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ACOUSTIC COLLECTIVE EXCITATIONS AND STATIC DIELECTRIC RESPONSE IN INCOMMENSURATE CRYSTALS WITH REAL ORDER PARAMETER

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Dedicated to Professor Boran Leontić on the occasion of his 70$^{\text{th}}$ birthday

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Starting from the basic Landau model for the incommensurate-commensurate materials of the class II, we derive the spectrum of collective modes for all (meta)stable states from the corresponding phase diagram. It is shown that all incommensurate states posses Goldstone modes with acoustic dispersions. The representation in terms of collective modes is also used in the calculation and discussion of static dielectric response for systems with the commensurate wave number in the center of the Brillouin zone.

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1. Introduction

The uniaxial incommensurate-commensurate (IC) materials of the II class have the wave number of commensurate ordering, q_c, either at the center ($q_c = 0$) or at the border ($q_c = \pi$) of the Brillouin zone. Here the unit length is taken equal to the lattice constant. The corresponding Landau free energy functional is then an expansion in terms of a real order parameter $u(z)$ [1–4],

$$f[u] = \frac{1}{2L}\int_{-L}^{L}\left[c\left(\frac{\mathrm{d}u}{\mathrm{d}z}\right)^2 + d\left(\frac{\mathrm{d}^2u}{\mathrm{d}z^2}\right)^2 + au^2 + \frac{1}{2}bu^4\right]\mathrm{d}z\,. \tag{1}$$

Since the parameter c may acquire negative values, it is necessary to include into the expansion (1) the further, second derivative term, with a coefficient d presumably positive.

The mean-field phase diagram follows from the simple variational procedure for the functional (1). It contains disordered, commensurate, and various stable [2,3,5] and metastable [4] periodic phases. The most important among the latter is almost sinusoidal,

$$u_s(z) \approx \sqrt{\frac{4}{3b}\left(\frac{c^2}{4d} - a\right)}\,\sin\left(\sqrt{-\frac{c}{2d}}z\right)\,, \tag{2}$$

with weak higher harmonics [2,4].

Although represented in terms of the one-component (real) order parameter, the periodic phases like (2) are generally incommensurate with respect to the underlying lattice. From the other side, it was stated [6] that incommensurate orderings, including those close to the commensurabilities of the II class, should have to be represented by at least two quantities, i.e., by the amplitude and the phase of some periodic modulation. This expectation originates from the experience with the I class of IC systems, characterized by at least two-dimensional order parameters. More specifically, the incommensurate orderings are then most often represented by the modulation of the phase of a complex order parameter. Since the model (1) apparently does not comprise a phase variable, it was interpreted as a reduction, appropriate only for the description of the commensurate ordering, of some richer physical models that include at least two coupled modes, i.e., one-component order parameters. The explicit Landau model with this property was formulated by Levanyuk and Sannikov [7], and widely explored afterwards [8,6,9,10]. The alternative approaches along the same lines, attempting primarily to explain the phase diagram for betaine calcium chloride dihydrate (BCCD), were also proposed [11,12]. The physical arguments for such general approach to insulators from the II class were given by Heine and McConnell [13].

Coming back to the model (1), it is important to emphasize that, either already bearing the whole physical relevance (like in charge density wave materials [14]), or being derived from a more complex starting scheme [13], it accounts for the crossover between orderings with real and complex order parameters. In that sense the solutions like (2) are examples of the mean field approximation for the latter. This can be most easily recognized by looking at the dispersion of the quadratic part of the expansion (1) in the reciprocal space, with the biquadratic ("bottle bottom") dependence on the wave number (see Eq. (6)). This dispersion is an expansion around a pair of symmetry related minima, that in addition takes properly into account the symmetry condition on evenness with respect to the center (or the boundary) of the Brillouin zone. In this sense the model (1) can be qualified as the basic one for the II class, while the more complex Landau expansions [7] are necessary in, physically possible, but non-generic cases when two or more hybridized modes are simultaneously close to instability.

In order to justify the above statement at the mean-field level, one has to prove that incommensurate periodic states of the model (1) fulfill the crucial general property of incommensurately modulated orderings, namely that for each of them there exists a Goldstone mode with the frequency $\Omega_0(k)$ that vanishes at $k = 0$, and generally has a finite slope (phase velocity) $\partial\Omega_0(k)/\partial k \equiv v_{\mathrm{G}}$ in the long wavelength limit $k \to 0$. Such mode should exist in the whole control parameter (e.g. temperature) range of (meta)stability for a given state. It would correspond to standard acoustic phason branches for IC orderings in the materials of the I class. The existence of the Goldstone mode in incommensurate states like (2) for the materials of the II class is to be contrasted to a widely accepted belief [9] that these states do not have a phason mode.

