PHASE DIAGRAMS OF CRYSTALS WITH ONE-DIMENSIONAL MODULATED PHASES INDUCED BY 2d ACTIVE REPRESENTATIONS

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A one-dimensional model of particles with a displacive degree of freedom for crystals possessing incommensurate phases which arise as a result of the condensation of either real two-dimensional or complex one-dimensional irreducible representations, has been proposed. For these representations all invariants of the free energy expansion can be divided to four general forms. For the active irreducible representations for which the invariants belong to the first form a complete list of invariants is derived. In this case the incommensurate modulation propagates along the symmetry axis and for such crystals a proposed one-dimensional model may be a good approach to describe the main features of the devil's staircase curve. The particles of the model interact with harmonic and anharmonic terms. The last ones may contain an additional third order term provided a soft phonon branch has a symmetry τ^1. The calculated phase diagrams show sequences of the incommensurate and commensurate one-dimensional phases. In the presence of the third order anharmonic term the incommensurate phase proves to be stable closer to the phase boundary to the normal phase.

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1. Introduction

In recent years considerable attention, both theoretical and experimental, has been drawn to the properties of incommensurate crystal phases. The occurrence of transitions from a normal crystalline phase to a structure with an incommensurate modulation has been observed in many different materials [1, 2]. The phase transitions from the high-temperature normal phase to the low-temperature one are often induced by the so-called soft modes. The model mechanism of them is that one of the phonon branch "softens" with decreasing temperature. The wave

vector of its minimum frequency describes the modulated degrees of freedom in the low-temperature phase.

The great majority of structural phase transitions belong to the commensurate–commensurate type. For these phase transitions the soft phonon frequency has a minimum value characterized by a wave vector lying at a special point of the Brillouin zone of the high-temperature phase. Then, the low-symmetry phase, which arises as a result of such phase transitions, is commensurate and is described by one of 230 three-dimensional crystallographic space groups. If, however the minimum value of frequency is characterized by the wave vector which is not localized at a high-symmetry point of the Brillouin zone of the normal phase but is to be found at an arbitrary point, the low-temperature phase is an incommensurate one. The symmetry of an incommensurate phase can be specified by a crystallographic space group in a higher-dimensional space [3].

The Landau theory of phase transitions [4] supplies the method to derive the symmetry changes which can take place at the continuous phase transition. In order to predict all such phase transitions it is sufficient to consider irreducible representations of space groups complying certain symmetry criteria. The essential aspects of various phenomena related to the normal–incommensurate and the incommensurate–commensurate phase transitions can be also explained within the framework of the phenomenological Landau theory of phase transitions [5–10]. The Landau theory is symmetry-based and can account for the space group symmetries of the low-temperature phases. According to this theory it will be assumed that the thermodynamic state of the crystal above, below and at the critical point may be described by the free energy which depends on a set of thermodynamical variables and components of the primary and secondary order parameter [11]. The free energy is invariant under symmetry operations of the high-symmetry group G_o. This requirement concerning symmetry is fulfilled when writing the free energy in terms of the invariant polynomials of the order parameter components. The low-symmetry phases are described by the minimum of the free energy with respect to the order parameter components. The order parameter has a symmetry of a given irreducible or physically irreducible representation of the space group G_o. The symmetry reduction from the space group G_o to the incommensurate one is driven by the active representation which usually is equal to one irreducible or physically irreducible representation. This representation is characterized by the wave vector k_c which does not belong to a high-symmetry point of the Brillouin zone and is incommensurate with reciprocal lattice vectors. For such incommensurate phase the free energy has a minimum at the wave vector k_c. The free energy minima lie at several symmetry-equivalent points of the reciprocal space and are related by symmetry operations of the high-temperature space group. The possible modulated structures arise as a result of condensation of one, two or three pairs of wave vectors, denoted as $1q$, $2q$ or $3q$, respectively. Condensation of one pair $(k_c, -k_c)$ leads to one-dimensional modulation which propagates as a single static wave along one direction determined by the wave vector k_c. Condensation of two or three pairs of non collinear wave vectors leads to the modulated structure given by a superposition of several waves, $2q$ or $3q$ phase, respectively. The representations constructed from each star $(k_c, -k_c)$ are active two-dimensional representations.

In our previous study of one-dimensional incommensurate phases [12] for such active representations and for all space groups we have given a complete list of invariants from which one constructs the free energy expansion. It can contain one of four forms of invariants determined by the wave vector conservation law. In the case when the free energy expansion contains only the first form of invariants, it is possible to construct the one-dimensional displacive model with one degree of freedom per unit cell. In others cases one has to increase the number of freedom per unit cell or the lattice dimension.

Experimentally, the majority of phase transitions leading to incommensurate structures are described by one-dimensional modulation ($1q$). This is commonly found in systems having orthorhombic symmetry in which as a rule the modulation wave vector is parallel to a symmetry axis [1].

