Zeitschrift: Helvetica Physica Acta
Band: 56 (1983)
Heft: 1-3

Artikel: Incommensurate crystal phases
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DOI: https://doi.org/10.5169/seals-115408

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Helvetica Physica Acta,
Vol. 56 (1983) 665-675

0018-0238/83/010665-11$1.50+0.20/0
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INCOMMENSURATE CRYSTAL PHASES

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1. Introduction

The aim of the present paper is to explore how the superspace description of an incommensurate modulated crystal can be used for investigating crystal phase transitions.

The superspace group approach is explained briefly in section 2. For more details the reader is referred to the references given there. Then, the relevant ideas and results of two specific one-dimensional microscopic models leading to phase diagrams involving incommensurate crystal structures are briefly reviewed. Subsequently the same models are considered again but now in a superspace-adapted formulation, the advantage of the approach being more that of a symmetry-adapted formulation than that of a group-theoretical use of the crystallographic superspace symmetry occuring in these models.

In order to investigate the latter aspect as well, the classical theory of Landau for continuous phase transitions is considered and extended to allow the use of superspace symmetry as present in incommensurate crystals. In the last part of this paper such an extension is presented, which indeed allows to characterize second-order phase transitions involving incommensurate phases as well. This even when different modulation dimensionalities (the so-called internal dimensions) or when commensurate phases occur . As one intuitively expects, in these phase transitions the Lifshitz condition plays an important role. One can show that the existence of Lifshitz invariants is required in second-order phase transitions between crystal phases of different internal dimension. The present treatment has necessarily a sketchy character and more details will be given in another paper.

2. The Symmetry of Incommensurate Crystal Phases

The fundamental structural property of an ideal incommensurate crystal is to have a density ρ whose Fourier wave vectors span a Z-module M^* of dimension 3 and of rank 3 + d :

$$\rho(\vec{r}) = \sum_{\vec{k}\in M^*} \hat{\rho}(\vec{k})\, e^{i\vec{k}\vec{r}} . \tag{2.1}$$

This means that the wave vectors $\vec{k}$ are of the general form :

$$\vec{k} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^* + m_1\vec{q}_1 + \ldots + m_d\vec{q}_d \tag{2.2}$$

where $h,k,l,m_1,\ldots,m_d$ are integral coefficients (the indices). The basis vectors appearing in (2.2) are linearly independent over the rational numbers. We suppose that $\vec{a}^*$, $\vec{b}^*$ and $\vec{c}^*$ span the 3-dimensional reciprocal lattice Λ^* of a basic crystal structure, and that $\vec{q}_1,\ldots,\vec{q}_d$ are modulation wave vectors. This is not necessary but useful.

The 3-dimensional space V is then extended to a (3+d)-dimensional one by considering the above basis of M^* in V as a 1-to-1 orthogonal projection of a basis of a so-called superspace V_s. Then the Fourier wave vectors $\vec{k}$ are projections of reciprocal lattice vectors k_s :

$$k_s = hc^* + kb^* + lc^* + m_1d_1^* + \ldots + m_dd_d^* \in \Sigma^*. \tag{2.3}$$

The (3+d)-dimensional vector $k_s = (\vec{k},\vec{k}_I)$ has an internal component denoted by $\vec{k}_I$. In terms of the indices we can write :

$$\vec{k} = (h,k,l,m_1,\ldots,m_d) \quad \text{as well as} \quad k_s = (h,k,l,m_1,\ldots,m_d) \tag{2.4}$$

but of course those (same) components refer to different bases. This allows to interpret $\hat{\rho}(\vec{k})$ as a Fourier component $\hat{\rho}(k_s)$ of a function ρ_s defined in the superspace (the supercrystal) by :

$$\rho_s(r_s) = \sum_{k_s\in\Sigma^*} \hat{\rho}(k_s)\, e^{ik_sr_s} \tag{2.5}$$

with

$$r_s = (\vec{r},\vec{t}), \quad k_sr_s = \vec{k}\vec{r} + \vec{k}_I\vec{t} \quad \text{and} \quad \hat{\rho}(k_s) = \hat{\rho}(\vec{k}). \tag{2.6}$$