The requirement $\Omega_0(k = 0) = 0$ guarantees the presence of translational degeneracy of the ordered state. In the particular case (1), this means that the periodic solutions should be invariant to translations $z \to z + z_0$ with arbitrary z_0. This is obviously fulfilled, since the kernel in the functional (1) does not depend explicitly on z.

It remains to find out whether there exists a Goldstone mode with a *nontrivial* dispersion [$\Omega_0(k)\neq 0$ for $k\neq 0$], and, if so, to determine its properties at the critical lines of the phase diagram for the model (1). With this aim, we calculate in the present work the spectra of collective modes for all basic orderings that follow from the corresponding Euler-Lagrange equation. To this end, we generalize the usual eigenvalue problem for collective modes to the systems with non-standard free energy densities, in particular to those like (1) with higher-order terms in the gradient expansion. Details of this method are presented in Ref. [15]. Combining analytic and numerical analysis, we show that the Goldstone modes for the incommensurate orderings like (2) exist in the whole range of their stability. Furthermore, it appears that collective modes of the model (1) have some peculiar, experimentally observable, properties. For illustration we discuss the contribution of collective modes to the dielectric response of the II class materials for which the order parameter coincides with their electric polarization.

In Sect. 2 we continue by considering collective modes for the sinusoidal state (2) and for the disordered state of the free energy (1). The expressions for corresponding dielectric susceptibilities are derived in Sect. 3. The concluding remarks are given in Sect. 4.

2. *Collective modes*

The Euler-Lagrange equation for the model (1) reads

$$d\frac{\mathrm{d}^4u}{\mathrm{d}z^4} + c\frac{\mathrm{d}^2u}{\mathrm{d}z^2} + au + bu^3 = 0. \tag{3}$$

Given a solution $u_0(z)$ of this equation that also satisfies additional extremalization requirements [16], the corresponding eigenvalue problem is defined by

$$\mathcal{D}\eta_\Omega \equiv d\eta_\Omega''''(z) - c\eta_\Omega''(z) + \left[a + 3bu_0^2(z)\right]\eta_\Omega(z) = \Omega^2\eta_\Omega(z). \tag{4}$$

The spectrum of collective modes for a given (meta)stable solution $u_0(z)$ is defined by those non-negative values of Ω^2 for which the problem (4) has normalizable solutions $\eta_\Omega(z)$. For periodic orderings, $u_0(z+2\pi/Q) = u_0(z)$, we adopt the Floquet analysis of this problem [15]. In particular, it is convenient to use for such orderings the Bloch representation $\eta_\Omega(z) \to \eta_{n,k}(z)$, with

$$\eta_{n,k}(z) = e^{ikz}\Psi_{n,k}(z), \qquad \Psi_{n,k}\left(z + \frac{2\pi}{Q}\right) = \Psi_{n,k}(z)\,. \tag{5}$$

The wave number k is limited to the first Brillouin zone formed by the incommensurate modulation, $-Q/2 \le k \le Q/2$, and n is the branch index. The formulation (5) enables the extension of the numerical method, developed for finding the solutions $u_0(z)$ [4], to the calculation of dispersions $\Omega_n(k)$ and Bloch functions $\Psi_{n,k}(z)$.

While the previous calculations of the spectrum of collective modes for the incommensurate solution u_s given by Eq. 2 were approximative [17], the present approach (4,5) enables exact results, as shown in Fig. 1. The necessary condition for the (meta)stability of this and other periodic solutions is $c < 0$. Then it is convenient to introduce the parameter $\lambda \equiv ad/c^2$ and reduce the model (1) to a single parameter problem [4]. The lowest among branches from Fig. 1, that with the long wavelength dispersion $\Omega_0(k) = v_\mathrm{G}k$, is the Goldstone mode. As is seen from Fig. 1c, the phase velocity v_G tends to zero as λ approaches the lower stability edge at $\lambda_s = -1.835$ (Fig. 1a), and remains finite at the second-order phase transition to the disordered state at $\lambda_{id} = 0.25$ (Fig. 1b). In the latter figure we use both, Brillouin and extended, schemes for the k-space, since the former becomes irrelevant for $\lambda \ge \lambda_{id}$. The collective modes then reduce to the unique dispersion curve for the disordered state,

$$\Omega_d^2(k) = a + ck^2 + dk^4, \tag{6}$$

defined by the gradient expansion in Eq. (1).