The any other type of theoretical treatments of incommensurate phases is related to the semi-microscopic theories which take into account the discrete structure of the crystal. In particular we turn the attention to the discrete ϕ^4 model with a competing interaction [13], the Frenkel–Kontorova model [14] and the ANNNI model [15]. Microscopic theories which take into account more realistic interactions, have clarified the origin of an incommensurability in thiourea [16], $NaNO_2$ [17, 18].

In this article we have tabulated a complete list of all space groups, two-dimensional active representations and invariants for which the free energy expansions contain only the first form of invariants. For these cases it is possible to reduce the number of degrees of freedom to one per unit cell. Further, we propose a displacive one-dimensional model simulating such a phase transition in which the symmetry reduction from a crystallographic high-symmetry group to a low-symmetry phase of the crystal with $1q$ modulation is driven by an active two-dimensional irreducible representations having one of the four general forms of invariants. The wave vector which characterizes them does not belong to the high-symmetry points of the Brillouin zone. To make the computer simulation enable we have assumed that during the phase transition to the commensurate or incommensurate phases the number of degrees of freedom can be reduced to one relevant, only. This degree of freedom, which gives the largest contribution to the symmetry changes in a phase transition, is described by the given active representation. Therefore, we can build the one-dimensional model for the computer simulation from this degree of freedom with the simple form of the potential energy. Performing computer calculations we can search for the ground-state energy, configurations and the devil's staircase of the ground-state behaviour at zero temperature. Finally, we built the phase diagram of our model containing modulated phases and low-index commensurate phases.

The paper is organized as follows: In Sec. 2 we give two tables containing invariants of the first general form of all real two-dimensional irreducible and physical representations characterized by the incommensurate wave vectors of the space groups for triclinic, monoclinic, orthorhombic, tetragonal, trigonal and hexagonal systems which condensation can produce phases with one-dimensional modulation. In Sec. 3 we propose a displacive one-dimensional model and write the corresponding potential energy. Analytical solutions of the model in terms of a simple

cosine wave is derived in Sec. 4. In Sec. 5 we describe the method of finding the ground-state energy and the ground-state configurations of particles at zero temperature for a one-dimensional modulation. Section 6 reports the model phase diagram. Final conclusions close the paper.

2. Free energy expansion

In the phenomenological Landau theory of phase transitions the free energy of the crystal is expanded into a power series of the order parameter components and is invariant with respect to all symmetry elements of G_o. To construct the free energy expansion and to discuss the incommensurate phases one should find invariants of the relevant order parameter components. The order parameter has a symmetry of a given active irreducible representation $T^{(k,j)}$ of G_o. The wave vector k does not belong to the high-symmetry point of the reciprocal space and j indices the ray representation [19].

When the incommensurate phase is described by the active two-dimensional irreducible representation the modulation is one-dimensional and propagates along one direction. Such an active irreducible representation is either real two-dimensional one provided $T^{(k,j)}$ is real, or it becomes a direct sum $T^{(k,j)} \oplus T^{\star(k,j)}$ of $T^{(k,j)}$ and its conjugate representation $T^{\star(k,j)}$, when $T^{(k,j)}$ is a complex one-dimensional representation. We denote the basic functions of the active real representation by $\rho_j(k)$ and $\rho_j(-k)$. For $T^{(k,j)}$ complex the basic functions of $T^{(k,j)} \oplus T^{\star(k,j)}$ representation are $\rho_j(k)$ and $\rho_j^\star(k)$. In this case $\rho_j^\star(k) = \rho_{j'}(-k)$ and the indices of irreducible representation j and j' can be different.

From these basic functions one can construct the invariants using the projection operator technique [20]. The analysis of invariants for *all* crystallographic space groups and *all* real two-dimensional, complex one-dimensional irreducible representations showed that there exists only *four* forms of invariants [12]. In this paper we shall consider the first form of the invariants only. The n-th order invariant of the first form reads

$$I_1^n(k_1, k_2, \ldots, k_n) =$$

$$(1/2) \left[\rho_j(\pm k_1) \rho_j(\pm k_2) \cdots \rho_j(\pm k_n) + \rho_j(\mp k_1) \rho_j(\mp k_2) \cdots \rho_j(\mp k_n) \right]$$

$$\times \delta(\pm k_1 \pm k_2 \pm \cdots \pm k_n - K), \tag{1}$$

where $K = l_1 b_1 + l_2 b_2 + l_3 b_3$ is the reciprocal lattice vector with l_1, l_2, l_3 to be integers and b_1, b_2, b_3 representing the basic reciprocal lattice vectors.

