi_3 + \sin \xi_2 \cos \xi_3)]\, d\xi_1\, d\xi_2\, d\xi_3. \tag{49}$$

The right-hand side of equation (48) is positive [see the remark in §4 as to the sign of $I_1^{(1)}$] and thereby σ_3 must be negative since $\sigma_1 < 0$. Numerical calculation shows that this right-hand side tends to unity as $\beta_1 \to 0$ or $\beta_1 \to \infty$, and has a minimum equal to 0.7890 at $\beta_1 = 1.6089$. Hence, the C_{2v}^9 phase under study can exist only if $0.7890 < \sigma_3/\sigma_1 < 1$. Equation (48) admits two solutions for each value of σ_3/σ_1 from this interval. The temperature at which the phase transition to the C_{2v}^9 phase occurs can be found from the first equation of (46) in the same limit as $\beta_3 \to 0$ with $\beta_1 = \beta_2$ found from equation (48). With use made of equation (48) the relevant dimensionless temperature can be conveniently written as

$$\tilde{\theta} \equiv \frac{\theta}{\rho_0 |\sigma_1|} = 4 \frac{\sigma_3 I_{31}^{(2)}(\beta_1)}{\sigma_1 I_0^{(1)}(\beta_1, \beta_1)}. \tag{50}$$

The behaviour of α_1, α_2, α_3 and of the free energy F_c of equation (47) near the phase-transition point can be elucidated by expanding the integrals of equations (39)–(42) in powers of β_3 with account taken of the fact that $\beta_1 \neq \beta_2$ in the emerging phase, although $\beta_1 = \beta_2$ in the parent phase. The relevant procedure is similar, though more involved, to the one employed for deducing equations (6.13) and (6.14) in Golovko (2004). Here we shall not describe the procedure and shall not adduce the resulting cumbersome formulae, which are of only academic interest, by limiting ourselves to the results of numerical calculations for the entire temperature region where the C_{2v}^9 phase exists. The calculations were performed for $\sigma_3/\sigma_1 = 0.9$. The second-order phase transition into the C_{2v}^9 phase happens at $\tilde{\theta} = 0.726$; as the temperature lowers, the value of β_3 increases from 0 to 0.522 and thereafter begins to decrease and eventually vanishes at $\tilde{\theta} = 0.149$, where an inverse second-order transition from the C_{2v}^9 phase to the D_{2h}^{16} phase occurs. We do not represent the curve describing the C_{2v}^9 phase in Fig. 2 as long as the curve, passing slightly below curve 2, will practically merge with the last at the scale of the figure. The existence of the inverse phase transition may be due to the peculiarities of space group D_{2h}^{16} for the intermolecular interactions implied in this paper as pointed out in §1.

Closing the section, it is worthy of remark that the role of the order parameter in the present case is played by β_3, more

precisely by $\alpha_3 = -a_{110}$, i.e. by the Fourier coefficient a_{110}. A similar situation holds for the phase transition considered by Golovko (2004) [see the discussion of equation (6.16) in that paper].

6. Incommensurate phase

First of all, it is necessary to establish the form of the density $\rho(\mathbf{r})$ for the incommensurate phase. In view of the remark at the end of the preceding section, the role of the order parameter in the present approach is played by Fourier coefficients a_{lmn}. According to the Landau theory (§2) the order parameter in the incommensurate phase is spatially modulated. Consequently, the coefficients a_{lmn} in the incommensurate phase should be of the form

$$a_{lmn} = \sum_{p=-\infty}^{\infty} a_{lmnp} \exp(ipka_2' y), \tag{51}$$

where, for convenience, we have introduced a_2' into the exponent in order that the parameter k be dimensionless. Being irrational, the parameter characterizes the periodic modulation of a_{lmn} in the incommensurate phase.

Substituting equation (51) into equation (19) with $a_2 \to a_2'$ (we should have the C_{2v}^9 phase if $k = 0$) yields

$$\rho(\mathbf{r}) = \sum_{l,m,n,p=-\infty}^{\infty} a_{lmnp} \exp[i(la_1 x + ma_2' y + na_3 z + pka_2' y)]. \tag{52}$$