Note that

$$\rho(\vec{r}) = \rho_s(\vec{r},\vec{t})|_{\vec{t}=0} . \tag{2.7}$$

The symmetry of the incommensurate crystal is then the Euclidean symmetry

group G_s of ρ_s, i.e. a (3+d)-dimensional space group called superspace group. In terms of the Fourier components the symmetry condition takes the form :

$$\hat{\rho}(\vec{k}) = \hat{\rho}(R\vec{k})\, e^{iR_s k_s \cdot v_s} \tag{2.8}$$

for $g_s = \{ R_s \mid v_s \} \in G_s$ and $R_s=(R,R_I)$, with R and R_I orthogonal transformations in 3 and d dimensions, respectively, and v_s the translational component. The theory of superspace groups and their application to crystallographic problems are discussed in refs.[1] and [2].

3. One-Dimensional Model for Thiourea

Thiourea, $SC(NH_2)_2$ (and also the deuterated one), shows [3] a high temperature paraelectric phase (P) with space group D_{2h}^{16} = Pnma ; it has between T_I = 201 K (and 212 K respectively) and T_c = 169 K (and 185 K respectively) an incommensurate displacively modulated phase (I) with superspace group Pnma(0,β,0)(0,0,s) = $P^{Pnma}_{11\bar{1}s}$ (see [4] and for the notation [5] where this superspace group is listed as 62b.2), and has a temperature-dependent modulation wave vector $\vec{q}$ along the $\vec{b}$ direction ($\vec{q} = \beta\vec{b}^*$), the modulation wave being transversal. Finally at low temperature ($T < T_c$) it becomes ferroelectric (F). The modulation can be described in terms of a rotation angle ϕ of the polar thiourea molecules. This is the basis of a one-dimensional model investigated by Parlinski and Michel [6] having the following expression for the free energy :

$$F = \frac{1}{N} \sum_n^N \{V(\phi_n) + \sum_p^P W_p(\phi_n-\phi_{n-p}) + W_p(\phi_n-\phi_{n+p})\} \tag{3.1}$$

at molecular positions na (n any integer) with local potential $V(\phi_n)$ given by :

$$V(\phi_n) = \underline{a}\phi_n^2 + \underline{h}\phi_n^3 + \underline{b}\phi_n^4 \tag{3.2}$$

(where $\underline{a}$ describes the harmonic term and $\underline{h}$ and $\underline{b}$ the anharmonic ones) and an intermolecular potential (essentially due to the dipole-dipole interactions)

$$W_p(\phi_n-\phi_{n\pm p}) = \alpha_p(\phi_n-\phi_{n\pm p})^2 + \beta_p(\phi_n-\phi_{n\pm p})^4 \quad . \tag{3.3}$$

From this model, by numerical calculation and by adjusting a number of parameters, the authors have been able to describe phonon dispersion curves in the paraelectric phase leading through softening of phonon branches to the modulated phase, to derive a phase diagram (as a function of $\underline{h}$ and α_1) involving commensurate as well as incommensurate regions and to get also information on the form of the modulation wave. The main ideas can be illustrated on the basis of the simple harmonic modulation :

$$\phi_n = (-1)^n \rho \cos(nqa). \tag{3.4}$$

One then gets the free energy (3.1) in the form :

$$F = \frac{A}{2}\rho^2 + \frac{B}{4}\rho^4 \tag{3.5}$$

from which by extremalization with respect to the amplitude of the modulation the different crystallographic phases follow :

$$\frac{\partial F}{\partial \rho} = \rho\ (A + \rho^2 B) = 0, \tag{3.6}$$

i.e. the P-phase for $\rho = 0$ and the I and the F phases for $\rho^2 = -A/B$. The phonons in the P phase are then obtained from:

$$\frac{\partial^2 F}{\partial \rho^2}\Big|_{\rho=0} = -\ \omega^2(q) \tag{3.7}$$

and the modulation wave vector q_m from :

$$\frac{\partial F}{\partial q} = 0 \quad \text{(in the I and F phases).} \tag{3.8}$$