Using the invariants of Eq. (1) one can express the general form of the free energy expansion in terms of basic functions of the active irreducible representation

$$F = (1/2) \sum_{n=2} \sum_{k_1, k_2, \ldots, k_n, K} F_n(k_1, k_2, \ldots, k_n) \rho_j(k_1) \rho_j(k_2) \ldots \rho_j(k_n)$$

$$\times \delta\left(\pm k_1 \pm k_2 \pm \cdots \pm k_n - K \right), \tag{2}$$

where in a displacive system $F_2(k, -k)$ is the square of the soft phonon frequency. All the expansion coefficients F_n depend on the wave vectors, temperature, pressure and have to be found from a microscopic model. In practice, the anharmonic

coefficients F_3, F_4, ... are usually kept constant. In a strictly incommensurate phase no Umklapp terms ($K \neq 0$) are present. The Umklapp invariants can lower the free energy and in some temperature range make the commensurate phase more stable than the incommensurate one [6]. For any phase the summation over K is limited to a few types of Umklapp invariants. The incommensurate phase is described by the minimum of F with respect to the basic functions and to the wave vector k. This minimization condition allows one to establish the behaviour of the first harmonic being the primary order parameter and all higher order harmonics playing a role of secondary order parameters [5, 6].

In principle, the free energy expansion, Eq. (2), may contain even and odd order terms (except the first order one). The symmetry of the active representation requires very often that odd order terms vanish. We were considered this problem in details. In Table I we show a complete list of these crystallographic space groups and real two-dimensional irreducible representations, for which the free energy expansion written in terms of the basic function of these irreducible representations has the general form given by Eq. (2). Similarly, the crystallographic space groups for complex one-dimensional irreducible representations extended to two-dimensional physical representations are listed in Table II. The tables contain the groups ordered according to the crystal systems and Bravais lattices.

It proves that the free energy, Eq. (2), always has even order terms. But only the free energy for the active irreducible representation $T^{(k_m,1)}$ contains the odd order terms as well. In Table I and II the notation of the irreducible representation $T^{(k_m,j)}$ is abbreviated to $km(j; n)$, where n = e or n = a if only *even* or *any* order invariants are allowed. For a given irreducible star k_m and ray representation j we have used a symbol of an allowed invariant [12] as

$$km(j; n) - 1(X, Y, Z \mid l_1, l_2, l_3). \tag{3}$$

The index 1 denotes the first form of invariants from the set of four classes. The X, Y, Z denote that the wave vector conservation law like in Eq. (1) contains the product of δ-functions for x, y and z components $\delta(k_{1x} + k_{2x} + \cdots + k_{nx} - K_x) \times \delta(k_{1y} + k_{2y} + \cdots + k_{ny} - K_y) \times \delta(k_{1z} + k_{2z} + \cdots + k_{nz} - K_z)$, respectively. If one or two of X, Y, Z indices are 0 then in the conservation law the one or two δ-functions, respectively should be omitted. Finally, the indices (l_1, l_2, l_3) indicate the allowed multiplicity of the basic reciprocal vectors in the conservation law and $l_1, l_2, l_3 = 0, \pm 1, \pm 2, \ldots$. For many cases the allowed types of invariants are the same for all the irreducible representations of the same irreducible star. To simplify the tables in this case, we have abbreviated the notation to

$$km(n) - 1(X, Y, Z \mid l_1, l_2, l_3) \tag{4}$$

disregarding the index j, and having in mind that all j irreducible representations of k_m produce this invariant. The fact that all ray representations of a given star k_m have the same even order invariants is indicated in the tables by $km(e)$. However, the complete analysis showed that often for the representation $j = 1$ even and odd order of invariants are permitted. This fact is explicitly stated in the tables by writing a symbol $km(1, a)$. The irreducible representations described by the different irreducible stars $k_1, k_2, \ldots$, but the same set of ray representations $j_1, j_2, \ldots$ are denoted by $k1, 2, \ldots (j_1, j_2, \ldots; e)$.

TABLE I

Crystallographic space groups and invariants for real two-dimensional irreducible representations which can produce one-dimensional incommensurate and commensurate modulations of $1q$ type.