This nonperiodical three-dimensional density $\rho(\mathbf{r})$ is characterized by four parameters a_1, a_2', a_3 and ka_2'. It is worth remarking that the symmetry of such a density may be described with the aid of superspace groups (Janssen & Janner, 1987; Janssen et al., 2007). By equation (11) analogously with equation (14), we can also calculate the potential $U(\mathbf{r})$ if $\rho(\mathbf{r})$ is given by equation (52):

$$U(\mathbf{r}) = \sum_{l,m,n,p=-\infty}^{\infty} a_{lmnp} \sigma\{[l^2 a_1^2 + (m + kp)^2 a_1'^2 + n^2 a_3^2]^{1/2}\}$$

$$\times \exp[i(la_1 x + ma_2' y + na_3 z + pka_2' y)]. \tag{53}$$

The present approach leans heavily on the symmetry of Fourier series in the case of space groups. At the same time, the series of equation (52) is not a Fourier series if k is irrational. For this reason we adopt the following strategy. An irrational number k can be represented with any desired precision by a ratio of two integers μ and ν, namely $k = \mu/\nu$, if ν and $\mu \to \infty$. When $k = \mu/\nu$, from equation (52) it follows that the period of $\rho(\mathbf{r})$ along the y axis is $D_2 = \nu d_2' = 2\pi\nu/a_2'$. This consideration suggests an idea of representing the incommensurate phase as the limit of a sequence of long-period commensurate phases when $D_2 \to \infty$.

This idea, however, encounters a serious difficulty. In the case where $k = \mu/\nu$ while ν and μ change, one has in fact a devil's staircase (see Golovko & Levanyuk, 1981a,b, and references therein). Even if a variation of $k = \mu/\nu$ is arbitrarily small, symmetry and some physical quantities undergo irregular jumps (Golovko & Levanyuk, 1981a,b), so that no

definite limit exists as $v, \mu \rightarrow \infty$. Let us analyse the commensurate phases at the devil's staircase relevant to ammonium fluorberyllate. Inside the Brillouin zone, the irreducible representation T_2 considered in §5 splits into two irreducible representations T_2 and T_4 under number $T31$ in Kovalev's (1986, 1993) tables. It is unknown which of these two representations corresponds to curve 2 (the soft-mode branch) in Fig. 1(b). An analysis akin to the one performed by Golovko & Levanyuk (1981a,b) shows that, if in $K = ma_2/n$ we take the integers m and n to be odd and even, respectively, both the representations give point group C_{2v} with the z polar axis as in the preceding section. Therefore with these m and n we avoid the symmetry jumps when changing K.

Still another condition should be met. The above symmetry concerns in fact the supercell with the period $D_2 = vd_2'$. When, according to §2, the incommensurate phase becomes domain-like (near the lock-in transition), the cells of period d_2' inside the domains have the structure of the low-temperature commensurate phase, which amounts to saying that they are of C_{2v}^9 symmetry as well. The C_{2v}^9 symmetry transformations contain a translation by $d_2'/2$, which signifies the translation by $D_2/2 = vd_2'/2$ for the supercell (the translations along the x and z axes are identical in the cell and supercell). If v is odd ($v = 2v' + 1$), one has $D_2/2 = v'd_2' + d_2'/2$, that is to say, one finds oneself after the translation in the middle of the cell as one should. Hence, the integer v in $k = \mu/v$ must be odd. From Fig. 1 and the fact that $a_2' = a_2/2$ in equation (52) it follows that the fraction m/n in $K = ma_2/n$ and $k = \mu/v$ are interrelated by $m/n = 1/2 - k/2 = (v - \mu)/(2v)$. Inasmuch as we should have $m/n =$ odd/even while v is odd, the integer μ must be even. As a result, we see that, if the integer v is odd while the integer μ is even in $k = \mu/v$, in the limit as μ and $v \rightarrow \infty$ we should arrive at the required incommensurate phase without any irregular jumps characteristic of the devil's staircase. In what follows we assume that the fraction μ/v is irreducible, which is equivalent to saying that the integers μ and v are relatively prime.

We now turn to the long-period phases. Upon putting $k = \mu/v$ we apply the C_{2v}^9 symmetry operations to equation (52) to obtain

$$a_{lmnp} = a_{-l,-m,n,-p}(-1)^{l+vm+n} = a_{-l,m,n,p}(-1)^{vm}$$
$$= a_{l,-m,n,-p}(-1)^{l+n}. \tag{54}$$