4. An Elastic Chain Model

The one-dimensional model proposed by Janssen and Tjon [7] for studying dynamical (and thermodynamical) properties of incommensurate crystal phases driven by elastic forces, involves competing harmonic interaction terms between first, second and third nearest-neighbours and a (stabilizing)

anharmonic fourth-order term. Starting from atomic positions at

$$r_n = na + u_n \qquad n \text{ any integer} \tag{4.1}$$

the Hamiltonian is given by :

$$H = \sum_n \frac{p_n^2}{2m} + V \tag{4.2}$$

with

$$V = \frac{1}{2} \sum_n \{\alpha(u_n-u_{n-1})^2+\beta(u_n-u_{n-2})^2+\delta(u_n-u_{n-3})^2+\frac{1}{2}(u_n-u_{n-1})^4\}. \tag{4.2a}$$

The equilibrium positions u_n^o then follow from the condition :

$$\frac{\partial V}{\partial u_n} = 0 , \qquad \text{any } n \tag{4.4}$$

and one gets the vibrational modes by considering the dynamical equations for $u_n = u_n^o + \varepsilon_n$:

$$\sum_m \frac{\partial^2 V}{\partial \varepsilon_n \partial \varepsilon_m} \varepsilon_m = m\, \omega^2 \varepsilon_n. \tag{4.5}$$

This eventually leads to soft modes and to a modulated phase for the appropriate values of the parameters. Describing the I-phase in terms of a one-dimensional modulation function $u_n = u\,(nqa)$ one gets the modulation wave vector q from :

$$\frac{\partial V}{\partial q} = 0 \qquad \text{and} \qquad \frac{\partial^2 V}{\partial q^2} > 0 \tag{4.6}$$

and by comparing the corresponding values of the energy. In this way, by numerical calculation a phase diagram (in the α,δ parameter plane) has been obtained. Analytical expressions have also been derived in the continuum limit, for which the potential energy takes the form :

$$V = \int \frac{dx}{a} \left\{ \frac{1}{2}\sigma\xi^2 + \frac{1}{4}\xi^4 + \frac{1}{2}\rho\xi'^2 \right\}. \tag{4.7}$$

The extremality condition for V leads by the Euler-Lagrange formula to the equation :

$$\rho\, \xi'' = \sigma\, \xi + \xi^3. \tag{4.8}$$

The solutions are Jacobi elliptic functions whose type depends on the values of the parameters. The potential energy is then expressible in terms of complete elliptic integrals. From all that follows also the wave-length and the form of the modulation. A thermodynamical treatment (in the mean-field approximation) allows to derive further properties [8], but the essential features appear to be already correctly described by the simple Hamiltonian approach discussed above.

5. Superspace adapted formulation of the models

The reformulation of the microscopic models presented above will be done now for the Janssen-Tjon model. The same can be done for the Parlinski-Michel model as well.

The first step is a restriction of the considerations to modulated displacements u_n which are periodic (but not necessarily incommensurate with the underlaying basic structure) with wave vector q, and involves thus a phase variable τ according to :

$$u_n(\tau) = u\,(nqa + \tau) = u_n(\tau + 2\pi) \tag{5.1}$$

for any τ real. Introducing that dependency in eq. (4.2) one gets a family of τ-dependent Hamiltonians :

$$H\,(\tau) = \sum_n \left\{ \frac{p_n^2}{2m} + \frac{1}{2}\alpha[u_n(\tau) - u_{n-1}(\tau)]^2 + \ldots \right\} \tag{5.2}$$

showing two-dimensional lattice translational invariance in the superspace, i.e. in the space which extends the space of positions of the chain mass points with an extra dimension associated with the phase of the modulation. The generators of these lattice translations are given by the following transformations :

$$(a,\Delta a) : \quad n \to n+1 \quad \text{and} \quad \tau \to \tau - qa \tag{5.3a}$$

$$(0,b) : \quad n \to n \quad \text{and} \quad \tau \to \tau + 2\pi \tag{5.3b}$$

Incommensurability occurs for :

$$q = \nu \frac{2\pi}{a} \quad (\ \nu \text{ irrational}). \tag{5.4}$$

The potential energy (4.3) can be expressed by the integral :