Crystalline system	Bravais lattice	Space group	Irreducible representation	Invariants
Triclinic	Γ_{tr}	C_i	$k0^*(1,a)$	$1(X,Y,Z \mid l_1,l_2,l_3)$
Monoclinic	Γ_m	C_{2h}^1	$k1^*(1,a),$ $k1^*,2^*(e)$	$1(X,Y,0 \mid l_1,l_2,0),$
			$k3(1,a),$ $k3,4^*,5^*,6^*(e)$	$1(0,0,Z \mid 0,0,l_3)$
		C_{2h}^2	$k1^*(1,a),k1^*(e)$	$1(X,Y,0 \mid l_1,l_2,0)$
		C_{2h}^4	$k3(1,a),k3,5^*(e)$	$1(0,0,Z \mid 0,0,l_3)$
	Γ_m^b	C_{2h}^3	$k1^*(1,a),k^*1(e)$	$1(X,Y,Z \mid l_1,l_2,l_2)$
			$k2^*(1,a),k2^*,3^*(e)$	$1(0,Y,Z \mid 0,l_2,-l_2)$
		C_{2h}^6	$k2^*(1,a),k2^*(e)$	$1(0,Y,Z \mid 0,l_2,-l_2)$
Orthorhombic	Γ_o	D_2^1,D_{2h}^1	$k7(1,a)$ $k7,10^*,11^*,12^*(e)$	$1(X,0,0 \mid l,0,0)$
			$k8(1,a)$ $k8,13^*,14^*,15^*(e)$	$1(0,Y,0 \mid 0,l_2,0)$
			$k9(1,a)$ $k9,16^*,17^*,18^*(e)$	$1(0,0,Z \mid 0,0,l_3)$
		$D_2^2,D_{2h}^{3,5}$	$k7(1,a),k7,10^*(e)$	$1(X,0,0 \mid l_1,0,0)$
			$k8(1,a),k8,13^*(e)$	$1(0,Y,0 \mid 0,l_2,0)$
		$D_2^3,D_{2h}^{4,9,11,13}$	$k9(1,a),k9(e)$	$1(0,0,Z \mid 0,0,l_3)$
		D_{2h}^7	$k8(1,a),k8(e)$	$1(0,Y,0 \mid 0,l_2,0)$
		D_{2h}^8	$k7(1,a),k7(e)$	$1(X,0,0 \mid l_1,0,0)$
	Γ_o^b	$D_2^5,D_{2h}^{17,18,20,22}$	$k8(1,a),k8(e)$	$1(X,0,0 \mid l_1,-l_1,0)$
			$k10(1,a),k10(e)$	$1(0,Y,0 \mid l_1,l_1,0)$
		$D_2^6,D_{2h}^{19,21}$	$k6(1,a),k6,7^*(e)$	$1(0,0,Z \mid 0,0,l_3)$
			$k8(1,a),k8,9^*(e)$	$1(X,0,0 \mid l_1,-l_1,0)$
			$k10(1,a),k10,11^*(e)$	$1(0,Y,0 \mid l_1,l_1,0)$
	Γ_o^f	D_2^7,D_{2h}^{23}	$k4(1,a),k4,5^*(e)$	$1(X,0,0 \mid 0,l_2,l_2)$
			$k6(1,a),k6,7^*(e)$	$1(0,Y,0 \mid l_1,0,l_1)$
			$k8(1,a),k8,9^*(e)$	$1(0,0,Z \mid l_1,l_1,0)$
	Γ_o^v	$D_2^{8,9},D_{2h}^{25,26,27,28}$	$k7(1,a),k7(e)$	$1(X,0,0 \mid -l_1,l_1,l_1)$
			$k8(1,a),k8(e)$	$1(0,Y,0 \mid l_1,-l_1,l_1)$
			$k9(1,a),k9(e)$	$1(0,0,Z \mid l_1,l_1,-l_1)$
Tetragonal	Γ_q	S_4^1	$k13(1,a),$ $k13(e),14^*(1;e)$	
		C_{4h}^1	$k13(1,a),$ $k13(e),14^*(1,3;e)$	
		C_{4h}^3,D_4^2	$k13(1,a),k13(3;e)$	
		$D_{2d}^{1,5}$	$k13(1,a),$ $k13(e),14^*(1,2;e)$	$1(0,0,Z \mid 0,0,l_3)$
		$D_{2d}^{3,7}$	$k13(1,a),k13(2;e)$	
		D_4^1	$k13(1,a),$ $k13,14^*(1,3;e)$	
		$D_4^2,D_{4h}^{3,5,7}$	$k13(1,a),k13(e)$	
		D_{4h}^1	$k13(1,a),k13,14^*(e)$	

TABLE I (cont.)

Tetragonal	Γ_q^v(a)	S_4^2	$k10(1,\text{a})$	
		C_{4h}^5, D_4^9	$k10(1,\text{a}), k10(3;\text{e})$	$1(0,0,Z \mid l_1,l_1,-l_1)$
		D_{2d}^{11}	$k10(1,\text{a}), k10(2;\text{e})$	
		$D_{4h}^{17,18}$	$k10(1,\text{a}), k10(2,3,4;\text{e})$	
Trigonal	Γ_{rh}	S_6^2, D_3^7, D_{3d}^5	$k6(1,\text{a})$	$1(0,0,Z \mid l_1,l_1,l_1)$
		D_{3d}^5	$k6(1,\text{a}), k6(2;\text{e})$	
Hexagonal	Γ_h	$S_6^1, C_{3h}^1, D_3^{1,2}$	$k11(1,\text{a})$	
		$D_{3d}^{1,3}, D_{3h}^{1,3}$	$k11(1,\text{a}), k11(2;\text{e})$	$1(0,0,Z \mid 0,0,l_3)$
		C_{6h}^1, D_6^1	$k11(1,\text{a}), k11(4;\text{e})$	
		D_{6h}^1	$k11(1,\text{a}), k11(2,3,4;\text{e})$	

TABLE II

Crystallographic space groups and invariants for real two-dimensional physical representations which can produce one-dimensional incommensurate and commensurate modulations of $1q$ type. These representations have been generated from the complex one-dimensional irreducible representations.