Other collective modes for u_s are massive. The dispersion curves for three of them are also shown in Fig. 1. The gap of the lowest-lying one, $\Omega_1(0)$, tends to zero as $\lambda \to \lambda_{id}$. As is seen in Fig. 1b, at the very transition to the disordered state, $\lambda = \lambda_{id}$, this mode has an acoustic dispersion, with the phase velocity equal to v_G, i.e., to that of the Goldstone mode.

The spectra of collective modes for other, metastable, periodic solutions of Eq. (3) resemble to that of u_s. In particular, for all of them the phase velocities of Goldstone modes vanish as the parameter λ tends towards both edges of metastability for a given solution [15]. This is to be contrasted to $v_{\rm G}$ for u_s, which remains finite at one edge, i.e., at λ_{id} (Fig. 1c).

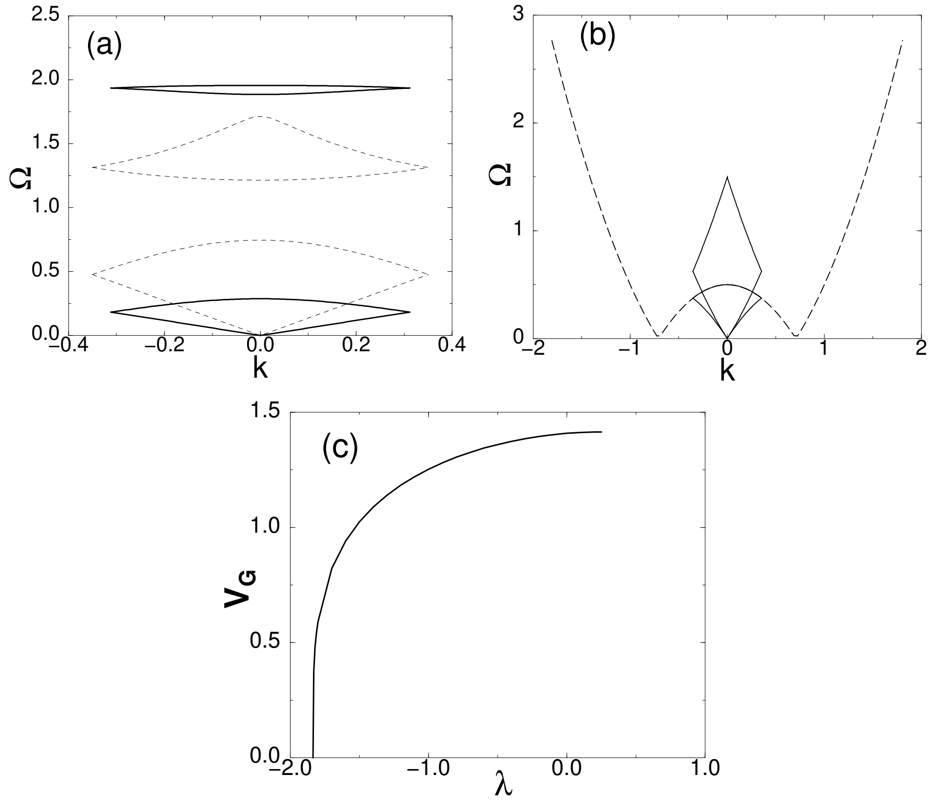

Fig. 1. The dispersion curves for the lowest collective modes of the incommensurate state (2), for $\lambda = -1.8 > \lambda_s$ (full lines), $\lambda = -0.5$ (dashed lines) (Fig. 1a), and for $\lambda = \lambda_{id} = 0.25$ in the Brillouin (full lines) and extended (dashed line) schemes (Fig. 1b). The dependence of the phase velocity of the Goldstone mode on the parameter λ is shown in Fig. 1c.

3. Dielectric susceptibility

The straightforward use of the above Bloch basis (5) leads to the dielectric susceptibility for the incommensurate state u_s, expressed in terms of branches of collective modes. In the static limit which is under consideration here, it is given by

$$\alpha_i \;=\; \frac{d}{c^2}\left[\frac{|g|^2}{v_G^2}+\sum_{n\neq 0}\frac{|\psi_n|^2}{\Omega_n^2(0)}\right]. \tag{7}$$