$$V = \frac{N}{2\pi} \int_0^{2\pi} d\tau \left\{ \frac{1}{2}\alpha x(\tau)^2 + \frac{1}{2}\beta[x(\tau) - x(\tau-\tau_1)]^2 + \right. \tag{5.5}$$

$$\left. + \frac{1}{2}\delta[x(\tau) - x(\tau-2\tau_1)]^2 + \frac{1}{4}x(\tau)^4 \right\}$$

for $x_n = x(nqa)$ and $\tau_1 = qa$. In order to investigate (5.5) let us first consider $x(\tau-\tau_1)$ and $x(\tau-2\tau_1)$ in Taylor expansion at $x(\tau)$ up to the first order. One gets :

$$V = \frac{N}{2\pi} \int_0^{2\pi} d\tau \left\{ \frac{1}{2}\alpha x^2 + \frac{1}{4}x^4 + \frac{1}{2}(\beta + 2\delta)\tau_1^2 x'^2 \right\}. \tag{5.6}$$

Extremalization using the Euler-Lagrange equations leads to the following condition for the equilibrium positions :

$$\rho\, x'' = \sigma\, x + x^3 \tag{5.7}$$

with exactly the same parameter values as found in (4.9) for the continuum limit.

Taking now the full Taylor expansion into account, extremalization requires instead of the usual Euler-Lagrange equation the condition :

$$\frac{\partial L}{\partial x} + \sum_{m=1}^{\infty} (-1)^m \frac{d^m}{d\tau^m} \frac{\partial L}{\partial x^{(m)}} = 0 \tag{5.8}$$

with $x^{(m)} = \partial^m x/\partial\tau^m$. An alternative possibility is to take into account eq. (4.4) first and only then to go over to the phase-dependent description. One then gets an expression for the potential which depends on $\tau_1 = qa$ in

the form :

$$V_o = V|_{x_n^o} = \int_0^{2\pi} d\tau\, f(\tau,\tau_1). \tag{5.9}$$

A condition for q follows from the extremalization :

$$\frac{\partial V_o}{\partial \tau_1} = 0 \tag{5.10}$$

which leads to the equation :

$$y'(\,2\tau_1\,) = \frac{\beta}{2\delta}\, y'(\,\tau_1\,) \tag{5.11}$$

for

$$y\,(\tau_1) = \int_0^{2\pi} d\tau\; x(\tau)\; x(\tau-\tau_1). \tag{5.12}$$

For getting a better feeling of these equations let us consider the sinusoidal modulation case :

$$x_n = \rho \sin\,(nqa), \quad x(\tau) = \rho \sin\,(\tau)\,, \tag{5.13}$$

then eq. (5.9) becomes :

$$V_o = \int_0^{2\pi} d\tau\, f(\tau,\tau_1) = A + \rho^2 B + C\rho^2 \cos\tau_1 + D\rho^2 \cos 2\tau_1\,, \tag{5.14}$$

and condition (5.10) leads to :

$$(\beta + 4\delta\, \cos\tau_1)\, \sin\tau_1 = 0\,, \tag{5.15}$$

i.e. to the non-modulated case (for $\sin\,\tau_1 = 0$) and to the modulated one (for $\cos(qa) = -\beta/4\delta$), a result which has been discussed in the paper of Janssen and Tjon as well.

Note that in the present case we have $y(\tau_1) = \frac{1}{2}\cos\tau_1$ and equation (5.11) leads also to (5.15) .

6. Landau Theory for Continuous Phase Transitions

What follows simply recalls the basic ideas of Landau's theory and fixes the notation. One starts from a high temperature ($T > T_c$) crystal density $\rho_o(\vec{r})$ having space group G_o as symmetry :

$$G_o\,\rho_o = \rho_o. \tag{6.1}$$

Then the low-temperature ($T < T_c$) phase is described by a density ρ with symmetry group G and one supposes that G is a subgroup of G_o :

$$G\,\rho = \rho \quad \text{and} \quad G \subset G_o. \tag{6.2}$$

The difference density ψ is expressed in terms of irreducible representations D^α of G_o with basis functions $\phi_j^\alpha(\vec{r})$:

$$\rho = \rho_o + \psi \tag{6.3}$$

and

$$\psi(\vec{r}) = \sum_{\alpha j} c_j^\alpha\,\phi_j^\alpha(\vec{r}). \tag{6.4}$$