Crystalline system	Bravais lattice	Space group	Irreducible representation	Invariants
Triclinic	Γ_{tr}	C_o^1	$k0^\star(1,\text{a})$	$1(X,Y,Z \mid l_1,l_2,l_3)$
Monoclinic	Γ_m	C_s^1	$k1^\star(1,\text{a}), k1^\star, 2^\star(\text{e})$	$1(X,Y,0 \mid l_1,l_2,0)$
		C_2^1	$k3(1,\text{a}), k3, 4^\star, 5^\star, 6^\star(\text{e})$	$1(0,0,Z \mid 0,0,l_3)$
	Γ_m^b	C_s^3	$k1^\star(1,\text{a})$	$1(X,Y,0 \mid l_1,l_2,l_2)$
		C_2^3	$k2^\star(1,\text{a}), k2^\star, 3^\star(\text{e})$	$1(0,0,Z \mid 0,l_2,-l_2)$
Orthorhombic	Γ_o	C_{2v}^1	$k9(1,\text{a}), k9, 16^\star, 17^\star, 18^\star(\text{e})$	
		C_{2v}^4	$k9(1,\text{a}), k9, 18^\star(\text{e})$	$1(0,0,Z \mid 0,0,l_3)$
		C_{2v}^8	$k9(1,\text{a})$	
	Γ_o^b	C_{2v}^{11}	$k6(1,\text{a}), k6, 7^\star(\text{e})$	$1(0,0,Z \mid 0,0,l_3)$
		$C_{2v}^{14,15}$	$k8(1,\text{a}), k8, 9^\star(\text{e})$	$1(X,0,0 \mid l_1,-l_1,0)$
		$C_{2v}^{16,17}$	$k8(1,\text{a})$	
	Γ_o^f	C_{2v}^{18}	$k8(1,\text{a}), k8, 9^\star(\text{e})$	$1(0,0,Z \mid l_1,l_1,0)$
	Γ_o^v	$C_{2v}^{20,21,22}$	$k9(1,\text{a})$	$1(0,0,Z \mid l_1,l_1,-l_1)$
Tetragonal	Γ_q	C_4^1	$k13(1,\text{a}), k13(\text{e}), 14^\star(1,3;\text{e})$	
		C_{4v}^1	$k13(1,\text{a}), k13(\text{e}), 14^\star(\text{e})$	$1(0,0,Z \mid 0,0,l_3)$
		C_{4v}^2	$k13(1,\text{a})$	
	Γ_q^v(a)	C_4^5	$k10(1,\text{a}), k10(3;\text{e})$	$1(0,0,Z \mid l_1,l_1,-l_1)$
		$C_{4v}^{9,10}$	$k10(1,\text{a})$	
Trigonal	Γ_{rh}	C_3^4	$k6(1,\text{a})$	$1(0,0,Z \mid l_1,l_1,l_1)$
		C_{3v}^5	$k6(1,\text{a}), k6(2;\text{e})$	
Hexagonal	Γ_h	$C_3^1, C_{3v}^{1,2}, C_{6v}^1$	$k11(1,\text{a})$	$1(0,0,Z \mid 0,0,l_3)$
		C_6^1	$k11(1,\text{a}), k11(4;\text{e})$	

Inspection of Table I and II shows that the one-dimensional modulation propagates usually along the high-symmetry lattice direction. The fact that the modulation wave vector k_m propagates not along a high-symmetry direction, although being parallel to the unique symmetry plane, is indicated in Tables I and II by the star ($\star$) put after the active representation symbol.

3. The model

Tables I and II indicate what symmetry of order parameter produces the incommensurate and commensurate modulations of $1q$ type. However, the magnitude of the wave vector of the modulation is not specified by the symmetry requirements. On the other hand, one knows that the temperature behaviour of the modulation wave vector shows plateaux which correspond to the regions of stability of commensurate phases. Such a behaviour carries on the name of the devil's staircase curve. In this section we are going to sketch the devil's staircase curves for two general cases for the free energy expansion containing the even order terms only and the free energy with even and odd order terms. We apply for this such a simple microscopic displacive model with one degree of freedom per unit cell, whose free energy corresponds to the form of Eq. (2). We are aware that this approach is a simplification to the real crystals, since it accepts a considerable reduction of the number of degrees of freedom. Nevertheless, we expect that in each case the main features of the devil's staircase curves will be correctly reflected. A reduction of a realistic model to a model with one degree of freedom per unit cell can be performed for the crystal with modulation propagating along the high-symmetry directions only. In such a case the interaction range of the harmonic potential can be limited to a few neighbours. Indeed, in this case the crystal planes can be projected on the selected high-symmetry direction and the projected sites still form a one-dimensional chain with the same lattice constant. That situation occurs for these irreducible representations listed in Tables I and II which are *not* labelled by the star. In contrary, for cases labelled by the star any projection of the crystal sites on the non-high-symmetry direction, moreover, a direction with incommensurate inclination with respect to the basic lattice vectors, will result in dense coverage of the sites on the projected line. That excludes the possibility to approximate the incommensurate phase of a crystal by a one-dimensional chain and forces to treat these cases by taking into account a considerable number of degrees of freedom of the unit cell. Therefore, in what follows we consider further only a model appropriate for the irreducible representations not labelled by a star. We assume that in each of these cases the crystal lattice can be projected to a one-dimensional chain with one degree of freedom per unit cell and with an effective interacting potential.

