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Statics and dynamics of incommensurate crystal phases

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We present a formulation of the statics and dynamics of displacive incommensurately modulated structures with modulation vector **q** based on a Taylor expansion of the interaction energy and of the dynamical matrix. For a given interaction potential, this approach allows the consistent calculation of the incommensurate distortion and the vibrational frequencies, including the phase and amplitude modes, and the intensities of the modes activated by the distortion. The necessary approximations are discussed; the coupling and selection rules are easily visualized in terms of the space group symmetry of the parent structure. Finally, we work out in detail a simple example of an idealized three-dimensional crystal, calculating the static incommensurate distortion, the Γ point modes of the modulated structure, and the relative optical intensities of the activated modes. [S0163-1829(96)05445-8]

I. INTRODUCTION

Incommensurate (IC) modulated phases have been the focus of special interest over many years; reviews spanning the more relevant experimental and theoretical features of these phases have been published,[1–4] and, in particular, the problem of their dynamical properties has been approached from different viewpoints. On one side, phenomenological Landau theory has been used to study the dynamics of systems undergoing phase transitions driven by soft modes, with special emphasis on the resulting phase and amplitude modes.[5,6] On the other, a more general formulation of the dynamics of the IC phases was performed using essentially two different approaches. In the first one[7] the study was based on the symmetry group of the crystal, a superspace group; the normal modes were shown to be characterized by irreducible representations of this group, and the selection rules for infrared absorption were derived. The second approach[8] provides a more direct visualization of the dynamics of the IC phases: Using the normal modes of the high-temperature phase as a basis for the modes of the IC structure, the couplings between modes of wave vector **k** and $\mathbf{k}+n\mathbf{q}$ ($\mathbf{q}$ the modulation vector an n an integer) were explicitely obtained, generalizing the expressions introduced in the framework of Landau theory.

The existence of generic theories, however, has not had its counterpart in explicit calculations on real crystals: To our knowledge, these have been limited mostly to simple one-dimensional chains, f.i. using the modulated spring model[9] [which has also been employed to describe qualitatively the observed vibrational frequencies of $\mathrm{Rb_2ZnBr_4}$ (Ref. 10)] or the Frenkel-Kontorova model,[3,11] and considering long-wavelength commensurate systems; on the other hand, Hlinka *et al.*[12] have studied a three-dimensional crystal with a limited number of degrees of freedom, using a rational approximant; they considered only some fourth-order anharmonic terms.

This scarcity could be attributed, on the one hand, to the difficulty of determining interatomic potentials, empirical or otherwise, appropiate to explain the instabilities which lead to IC phases, and, on the other, to the lack of a simple model for realistic calculations. Recently, empirical potentials which account for instabilities in the normal structure of most compounds of the A_2BX_4 family have been proposed:[13,14] This could open a valuable path for the calculation of their IC phase properties, and renews interest in the formulation of a practical theoretical approach to the problem.

As in the case of commensurate crystals, both the static and the dynamical properties of IC phases are determined by the interaction potential, and information on it can be derived from the atomic equilibrium positions and the vibrational normal modes: The IC distortion and the resulting dynamics should be included consistently in the theory. The existing theories[7,8] for the lattice dynamics are formulated rigorously. The problem is approached by Fourier transforming the interaction potential; this has the advantage of taking into account the coupling between normal modes at **k** and $\mathbf{k}+n\mathbf{q}$, through all its possible paths, therefore giving an exact expression for it; however, the calculation involves the equilibrium atomic positions in the IC phase, and it is not clear how the IC distortion can be calculated consistently with the dynamics of the IC phase.

In this work we present a formulation of the dynamics of the IC phase of a crystal with an IC phase transition driven by a soft mode. We start from a known interaction potential; our approach follows the general lines of Ref. 8, but we use a Taylor expansion of the interaction energy and of the dynamical matrix. With this scheme we present a procedure for the consistent calculation of the distortion, the changes in the vibrational frequencies, and the optical intensities of the activated modes. The coupling scheme may be derived in a simple way, using space group symmetry; superspace symmetry considerations add to the simplification of the dynamical calculations. Finally, we apply the theory to an idealized, but more or less ''realistic'' crystal, and calculate the frequency shifts and relative optical intensities of the relevant modes as a function of the parameters which characterize the incommensuration.