Here we have used the fact that $(-1)^{\mu p} = 1$ for μ is even. To this must be added the condition $a_{lmnp}^* = a_{-l-m-n-p}$ as $\rho(\mathbf{r})$ is real. Now, instead of the general form of equation (53), we are in a position to write down the potential for the long-period phases which goes over into equation (37) if $k = 0$ (the fact that v is odd is also taken into account):

$$U(\mathbf{r}) = \rho_0\sigma(0) + 4\cos a_1 x \sin a_3 z \sum_{p=0}^{\infty} \alpha_{1p}\sigma_{1p} \cos pka_2'y$$

$$+ 4\cos a_3 z \sum_{p=-\infty}^{\infty} \alpha_{2p}\sigma_{2p} \sin(2 + pk)a_2'y$$

$$+ 4\sin a_1 x \sum_{p=-\infty}^{\infty} \alpha_{3p}\sigma_{3p} \sin(1 + pk)a_2'y, \tag{55}$$

where $\alpha_{10} = ia_{1010}$, $\alpha_{1p} = 2ia_{101p}$ if $p \neq 0$, $\alpha_{2p} = ia_{021p}$, $\alpha_{3p} = -a_{110p}$ and

$$\sigma_{1p} = \sigma[(a_1^2 + p^2k^2a_2'^2 + a_3^2)^{1/2}], \quad \sigma_{2p} = \sigma\{[(2 + pk)^2a_2'^2 + a_3^2]^{1/2}\},$$
$$\sigma_{3p} = \sigma\{[a_1^2 + (1 + pk)^2a_2'^2]^{1/2}\}. \tag{56}$$

Although the summation in equation (55) should not be extended up to infinity once the Kirkwood approximation is used, the potential of equation (55) contains a great many terms because the value of k is usually small [$k \sim 0.01$ for ammonium fluorberyllate (Iizumi & Gesi, 1977)].

As long as $k = \mu/v$, the potential $U(\mathbf{r})$ of equation (55) and thereby the density $\rho(\mathbf{r})$ in equation (9) are periodic and we can expand $\rho(\mathbf{r})$ in a Fourier series. We shall, however, obtain the coefficients a_{lmn} of equation (19), whereas we need the coefficients a_{lmnp} of equation (52). Therefore, an interrelation between a_{lmn} and a_{lmnp} is required. To this end we recast equation (19) for the long-period phases replacing a_2 by a_2'/v since $D_2 = vd_2'$; besides, we substitute s for m:

$$\rho(\mathbf{r}) = \sum_{l,s,n=-\infty}^{\infty} a_{lsn} \exp[i(la_1x + na_3z) + isa_2'y/v]. \tag{57}$$

Comparing this with equation (52) where $k = \mu/v$ we see that $s = vm + \mu p$. This is a Diophantine equation for m and p. As long as μ and v are relatively prime, the equation admits a solution with arbitrary s; moreover, it has an infinite number of solutions with the same s. If one writes $s = vm' + \mu p'$ for another solution and compares this with the first one, one arrives at

$$\frac{\mu}{v} = \frac{m - m'}{p' - p}. \tag{58}$$

The integers μ and v being relatively prime, this relation is satisfied only if $m - m' = t\mu$ and $p' - p = tv$ with an arbitrary integer t, from which $m' = m - t\mu$ and $p' = p + tv$ for any other solution.

We see now that, to obtain equation (57) from (52), at a given s we should add up all a_{lmnp} for which $vm + \mu p = s$ with the result

$$a_{lsn} = \sum_{t=-\infty}^{\infty} a_{l,m-t\mu,n,p+tv}. \tag{59}$$

The coefficients a_{lmnp} in equation (51) should tend to zero as $|p|$ tends to infinity; the same occurs if $|m| \rightarrow \infty$ because $a_{lmn} \rightarrow 0$ in this limit. Consequently, as $v, \mu \rightarrow \infty$, only the term with $t = 0$ remains in the sum of equation (59), which finally yields

$$a_{lmnp} = a_{l,vm+\mu p,n}. \tag{60}$$

With this formula at our disposition we can calculate the Fourier coefficients a_{lmn} with the help of the standard procedure, and we shall arrive at an equation of the type of equation (16) into which the potential $U(\mathbf{r})$ of equation (55) should be substituted. Afterwards, with use made of equation (60) we shall find the following equations for the coefficients α_{ip} ($i = 1, 2, 3$) that figure in equation (55):

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$$\frac{\alpha_{10}}{\rho_0} = \frac{J_{10}}{J_0}, \frac{\alpha_{1p}}{\rho_0} = \frac{2J_{1p}}{J_0} \quad \text{if } p \neq 0, \quad \frac{\alpha_{2p}}{\rho_0} = \frac{J_{2p}}{J_0}, \frac{\alpha_{3p}}{\rho_0} = \frac{J_{3p}}{J_0},$$

$$(61)$$

where

$$J_0 = \frac{1}{8\pi^3} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \exp[-U(\xi_1, \xi_2, \xi_3)] \, d\xi_1 \, d\xi_2 \, d\xi_3, \qquad (62)$$