Assume that a particle of the model has a displacive degree of freedom $\tilde{u}(n)$, where n denotes the index of a crystal site. Here, the displacement plays a role of a local order parameter. We assume further that each particle is placed in the local anharmonic potential and interacts with the first and second nearest neighbours via harmonic forces only. For simplicity the expansion up to the forth order term is considered for the local anharmonic potential. Then, the potential energy is

represented by

$$\widetilde{V} = \frac{1}{2} \sum_n \{\widetilde{A}(n)\widetilde{u}^2(n) + \widetilde{H}\widetilde{u}^3(n) + \widetilde{G}\widetilde{u}^4(n)$$

$$+ \sum_m \widetilde{V}_m^{(2)}\widetilde{u}(n)\left[\widetilde{u}(n+m) + \widetilde{u}(n-m)\right]\}. \tag{5}$$

It is a function of parameters $\widetilde{A}, \widetilde{H}, \widetilde{G}$ and $\widetilde{V}_m^{(2)}$. The Fourier transform for the particle displacements reads

$$\widetilde{u}(n) = \sum_k Q_k \exp(-2\pi i k R(n)), \tag{6}$$

where $R(n)$ denotes the position vector of particle n. Rewriting Eq. (5) for the potential energy in Fourier space, one finds

$$\widetilde{V} = \frac{1}{2} \left[\sum_{k_1,k_2,K} \omega^2(k_1) Q_{k_1} Q_{k_2} \delta(k_1 + k_2 - K) \right.$$

$$+ \widetilde{H} \sum_{k_1,k_2,k_3,K} Q_{k_1} Q_{k_2} Q_{k_3} \delta(k_1 + k_2 + k_3 - K)$$

$$\left. + \widetilde{G} \sum_{k_1,k_2,k_3,k_4,K} Q_{k_1} Q_{k_2} Q_{k_3} Q_{k_4} \delta(k_1 + k_2 + k_3 + k_4 - K) \right]. \tag{7}$$

Reducing the potential energy expansion to the soft mode one arrives formally to the expansion analogous to the free energy expansion, Eq. (2). However, the third order anharmonic terms $\widetilde{H}$ of Eq. (7) do not vanish only if the requirements set in Tables I and II are fulfilled. The dispersive curve is

$$\omega^2(k) = \widetilde{A} + \sum_m 2\widetilde{V}_m^{(2)} \cos(2\pi k R(m)), \tag{8}$$

where we have used the relation $\widetilde{V}_m^{(2)} = \widetilde{V}_{-m}^{(2)}$. It should have a minimum around the incommensurate modulation wave vector. To achieve that, the interaction at least to the second nearest neighbours should be taken into account. Renormalizing further the displacement $\widetilde{u}(n)$, the potential parameters $\widetilde{A}, \widetilde{V}_m^{(2)}, \widetilde{H}, \widetilde{G}$ and potential energy $\widetilde{V}$ [21] we arrive to the following simple potential energy form

$$V = \frac{1}{2} \sum_n \left[A u_n^2 + B u_n (u_{n+n_0} + u_{n-n_0}) \right.$$

$$\left. + u_n (u_{n+2n_0} + u_{n-2n_0}) + H u^3 + u^4 \right] \tag{9}$$

and dispersion curve

$$\omega^2(k) = A + 2B \cos(2\pi k) + 2 \cos(4\pi k), \tag{10}$$

where k is the wave vector number along the chain. The positions of the first and second nearest neighbour particles are denoted by the index $n \pm n_0$ and $n \pm 2n_0$ of crystal sites, respectively. The phase space of the model specified by Eqs. (9) and (10) is spaned by three parameters A, B and H. In this space the normal, commensurate and incommensurate phases will occur.