The first term is the response from the Goldstone mode. Here $g \equiv \frac{1}{2L}\int\limits_{-L}^{L}\Psi_0^{(1)}(z)\mathrm{d}z$, and $\Psi_0^{(1)}(z)$ is the coefficient in the long wavelength expansion of the corresponding Bloch function (5),

$$\Psi_{0,k}(z) \;=\frac{1}{\sqrt{\mathcal{N}}}\,\frac{\mathrm{d}u_s(z)}{\mathrm{d}z} \;+\; k\Psi_0^{(1)}(z)+\ldots, \tag{8}$$

where $\mathcal{N}$ is the normalization constant. The expansion of $\mathcal{N}$ in powers of k does not contain the term linear in k, i.e., in the lowest order approximation it is given by

$$\mathcal{N}=\frac{1}{2L}\int\limits_{-L}^{L}\left(\frac{\mathrm{d}u_s(z)}{\mathrm{d}z}\right)^2\mathrm{d}z\,. \tag{9}$$

The residual sum in Eq. (7) includes the contributions from massive collective modes, i.e., those with finite gaps $\Omega_n(0)$. Corresponding oscillatory strengths are given by

$$|\psi_n|^2 \;\equiv\; \left|\frac{1}{2L}\int\limits_{-L}^{L}\Psi_{n,k=0}(z)\mathrm{d}z\right|^2. \tag{10}$$

It can be shown [18] that the coefficient g remains finite as λ approaches the stability edge at $\lambda_s = -1.835$, so that then α_i diverges as v_G^{-2}. From the other side, this coefficient vanishes together with the function $\Psi_1(z)$ at the transition to the disordered state ($\lambda = \lambda_{id} = 0.25$). Since v_G remains constant, it becomes clear from the expression (7) that in this limit the finite contribution to α_i comes from the residual sum. When calculated directly, by expanding the linear response equation in powers of $\lambda_{id} - \lambda$, this contribution reads [18]

$$\alpha_i(\lambda) \approx \frac{d}{c^2}\,\frac{1}{\frac{1}{2}-\lambda}\left[1+\frac{2\left(\lambda_{id}-\lambda\right)^2}{\left(\frac{1}{2}-\lambda\right)\left(\frac{5}{2}-\lambda\right)}+\ldots\right]. \tag{11}$$

The previous calculations [3,19] were limited only to the leading term in this expansion.

A careful inspection of the residual sum in (7) shows that it contributes to the susceptibility (11) only via one mode, denoted by Ω_2 in Fig. 1. We note that the oscillatory strength (10) of the lowest massive mode Ω_1 vanishes, so that it does not contribute to the susceptibility (7). The mode Ω_2 "survives" the phase transition at λ_{id}, and remains the only contribution, presented by the dashed curve in Fig. 1b. The dielectric susceptibility in the disordered state at $\lambda > \lambda_{id}$ is given by

$$\alpha_d = \frac{1}{\Omega_d^2(0)} = \frac{1}{a} \quad . \tag{12}$$

Thus, at the phase transition from the incommensurate to the disordered state the dielectric susceptibility varies continuously, but with a finite jump in $\mathrm{d}\alpha/\mathrm{d}\lambda$ at $\lambda = \lambda_{id}$.

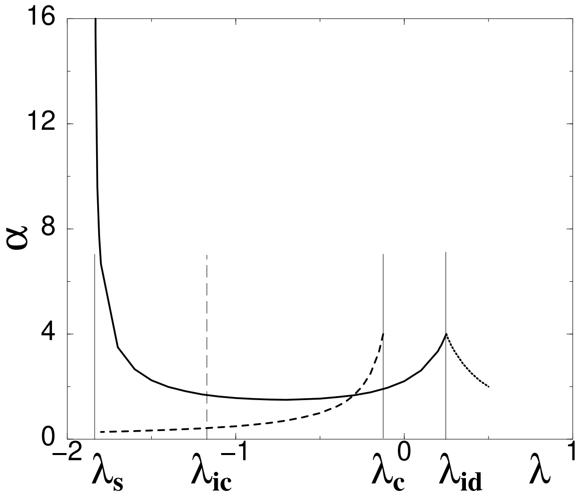

Fig. 2. Dielectric susceptibilities for the incommensurate state (full line), commensurate state (dashed line), and disordered state (dotted line) as functions of the parameter λ. The critical values of λ shown in the figure, are introduced in the text.

To summarize the above discussion of the dielectric responses α_i and α_d, we show in Fig. 2 their dependence on the parameter a (i.e. on temperature). Other parameters are fixed. Figure 2 also includes the susceptibility for the commensurate solution $u_c = \pm\sqrt{-a/b}$, which is stable in the ranges $\lambda < -\frac{1}{8}$ for $c < 0$, and $a < 0$ for $c > 0$. It is separated from the disordered state u_d by the second-order transition at the line $a = 0,\ c > 0$, and from the incommensurate state u_s by the first-order transition, defined by the line $c < 0,\ \lambda \approx -1.177$.