$$J_{1p} = \frac{1}{8\pi^3} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \cos\xi_1 \cos p\mu\xi_2 \sin\xi_3$$
$$\times \exp[-U(\xi_1, \xi_2, \xi_3)] \, d\xi_1 \, d\xi_2 \, d\xi_3, \qquad (63)$$

$$J_{2p} = \frac{1}{8\pi^3} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \sin(2\nu + p\mu)\xi_2 \cos\xi_3$$
$$\times \exp[-U(\xi_1, \xi_2, \xi_3)] \, d\xi_1 \, d\xi_2 \, d\xi_3, \qquad (64)$$

$$J_{3p} = \frac{1}{8\pi^3} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \sin\xi_1 \sin(\nu + p\mu)\xi_2$$
$$\times \exp[-U(\xi_1, \xi_2, \xi_3)] \, d\xi_1 \, d\xi_2 \, d\xi_3, \qquad (65)$$

$$U(\xi_1, \xi_2, \xi_3) = 4\cos\xi_1 \sin\xi_3 \sum_{n=0}^{\infty} \beta_{1n} \cos n\mu\xi_2$$
$$+ 4\cos\xi_3 \sum_{n=-\infty}^{\infty} \beta_{2n} \sin(2\nu + n\mu)\xi_2$$
$$+ 4\sin\xi_1 \sum_{n=-\infty}^{\infty} \beta_{3n} \sin(\nu + n\mu)\xi_2, \qquad (66)$$

$$\beta_{1n} = \frac{\alpha_{1n}\sigma_{1n}}{\theta}, \quad \beta_{2n} = \frac{\alpha_{2n}\sigma_{2n}}{\theta}, \quad \beta_{3n} = \frac{\alpha_{3n}\sigma_{3n}}{\theta}. \qquad (67)$$

From equations (62)–(65) it follows that

$$J_{1p} = -\frac{1}{4}\frac{\partial J_0}{\partial \beta_{1p}}, \quad J_{2p} = -\frac{1}{4}\frac{\partial J_0}{\partial \beta_{2p}}, \quad J_{3p} = -\frac{1}{4}\frac{\partial J_0}{\partial \beta_{3p}}. \qquad (68)$$

The next step is to find out the form of the above integrals in the limit as ν and $\mu \to \infty$ in order to arrive at the incommensurate phase. In view of equation (68) it is sufficient to consider the integral J_0 alone, which is done in the Appendix. As a result, we shall have for the incommensurate phase that

$$J_0 = \frac{1}{16\pi^4} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \exp[-U(\xi_1, \xi_2, \xi_3, \xi_4)] \, d\xi_1 \, d\xi_2 \, d\xi_3 \, d\xi_4,$$

$$(69)$$

$$U(\xi_1, \xi_2, \xi_3, \xi_4) = 4\cos\xi_1 \sin\xi_3 \sum_{n=0}^{\infty} \beta_{1n} \cos n\xi_4$$
$$+ 4\cos\xi_3 \sum_{n=-\infty}^{\infty} \beta_{2n} \sin(2\xi_2 + n\xi_4)$$
$$+ 4\sin\xi_1 \sum_{n=-\infty}^{\infty} \beta_{3n} \sin(\xi_2 + n\xi_4). \qquad (70)$$

It will be noted that k has disappeared explicitly off equations (69) and (70); it remains only implicitly in β_{in} through equation (56). The integrals J_{1p}, J_{2p} and J_{3p} can now be computed with the help of equation (68).

Combining equations (67) and (61) we arrive at a set of equations for β_{ip}:

$$\frac{\theta}{\rho_0 \sigma_1} = \frac{J_{10}}{\beta_{10} J_0}, \quad \frac{\theta}{\rho_0 \sigma_{1p}} = \frac{2J_{1p}}{\beta_{1p} J_0} \quad \text{if } p \neq 0, \quad \frac{\theta}{\rho_0 \sigma_{2p}} = \frac{J_{2p}}{\beta_{2p} J_0},$$
$$\frac{\theta}{\rho_0 \sigma_{3p}} = \frac{J_{3p}}{\beta_{3p} J_0}, \qquad (71)$$

where σ_1 is the same as in equation (22). Having found the β_{ip}'s from the set as functions of the temperature θ we are able, by equation (61), to compute the coefficients α_{ip} that describe the incommensurate phase. It is necessary also to have the Helmholtz free energy. It can be calculated on the basis of equation (4.27) of Golovko (2001) upon substituting equations (52) and (53) there:

$$F = \theta N \ln\left[\frac{1}{\gamma}\left(\frac{m}{2\pi\theta}\right)^{3/2}\right] + \theta N \ln C$$
$$- \frac{V}{2} \sum_{l,m,n,p} |a_{lmnp}|^2 \sigma\{[l^2 a_1'^2 + (m + kp)^2 a_2'^2 + n^2 a_3'^2]^{1/2}\}.$$