4. Analytical results

In this section we present some simple analytical solutions. The dispersion curve, Eq. (10), represents a single phonon branch with non-zero frequency at the Brillouin zone centre. When $\omega^2(k_m)$, Eq. (10), is negative at a minimum at k_m, the incommensurate phase with a wave vector k_m appears. However, we assume, that the form of the incommensurate modulation is sinusoidal. Then, the only non-zero amplitude η_{k_m} is that of the normal modes Q_{k_m} and Q_{-k_m} which belong to the opposite wave vectors $(k_m, -k_m)$. Leaving only the leading terms in the expansion, Eq. (9), the potential energy of the $1q$ incommensurate phase in the approximation of a single harmonic becomes

$$V_{k_m} = \omega^2(k_m)\eta_{k_m}^2 + 3\eta_{k_m}^4. \tag{11}$$

The amplitude of the ground-state energy specified by the extremum condition leads to

$$\eta_{k_m}^2 = -\frac{1}{6}\omega^2(k_m) \tag{12}$$

and

$$V_{k_m}^{(min)} = -\frac{1}{12}\omega^4(k_m). \tag{13}$$

The normal phase is defined by $|Q_{k_m}| = 0$ and hence, its potential energy, Eq. (9), is $V_n^{(min)} = 0$. The phase boundary between the normal and $1q$ incommensurate phases is defined by the relation $V_n^{(min)} = V_{k_m}^{(min)} = 0$. Using Eq. (13) one obtains that the stability of the normal phase is lost when $\omega^2(k_m) = 0$ and the minimum of the dispersion curve is located at k_m. So, the relation between the incommensurate wave vector of the modulation and the B parameter reads

$$B = -4\cos(2\pi k_m). \tag{14}$$

Hence, B lies within the range $-4 \leq B \leq 4$. From Eqs. (10) and (14) one finds that the value of $\omega^2(k)$ at the minimum equals to

$$\omega^2(k_m) = A - \frac{1}{4}B^2 - 2. \tag{15}$$

The condition $\omega^2(k_m) = 0$ gives the equation $A = (1/4)B^2 + 2$ for the phase boundary between the normal and $1q$ incommensurate phases.

5. Method of numerical solutions

The ground-state energy and the ground-state configuration of particles for $1q$ modulation were found numerically using the gradient method [22]. The incommensurate or commensurate phases are determined in the parameter space of A, B and H by minimizing the potential energy, Eq. (9). Our simulated chain consists of M unit cells and particles. The periodic boundary conditions were used. So, along the modulation direction it was possible to adjust the modulation waves which correspond to the commensurate phases with $k = (N/M)$, where N is integer and $N \leq M$. In the numerical calculations we started from initial configurations of particle displacements in the form of a simple cosine wave, characterized by a

commensurate wave vector $k = (N/M)$. Next, calculating the force acting on each particle the particle position was readjusted. The procedure was repeated till the potential energy had the minimum for a given wave vector k. This minimization procedure was performed for a set of $\{(N/M) = m/(m + 2n)\}$ wave vectors with $n = 0, 1, 2, \ldots, 14$ and $m = 0, 1, 2, \ldots, 7$. Although it yields only commensurate phases we consider $k_c = 0/1, 1/2, 1/3, 1/4, 1/5$ and $2/5$, as commensurate if it is stable in a sufficiently wide interval, and other higher-order commensurate phases as incommensurate.

6. Phase diagram

Here, the numerical results of the phase diagram of the model potential energy, Eq. (9), for various values of the parameters A, B, H and zero temperature are presented. Figure 1 and Fig. 2 show two sections for $H = 0$ and $H = -1.0$, respectively. In the $H = 0$ case the third order invariant of the order parameter vanishes by symmetry requirements. The phase diagram contains regions of the commensurate lock-in $0/1, 1/2, 1/3, 1/4, 1/5, 2/5$ and the incommensurate I phases. The modulated phases appear only in a small part of (A, B, H) space. The whole (A, B, H) space is divided into three main regions confined by two planes: $B = -4$, $B = 4$ and the surface $A = (1/4)B^2 + 2$, Eq. (15). The normal phase N exists only in a part of the parameter space confined by plains: $B = -4$ $B = 4$ and $A > (1/4)B^2 + 2$. The modulated phases exist within: $B = -4$, $B = 4$ and $A < (1/4)B^2 + 2$. Outside these two regions, $B < -4$ and $B > 4$, the normal or simple commensurate phases appear, only.
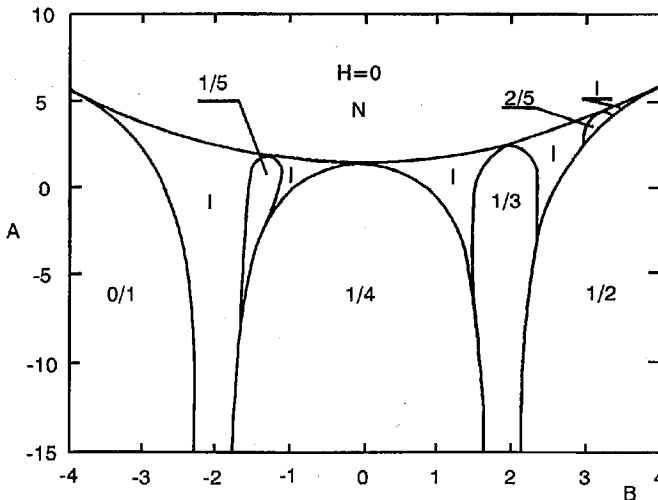