The static susceptibility of the commensurate state u_c is given by

$$\alpha_c = \frac{1}{a + 3bu_c^2} = \frac{1}{\Omega_c^2(0)} = -\frac{1}{2a} \ , \tag{13}$$

where

$$\Omega_c^2(k) = dk^4 + ck^2 - 2a \tag{14}$$

is the dispersion for the corresponding unique collective mode that follows from Eq. (4) after inserting $u_0(z) = u_c$. We see from Eqs. (12) and (13) that the static susceptibility shows a standard type of divergence at the line of the second-order transition from the disordered to the commensurate state, $a = 0$, $c > 0$. From the other side, α_c has a finite value at the stability edge $(c < 0, \lambda_c = -\frac{1}{8})$ for u_c in the regime of coexistence with the incommensurate state u_s. Thus, we propose an asymmetric behaviour of the susceptibility as one passes through the hysteresis range (in, e.g., temperature), bounded by the values λ_c and λ_s in the parameter λ. Namely, as shown in Fig. 2, by cooling through the incommensurate state one ends with the divergence of α_i before passing into the commensurate state at λ_s, while by heating through the commensurate state one passes into the incommensurate state at λ_c with the jump in the susceptibility equal to $[\alpha_c - \alpha_i]_{\lambda=\lambda_c}$.

Due to the existence of other metastable periodic solutions [4] in the above coexistence range of the parameter λ, the temperature variation of the susceptibility may be even more complicated than that schematically presented in Fig. 2. The more detailed analysis [15] shows that, provided that for a given material and in particular circumstances some of these states are stabilized, the static susceptibility will diverge at both edges of their stability ranges, again, like in the case of the state u_s, due to the vanishing of phase velocity for the corresponding Goldstone modes. Since these stability ranges are rather narrow in comparison with $\lambda_c - \lambda_s \approx 1.71$, the stabilization of highly nonsinusoidal periodic states [4] would be manifested by dramatic variation of susceptibility in relatively narrow temperature intervals.

4. *Conclusion*

In the above analysis it was clearly shown that the model (1), although formulated in terms of a single and real order parameter, provides for the existence of the acoustic Goldstone mode for the incommensurate ordering. For small wave numbers $(k \ll Q)$, this mode simply generates compressions and dilatations of the sinusoidal modulation $u_s(z)$, i.e., its physical content is same as that of standard phason mode for incommensurate orderings in the II class of IC systems. Amplitude fluctuations of this modulation are generated through higher, massive modes from Fig. 1. Still, the lowest among these massive modes have some peculiar properties. For one of them, the gap tends to zero by approaching the transition from, e.g., the sinusoidal state to the disordered state. However, this mode is not optically active. The whole optical activity at this transition comes from the other massive mode in order, as shown in Fig. 1.

In contrast to standard approaches [20], the dielectric functions of all (meta)stable states are here strictly represented in terms of collective modes. We are thus able to distinguish modes with finite contributions in the optical response from those with no dipolar polarization. Note that the present analysis of dielectric response is limited to systems with uniform commensurate orderings (those with $q_c = 0$). The extension to systems with dimerizations, as well as the equivalent treatment of collective modes and dielectric response of extended Landau models for IC systems of class I [21], are under current investigation.

The above analysis shows that incommensurate states that follow already from the simplest basic version of the model (1) for the IC systems of class II, have the same physical properties as those of class I, represented in terms of the complex order parameter. This model is still insufficient for the explanation of rich phase diagrams of some well-known representatives of class II, like thiourea and BCCD. In this respect the question which remains is, how to make an appropriate extension without invoking an additional order parameter, in a way analogous to the recent proposal for the class I [21], that would as well stabilize other commensurate states with wave numbers close to $q_c = 0$ or $q_c = \pi/a$.

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AKUSTIČNA KOLEKTIVNA POBUĐENJA I STATIČKI DIELEKTRIČNI ODZIV U NESUMJERLJIVIM KRISTALIMA S REALNIM PARAMETROM UREĐENJA

Polazeći od temeljnog Landauovog modela za nesumjerljive materijale II klase, izveli smo spektar kolektivnih grana za sva (meta)stabilna stanja iz odgovarajućeg faznog dijagrama. Pokazali smo da sva nesumjerljiva stanja posjeduju Goldstonove grane s akustičkim disperzijama. Reprezentaciju kolektivnih grana primijenili smo također u proračunu i raspravi statičkog dielektričnog odziva sustava sa sumjerljivim valnim brojem u središtu Brillouinove zone.