As a first simplification, Landau restricts the considerations to a single irreducible representation. Writing the free-energy density F as a function of ψ and $\vec{\nabla}\psi$ one has (due to continuity) invariance of F with respect to the group G_o. So one expands F in μth order (homogeneous) G_o-invariant terms :

$$F(\psi,\vec{\nabla}\psi) = F_o + \sum_{\mu s} A_{\alpha s}^{(\mu)}\,\phi_{j1}^\alpha\cdots\phi_{j\mu}^\alpha \tag{6.5}$$

where F_o is the high-temperature free-energy term and s labels the various invariants. Minimalization of F requires vanishing of second-order terms at $T = T_o$:

$$A_{\alpha}^{(2)}(T_c) = 0 \quad . \tag{6.6}$$

Stability of T_o requires absence of third-order invariant terms, i.e. :

$$(D^{\alpha}_{(3)} \mid D^1) = 0, \tag{6.7}$$

where $D^{\alpha}_{(3)}$ is the third-order tensor product of D^{α}, and D^1 is the identity representation. Homogeneity, i.e. the condition that the low temperature phase is a (commensurate) crystal leads to the Lifshitz condition:

$$(D^{\alpha}_{[2]} \otimes D^{v} \mid D^1) = 0, \tag{6.8}$$

where $D^{\alpha}_{[2]}$ is the antisymmetric tensor product of D^{α} with itself and D^{v} is the vector representation. As is well known, the presence of Lifshitz invariants is connected with incommensurate phase transitions [9] [10], and in what follows we briefly discuss its role in the superspace-adapted formulation.

7. Superspace Extension of Landau Theory

One embeds the crystal density (the high- and the low-temperature ones) in the superspace as soon as one of the two phases involved describes an incommensurate crystal. In the case that the internal dimension is different, one extends (possibly in a trivial way) the structure in order to have both crystals described in a same superspace. Then the conditions (6.1) to (6.4) are again verified for the appropriate superspace expressions. In particular for $T < T_c$ and in the notation of section 2 one has :

$$\rho_s(\vec{r},\vec{t}) = \rho_{os}(\vec{r},\vec{t}) + \psi_s(\vec{r},\vec{t}) \tag{7.1}$$

with $G_s\, \rho_s = \rho_s$, $G_{os}\rho_{os} = \rho_{os}$ and $G_s \subset G_{os}$. Then the free-energy density is considered as a function of the internal variable $\vec{t}$

$$F_s(\vec{r},\vec{t}) = F_s(\psi_s, \vec{\nabla}\psi_s) \tag{7.2}$$

where $\vec{\nabla} = \frac{\partial}{\partial \vec{r}}$. Then the group-theoretical steps indicated in eqs. (6.4) to (6.8) can be performed again.

As it will be shown in more detail in another paper, it follows that the transitions between crystal phases having the same internal dimension (commensurate → commensurate, 1-dimensional modulated → 1-dimensional modulated, and so on) requires :

$$(D^{\alpha}_{[2]} \otimes D^{v} \mid D^{1}) = 0, \tag{7.3}$$

i.e. absence of Lifshitz invariant terms. Note that in equation (7.3), D^{v} is the 3-dimensional vector representation involving the positional (and not the internal) space.

The presence of Lifshitz invariants leads to terms in the superspace free-energy density of the form :

$$F_s(\vec{r},\vec{t}) = A^{(2)}_{ij}\phi^{\alpha}_{i}(\vec{r},\vec{t})\ \phi^{\alpha}_{j}(\vec{r},\vec{t}) + \ldots \tag{7.4}$$

$$\ldots + B^{v}_{[2]ij}\ \phi^{\alpha}_{i}(\vec{r},\vec{t})\partial_{v}\phi^{\alpha}_{j}(\vec{r},\vec{t}) + \ldots$$

from which by extremalization using the Euler-Lagrange equation one gets superspace-periodic solutions, and in general thus incommensurate modulated crystal structures.

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