II. THEORY

We use as a basis for our calculations the normal modes of the undistorted parent structure; although this phase is unstable, the normal modes which are obtained span the complete crystal coordinate space, and possess the symmetries of the corresponding space group. The first step is, then, to calculate the dynamics of this (virtual) phase in the harmonic approximation. Restricting ourselves for simplicity to one-dimensional modulations, the atomic positions $\mathbf{r}_l^\mu$ are described through a distortion of a basic structure of the form

$$\mathbf{r}_l^\mu = \mathbf{r}_{0l}^\mu + \mathbf{u}^\mu(\mathbf{q}\cdot\mathbf{r}_{0l}^\mu), \tag{2.1}$$

where $\mathbf{r}_{0l}^\mu$ is the position of the μth atom of the basic structure in the lth unit cell and $\mathbf{u}^\mu$ is the periodic displacement field, which can be expressed as a Fourier series in terms of normal modes of the basic structure,

$$\begin{aligned}\mathbf{u}^\mu(\mathbf{q}\mathbf{r}_{ol}^\mu) &= \sum_n \mathbf{u}^\mu(n) e^{in\mathbf{q}\cdot\mathbf{r}_{0l}^\mu}\\ &= \sum_n \left[\sum_\lambda Q_s(n\mathbf{q},\lambda)\mathbf{e}^\mu(n\mathbf{q},\lambda)\right] e^{in\mathbf{q}\cdot\mathbf{r}_{0l}^\mu}, \end{aligned}\tag{2.2}$$

where $\mathbf{u}^\mu(n)$ are the Fourier amplitudes, $Q_s(n\mathbf{q};\lambda)$ the normal coordinate of the principal (soft) mode and all the secondary ones which have compatible symmetries, λ is the branch index, and $\mathbf{e}^\mu(n\mathbf{q},\lambda)$ are their mass-weighted polarization vectors.

The interatomic interaction energy in the IC phase may be written as a Taylor expansion in terms of the distortion, or, using Eq. (2.2), the normal coordinates Q_s:

$$\begin{aligned}E = E_0 + \sum_{j=2} \sum_{\mu\nu l} \sum_{\{n_j\}} \sum_{\{\lambda_j\}} \frac{1}{j!} \phi^{(j)}_{\alpha_1\cdots\alpha_j}(\mathbf{r}_{0l}^{\mu\nu})\\ \times \Delta e^{\mu\nu}_{\alpha_1 l}(n_1\mathbf{q},\lambda_1)\cdots\Delta e^{\mu\nu}_{\alpha_j l}(n_j\mathbf{q},\lambda_j)\\ \times Q_s(n_1\mathbf{q};\lambda_1)\cdots Q_s(n_j\mathbf{q};\lambda_j),\end{aligned}\tag{2.3}$$

where E_0 is the interaction energy in the basic structure, $\mathbf{r}_{0l}^{\mu\nu} = \mathbf{r}_{0l}^\nu - \mathbf{r}_{00}^\mu$, α labels Cartesian components, the n_i's are the integers appearing in Eq. (2.2) fulfilling the condition $\Sigma_i{}^j n_i = 0$, $\Delta\mathbf{e}_l^{\mu\nu}(n\mathbf{q},\lambda) = \mathbf{e}^\mu(n\mathbf{q},\lambda) - \mathbf{e}^\nu(n\mathbf{q},\lambda)e^{in\mathbf{q}\cdot\mathbf{r}_{0l}^{\mu\nu}}$, and $\phi^{(j)}_{\alpha_1\cdots\alpha_j}(\mathbf{r}_{0l}^\mu)$ is the jth derivative of the interatomic potential evaluated at the atomic positions in the parent structure; the ϕ's have the full symmetry properties of the basic space group. The total interaction energy E is minimized with respect to the distortion, by putting to zero the derivatives of Eq. (2.3) with respect to the Q_s's which are relevant to the problem: These are determined by the values of n which must be considered and by simple symmetry rules. In this way a system of nonlinear equations is obtained.

Likewise, the dynamical matrix of the IC structure may be expanded in terms of the distortion (the Q_s's). A general term in the expansion of the potential energy, coupling the basic modes $Q(\mathbf{k},\eta)$ and $Q^*(\mathbf{k}+m\mathbf{q},\eta')$,

$$\begin{aligned}D^{k,m}_{\eta\eta'} = \frac{1}{2}\sum_{j=0} \sum_{\mu\nu l} \sum_{\{n_j\}\{\lambda_j\}} \frac{1}{j!} \phi^{(j+2)}_{\alpha_1\cdots\alpha_j,\beta,\gamma}(\mathbf{r}_{0l}^{\mu\nu}) \Delta e^{\mu\nu}_{\alpha_1 l}(n_1\mathbf{q},\lambda_1)\cdots\Delta e^{\mu\nu}_{\alpha_j l}(n_j\mathbf{q},\lambda_j) e^\mu_\beta(\mathbf{k},\eta)\\ \times \Delta e^{\mu\nu}_\gamma(-\mathbf{k}-m\mathbf{q},\eta') Q_s(n_1\mathbf{q};\lambda_1)\cdots Q_s(n_j\mathbf{q};\lambda_j) Q(\mathbf{k},\eta) Q^*(\mathbf{k}+m\mathbf{q},\eta'),\end{aligned}\tag{2.4}$$

with the condition $\Sigma_i{}^j n_i = m$.