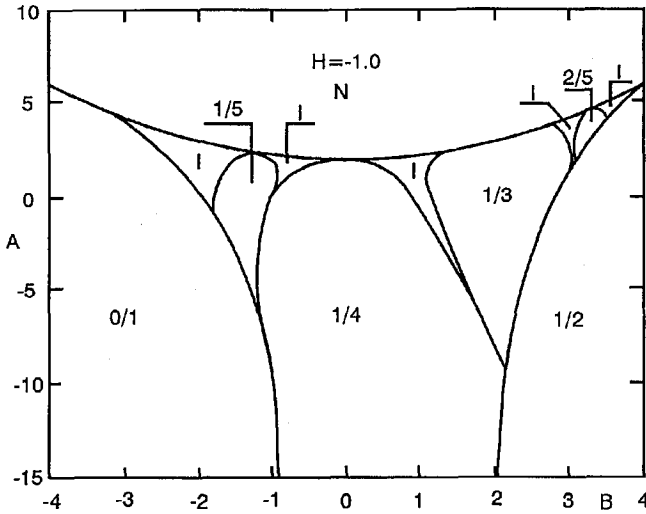Fig. 1. Phase diagram of the model for $H = 0$. N and I denote normal and incommensurate phases, respectively.

Fig. 2. Phase diagram of the model for $H = -1.0$. N and I denote normal and incommensurate phases, respectively.

The commensurate phases cover a large area of the phase diagram. Close to the phase boundary to the normal phase one can see regions of incommensurate phases existing between commensurate ones. At $H = 0$ one finds incommensurate and commensurate phases with wave vectors $0/1, 1/5, 1/4, 1/3, 1/2$. At $H < 0$ the phase boundaries change the slope and consequently the regions of stability of incommensurate regions increase in expense of incommensurate phases. Figures 1 and 2 show that commensurate phases are more stable than the others. This is because, for the commensurate wave vector k_c the free energy expansion, Eq. (7), contains also the Umklapp invariants ($K \neq 0$) which lower the free energy additionally. The commensurate 1/2 and 1/4 phases are stabilised by the second-, and fourth-order invariants. At $H = 0$, the lock-in phases, $1/3, 1/5, 2/5$, appear as a result of Umklapp invariants which couple higher-order modulation harmonics. The couplings are given by allowed invariants and they need that the relevant higher order harmonics already exist. The strength of these phases depend on the amplitudes of apparent higher-order harmonics and become non-zero only if they do not vanish. At $H = -1.0$ the free energy, Eq. (7), has the third-order invariant additionally. This invariant couples three modes with the wave vectors $k_c = 1/3$, stabilizing the free energy for the commensurate phase 1/3.

7. Final remarks

We have shown that the incommensurate modulation propagates in one direction of a crystal if the wave vector of the order parameter belongs to a real two-dimensional or to a complex one-dimensional irreducible star. Our earlier calculation has shown that in this case there are only four general forms of invariants.

In this paper we consider only the first form of the invariants. All symmetry reduction cases for crystallographic space groups are collected in Tables I and II. The tables show that the free energy expansion is represented by two types of power series: with all or only even order invariants. Moreover, the odd order invariants are present only if the phase transition to the incommensurate phase is induced by the soft mode of τ^1 symmetry.

To estimate the stability regions of commensurate and incommensurate phases a simple one-dimensional displacive model has been proposed. Its phase diagram, which has been found numerically, displays sequences of modulated and lock-in phases. The model contains a number of simplifications made to reduce the complexity of a real system. Thus, the number of particles and degrees of freedom of a real system is reduced to one particle per unit cell and to one essential degree of freedom. This degree of freedom enters the two-dimensional active irreducible representation which is responsible for the formation of the incommensurate modulation. Since, a realistic model of a crystal requires interactions between larger numbers of particles per unit cell, the larger number of neighbours should be taken into account. Consequently, the phase diagram boundaries might be shifted and the stability width of the commensurate phases might change. This, however, will not change the general scope of commensurate phases appearing in the phase diagram. We have considered the ground-state energy and particles configurations at zero temperature. At finite temperature, the configurations and phase diagrams will be modified because of the renormalization of potential parameters. The stability width of the commensurate phase will then diminish. The renormalization of the parameters will involve many degrees of freedom including those not considered explicitly in our model. In spite of these, the calculated phase diagram qualitatively describes many features of incommensurate systems.

Acknowledgments

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