$$(72)$$

The constant C herein, the same as in equation (9), is to be expressed in terms of the average density $\rho_0 = a_{000} = a_{0000}$ analogously to equation (3.10) of Golovko (2001). As a result, the first two terms on the right can be recast as in equation (18). For the example considered in the present section, one has

$$F = F_f - \theta N \ln J_0 - 2V\alpha_{10}^2 \sigma_1 - V \sum_{p=1}^{\infty} \alpha_{1p}^2 \sigma_{1p}$$
$$- 2V \sum_{p=-\infty}^{\infty} \alpha_{2p}^2 \sigma_{2p} - 2V \sum_{p=-\infty}^{\infty} \alpha_{3p}^2 \sigma_{3p}. \qquad (73)$$

As distinct from the previous sections, the equations of (71) represent a great number of equations since the value of the integer p can be very large in spite of the Kirkwood approximation employed, according to the remark concerning equation (55). It can be shown that, if $k = 0$, the above equations transform into the equations of §5 describing the C_{2v}^9 phase.

Considering the transition from the parent phase to the incommensurate one we set $\beta_{10} = \beta_{20} = \beta_1$, $\beta_{30} = 0$, and assume that only the first harmonics with the coefficients α_{31} and $\alpha_{3,-1}$ come into being initially because it is just these harmonics that correspond to the last term in equation (36). We expand the integrals J_0, J_{31} and $J_{3,-1}$ in powers of α_{31} and $\alpha_{3,-1}$ and retain only linear terms. The result is placed in the last equation of (61) with account taken of equation (67). In this manner we obtain the following two equations:

$$\left[\frac{\theta I_0^{(1)}(\beta_1, \beta_1)}{\rho_0} + 4\sigma_{31} I_{31}^{(2)}(\beta_1)\right]\alpha_{31} = 0,$$

$$\left[\frac{\theta I_0^{(1)}(\beta_1, \beta_1)}{\rho_0} + 4\sigma_{3,-1} I_{31}^{(2)}(\beta_1)\right]\alpha_{3,-1} = 0, \qquad (74)$$

where $I_0^{(1)}(\beta_1, \beta_1)$ and $I_{31}^{(2)}(\beta_1)$ are the same integrals as in equations (24) and (49) and, according to equation (56),

$$\sigma_{31} = \sigma\{[a_1^2 + (1+k)^2 a_2^2]^{1/2}\}, \quad \sigma_{3,-1} = \sigma\{[a_1^2 + (1-k)^2 a_2^2]^{1/2}\}. \tag{75}$$

It follows from equation (74) that one of the coefficients α_{31} or $\alpha_{3,-1}$ acquires a nonzero value if the expression in the relevant brackets vanishes, which gives two temperatures:

$$\frac{\theta}{\rho_0|\sigma_1|} = 4\frac{\sigma_{31} I_{31}^{(2)}(\beta_1)}{\sigma_1 I_0^{(1)}(\beta_1, \beta_1)}, \qquad \frac{\theta}{\rho_0|\sigma_1|} = 4\frac{\sigma_{3,-1} I_{31}^{(2)}(\beta_1)}{\sigma_1 I_0^{(1)}(\beta_1, \beta_1)}. \tag{76}$$

If $k = 0$, then $\sigma_{31} = \sigma_{3,-1} = \sigma_3$, and both the temperatures coincide with the temperature of equation (50). The quantities σ_{31} and $\sigma_{3,-1}$, however, cannot have an extremum at $k = 0$ because of the presence of terms linear in k. One of the quantities must be a maximum at $k \neq 0$ (for definiteness, we assume that $k > 0$). The maximum will yield the transition temperature to the incommensurate phase by virtue of equation (76) and the temperature will be higher than the one given by equation (50). Simultaneously, one will have the corresponding value of k.

The above reasoning is akin to the one concerning equation (8). In the Landau theory, the behaviour of the soft-mode branch at $K = a_2/2$ displayed in Fig. 1(b) is reflected in the presence of the Lifshitz invariant (see §2). In the statistical approach where the Lifshitz invariant does not figure, that behaviour manifests itself in the presence of linear in k terms in σ_{ip} of equation (56).

Having found the phase-transition temperature one can elucidate the further temperature behaviour of the incommensurate phase upon solving the equations (71) [to do this, one must, of course, know the concrete form of σ_{ip} that depends upon the intermolecular potential and the pair correlation function given by equations (15) and (12)]. The equations also contain k via σ_{ip}. The equilibrium value of k has to be computed by minimizing the Helmholtz free energy of equation (73) as far as it is implied in the present study that the external conditions are specified by the volume of the crystal (more precisely, by its periods) and by the temperature, so that the relevant thermodynamic potential is just the Helmholtz free energy.

One further point should be discussed. In the Landau theory, we had only two equations (5) and (6) that described the incommensurate phase (in the case of a two-component order parameter). In the present statistical theory, the incommensurate phase is described by a great many equations of (71) (although the equations are not differential). This is due to the following. In the Landau theory, one presumes that the order parameter is one of the normal coordinates while the normal coordinates are mutually independent in a linear

approximation. In the present statistical theory, the role of the order parameter is played by Fourier coefficients as mentioned at the outset of this section, whereas different Fourier coefficients are interrelated. It may be added that the neglect of other normal coordinates below the phase-transition point in the Landau theory is only an approximation whose validity is not clear (see the end of §2).

If the dispersion curves behave as the ones presented in Fig. 1(a), the quantities σ_{ip} should depend upon k quadratically as σ_{1p} of equation (56). One can also deduce an equation equivalent to equation (76). In this case the quantity, say σ_{11}, will have an extremum at $k = 0$. If, however, the extremum is not a maximum, the maximal possible value of σ_{11} and the relevant temperature θ will anew be at $k \neq 0$, which amounts to saying that one will again have an incommensurate phase, of type II in this event. Hence, the present approach enables one to treat the type-II incommensurate phases as well.

7. Concluding remarks

In the present paper, a mathematical apparatus has been worked out which permits one to study commensurate as well as incommensurate phase transitions and the relevant phases from the viewpoint of statistical mechanics. It is shown how one can carry out the preliminary symmetry analysis when one deals with a concrete crystal. The analysis can be performed analogously with the one in the Landau phase-transition theory where this analysis is well elaborated, although some refinements are required which are not obligatory in the Landau theory. After the analysis one is able to deduce a set of equations that describe the emerging phases and corresponding phase transitions. The equations of the statistical approach contain quantities that may be directly calculated once the intermolecular potential and the pair correlation function are known, while the equations of the Landau theory contain only phenomenological coefficients.

The Landau theory as applied to incommensurate phases leans heavily on the notion of the Lifshitz invariant. In the statistical approach, the Lifshitz invariant does not figure and the relevant behaviour of the soft-mode branch is reflected in another way. The treatment of an incommensurate phase in the statistical theory is substantially complicated because the symmetry of the phase cannot be described in terms of customary space groups. For this reason, a strategy of representing the incommensurate phase as the limit of a sequence of long-period commensurate phases whose period tends to infinity was adopted in the paper. The strategy, however, encounters a serious difficulty because a devil's staircase occurs in this situation. We have chosen a method of moving along the devil's staircase such that it was possible to avoid irregular jumps characteristic of the devil's staircase and to arrive at a definite limit. It should be added that the mathematical apparatus worked out in the paper can be used for the study of incommensurate phases of type I as well as of type II.

The studies in the paper were carried out using displacive phase transitions as an example because a soft

mode exists in this event and the situation occurring can be conveniently illustrated with the help of Fig. 1. All results of the paper remain valid for order–disorder phase transitions as well where occupation-modulated structures arise.

It should be emphasized that the present paper is a first, though essential, step in applying statistical mechanics to studying the incommensurate phases and the phase transitions relevant to them. We have shown that the phase-transition temperature and properties of the emerging phase are expressible in terms of the function $\sigma(A)$ of equation (15) whose form depends upon the pair correlation function. Consequently, the next step is to find an equation for this last function leaning on the second equation of the BBGKY hierarchy. Seeing that the pair correlation function should be directly dependent on the intermolecular potential, the second step will enable one to express the phase-transition temperature, peculiarities of the transition and properties of the incommensurate phase in terms of the intermolecular potential. At the same time, to find the pair correlation function is not a simple matter inasmuch as the second BBGKY equation contains a triplet correlation function as well. The problem is complicated by the fact that, as distinct from a fluid, the pair correlation function in a crystal is anisotropic and its form is rather involved, even in the case of an ordinary crystal (Golovko, 2007).

Some remarks should be made as to the approach where one describes the symmetry of an incommensurate phase in terms of superspace groups (Janssen & Janner, 1987; Janssen *et al.*, 2007). An especial investigation is needed in order to uniquely prescribe a superspace group for a given incommensurate phase, which requires elaborate techniques (Janssen *et al.*, 2007). At the same time, in the Landau theory it suffices to know the space group of the parent phase and that of the low-temperature commensurate phase in order to write down unambiguously the free energy of the type of equation (1) which enables one to investigate properties of the incommensurate phase. The same occurs in the present statistical approach, where we have obtained a unique system of equations for the incommensurate phase in the crystal under study on the basis of the above space groups alone.

It is instructive nevertheless to compare the present approach and the superspace-group one. In line with the superspace-group approach we replace y in the last term of the exponent of equation (52) by an independent variable, say u, implying that we may always put $u = y$ at the end; for convenience we set $ka'_2 = a_4$ as well. The same replacements are to be made in equation (53). Now equation (52) becomes an ordinary four-dimensional Fourier series for $\rho(\mathbf{r}, u)$ whose coefficients a_{lmnp} can be calculated in a standard way. With use made of equation (9) written for $\rho(\mathbf{r}, u)$ and $U(\mathbf{r}, u)$ we obtain a set of equations for a_{lmnp} analogous to equation (16). To achieve a full analogy one needs to single out the term with $\sigma(0)$ and to determine the constant C from the condition that $a_{0000} = \rho_0$. As a result, we arrive at the following set of equations:

$$a_{lmnp} = \frac{\rho_0}{16\pi^4 G} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \exp[-(1/\theta)U_4(\xi_1, \xi_2, \xi_3, \xi_4)$$
$$- i(l\xi_1 + m\xi_2 + n\xi_3 + p\xi_4)]\, \mathrm{d}\xi_1\, \mathrm{d}\xi_2\, \mathrm{d}\xi_3\, \mathrm{d}\xi_4, \qquad (77)$$

where

$$G = \frac{1}{16\pi^4} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \exp[-(1/\theta)U_4(\xi_1, \xi_2, \xi_3, \xi_4)]\, \mathrm{d}\xi_1\, \mathrm{d}\xi_2\, \mathrm{d}\xi_3\, \mathrm{d}\xi_4,$$
$$(78)$$

$$U_4(\xi_1, \xi_2, \xi_3, \xi_4)$$
$$= \sum_{l,m,n,p=-\infty}^{\infty\prime} a_{lmnp}\sigma\{[l^2 a_1^2 + (m + kp)^2 a_1'^2 + n^2 a_3^2]^{1/2}\}$$
$$\times \exp[i(l\xi_1 + m\xi_2 + n\xi_3 + p\xi_4)]. \qquad (79)$$

It may be noted that the auxiliary variable u has disappeared off these formulae so that there is no need to put $u = y$ here.

If one specifies $U_4(\xi_1, \xi_2, \xi_3, \xi_4)$ of equation (79) on the basis of equation (55) with the above replacements, one will see that G of equation (78) fully coincides with J_0 of equation (69). This result entails two important conclusions. First, the lengthy calculations of the Appendix are accurate. Secondly, the strategy of long-period commensurate phases chosen in §6 and the method of overcoming the peculiarities of the devil's staircase have led to a correct limit.

At the same time, the set of equations (77) by itself is of little use. The example of the set of equations (16) analogous to equations (77) demonstrates that the set becomes meaningful and yields definite results only if one specifies the set for a concrete space group, which is seen from §§4 and 5 above and from the paper by Golovko (2004). However, even if one knows a definite superspace group for a given incommensurate phase and can specify the set of equations (77) with this superspace group, this will be of little avail for studying the relevant phase transitions. For example, the general form of the potential $U(\mathbf{r})$ of equation (33) for space group C_{2v}^9 says nothing about possible phase transitions. Only the potential $U(\mathbf{r})$ of equation (37), which is a particular case of equation (33) and which was deduced from knowledge of the parent and low-temperature space groups, enabled us to study the phase transitions. The potential $U(\mathbf{r})$ of equation (55) that was used for studying the incommensurate phase transition was again obtained with the help of those space groups alone, and no superspace groups were required at all.

APPENDIX A
Limit of the integral J_0 as ν and $\mu \to \infty$

This limit concerns only the integration over ξ_2 and, instead of J_0 of equation (62), we shall consider the following integral with the same $U(\xi_1, \xi_2, \xi_3)$ as in equation (66):

$$I = \int_0^{2\pi} \exp[-U(\xi_1, \xi_2, \xi_3)]\, \mathrm{d}\xi_2. \qquad (80)$$

Recalling that $k = \mu/\nu$ we change the variable of integration according to $\xi_2 = y/\nu$, divide the new interval of integration into ν intervals of length 2π and represent the integral I as a sum of ν integrals in each of which we change the variables of integration so that the integration shall be from 0 to 2π. As a result,

$$I = \frac{1}{\nu} \sum_{j=0}^{\nu-1} \int_0^{2\pi} \exp[-U_j(y)] \, \mathrm{d}y, \qquad (81)$$

$$U_j(y) = 4\cos\xi_1 \sin\xi_3 \sum_{p=0}^{\infty} \beta_{1p}\cos(2\pi jpk + pky)$$

$$+ 4\cos\xi_3 \sum_{p=-\infty}^{\infty} \beta_{2p}\sin[2\pi jpk + (2+pk)y]$$

$$+ 4\sin\xi_1 \sum_{p=-\infty}^{\infty} \beta_{3p}\sin[2\pi jpk + (1+pk)y]. \quad (82)$$

Instead of the discrete variable j, we introduce a continuous variable t and consider the function (other variables are regarded as parameters)

$$f(t) = \exp\left\{ -4\cos\xi_1 \sin\xi_3 \sum_{p=0}^{\infty} \beta_{1p}\cos(2\pi pkt + pky) \right.$$

$$- 4\cos\xi_3 \sum_{p=-\infty}^{\infty} \beta_{2p}\sin[2\pi pkt + (2+pk)y]$$

$$\left. - 4\sin\xi_1 \sum_{p=-\infty}^{\infty} \beta_{3p}\sin[2\pi pkt + (1+pk)y] \right\}. \quad (83)$$

This function is periodic with the period $d = 1/k$ and can be expanded into a Fourier series:

$$f(t) = \frac{a_0}{2} + \sum_{n=1}^{\infty} (a_n \cos 2\pi knt + b_n \sin 2\pi knt), \qquad (84)$$

where

$$a_n = 2k \int_{-1/2k}^{1/2k} f(\tau) \cos 2\pi kn\tau \, \mathrm{d}\tau = \frac{1}{\pi} \int_0^{2\pi} f\left(\frac{\xi}{2\pi k}\right) \cos n\xi \, \mathrm{d}\xi,$$

$$(85)$$

the coefficient b_n being of no importance for the present calculations.

The integral I of equation (81) contains the sum

$$S = \sum_{j=0}^{\nu-1} f(j) = \frac{\nu a_0}{2} + \sum_{n=1}^{\infty} \sum_{j=0}^{\nu-1} (a_n \cos 2\pi knj + b_n \sin 2\pi knj).$$

$$(86)$$

Remembering that $k = \mu/\nu$, by virtue of equations (1.342.1, 2) of Gradshteyn & Ryzhik (1962, 1965) one has

$$\sum_{j=0}^{\nu-1} \cos 2\pi knj = \frac{\sin \pi\mu n}{\sin(\pi\mu n/\nu)} \cos[(\nu-1)\pi kn],$$

$$\sum_{j=0}^{\nu-1} \sin 2\pi knj = \frac{\sin \pi\mu n}{\sin(\pi\mu n/\nu)} \sin[(\nu-1)\pi kn]. \qquad (87)$$

It is seen that these sums vanish owing to $\sin \pi\mu n$ except for the case where $n = p\nu$ with $p = 1, 2, 3, \ldots$, when one has 0/0. In this case, $\cos 2\pi p\mu j = 1$ while $\sin 2\pi p\mu j = 0$, and equation (86) yields finally

$$S = \frac{\nu a_0}{2} + \nu \sum_{p=1}^{\infty} a_{p\nu}. \qquad (88)$$

The last sum should approach zero as $\nu \to \infty$ because the Fourier coefficients a_n of equation (84) tend to zero as $n \to \infty$. In the event of a function of the type of equation (83), the Fourier coefficients a_n tend to zero exponentially inasmuch as the function has all derivatives and they are continuous.

Substituting all of these into equation (81) and letting $\nu \to \infty$, in the end we obtain

$$I = \frac{1}{2\pi} \int_0^{2\pi} \mathrm{d}y \int_0^{2\pi} \exp[-U(\xi)] \, \mathrm{d}\xi, \qquad (89)$$

$$U(\xi) = 4\cos\xi_1 \sin\xi_3 \sum_{p=0}^{\infty} \beta_{1p}\cos p(\xi + ky)$$

$$+ 4\cos\xi_3 \sum_{p=-\infty}^{\infty} \beta_{2p}\sin[2y + p(\xi + ky)]$$

$$+ 4\sin\xi_1 \sum_{p=-\infty}^{\infty} \beta_{3p}\sin[y + p(\xi + ky)]. \qquad (90)$$

Replacing $\xi + ky$ by ξ_4 and y by ξ_2 (the integration over ξ_4 can again be from 0 to 2π for the integrand has a period equal to 2π) and putting the result into equation (62) we arrive at equation (69).

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