It is useful to analyze in some detail Eq. (2.4). The integer m indicates the distance, in terms of $\mathbf{q}$, of the modes which are coupled and j the expansion order of the dynamical matrix. For $j=0$, only terms with $m=0$ appear, and we reobtain the dynamics of the basic structure; for $j \geqslant 0$ and $m=0$ we have the dynamics of the average structure and if, as is usually the case, the symmetries of both structures coincide, the coupling occurs between branches with the same label. It is clear that these terms can only produce a shift in the normal mode frequencies, leaving out the more interesting features of the IC phase.

Terms with $j>0$ and $m \neq 0$ couple modes at different points of reciprocal space; these are anharmonic terms of the potential referred to the basis structure. Thus, the harmonic dynamics of the IC phase is formally identical to an anharmonic calculation of a normal phase, except for the fact that all but two of the normal modes in Eq. (2.4) are frozen (Q_s's); the well-known selection rules for this problem may be used and this applies, too, to the expression of the interatomic interaction energy (2.3). From the point of view of the symmetry analysis it is sufficient to consider successively the couplings through the principal mode of modes differing by $\mathbf{q}$. This has been already stated by Pérez-Mato *et al.*[15] in the framework of Landau theory: All the relevant information on the symmetry of the IC phase (the superspace symmetry) is determined by the symmetry of the principal mode. Following the general ideas of Ref. 15, superspace group considerations can be included in the present formalism, leading to the definition of new basis modes, linear combinations of modes belonging to the star of $n\mathbf{q}$ (with the addition of a phase related to the internal coordinate in the superspace formalism), with a definite symmetry in the superspace group. Beyond the formal character of this procedure, it may add to the simplification of the problem through further partition of the dynamical matrix: This is especially useful for modes which are closely connected to those at $\mathbf{k}=0$, i.e., those at $n\mathbf{q}$ for small values of n, and we will use this symmetry classification in the example below.

The expressions above are valid for any IC modulated phase; if only a few low values of n are found to be relevant, we are in the sinusoidal regime; if, on the contrary, higher n's appear in the modulation function, we will be in a discommensuration regime. In the latter case, very cumbersome calculations for real crystals may result; in any case it is necessary to make consistent approximations to render the procedure outlined above useful.

First, we consider a limited number of values for n in Eq. (2.2); these can be determined experimentally from the observation of the satellites of the Bragg reflections, but from the viewpoint of the calculation, successive values of n (starting with the principal mode) can be introduced in the minimization of the interaction energy until the values of the distortion do not change appreciably. This procedure also reduces the chances of not obtaining the absolute minimum which corresponds to the real distortion; the minimization problem may be further simplified *a priori* by observing the magnitude of the coupling terms. Second, we have to cut somewhere the chain of indirect couplings in Eq. (2.4). If we are interested in the modes at $\mathbf{k}=0$, which are coupled directly to those at some $m\mathbf{q}$, the latter will be coupled, in turn, to $2m\mathbf{q}$, and so on. Again, this convergence can be tested numerically. Finally, in the anharmonic expansion in Eqs. (2.3) and (2.4), we should consider only those terms which are relevant to each particular problem: This limits the number of direct couplings between normal modes. The nature of the IC transition may give useful indications in that respect; for instance, in the case of a second-order transition, probably only anharmonic coefficients up to fourth order will be relevant. The eigenvalue corresponding to the soft mode must be negative below the transition temperature T_I; in the framework of phenomenological Landau theory it is proportional to $T-T_I$, and this provides a connection between the temperature and our model via the interatomic force field. In a first-order transition, at least sixth-order coefficients are needed; the eigenvalue for the soft mode will now turn negative for some temperature below T_I.

Although a practical application of this formulation must use, by necessity, a number of approximations, it has the advantage of allowing a consistent treatment of the problem, by carrying out the expansions (2.3) and (2.4) to the same order, and by checking numerically, in successive steps of the calculation, the convergence of the results.

III. EXAMPLE

We will now illustrate the procedure outlined above with an example: We have constructed a simple three-dimensional crystal, with four identical atoms located on σ_a planes in its orthorhombic $Pmcn$ unit cell. We made this choice trying to avoid the greater difficulties of a real crystal but keeping its relevant features; furthermore, there are many crystals with this space symmetry which show IC transitions. We have simulated the interactions between atoms μ,ν separated by $\mathbf{r}$ using anharmonic springs, with coefficients

$$\phi^{(j)}_{\alpha_1,\cdots,\alpha_j}(r)=\frac{C_j(r)}{r^j}\,\frac{r_{\alpha_1}\cdots r_{\alpha_j}}{r^j},\quad j=2,3,4. \qquad (3.1)$$

The parameters relevant to the example are listed in Table I; arbitrary energy units are used for the C_j's. For the harmonic parameters C_2 we chose different values of opposite sign for consecutive interaction shells; those values shown in Table I succeed in producing a soft mode of Σ_2 symmetry (antisymmetric with respect to σ_a and σ_b), in the $\mathbf{c}^*$ direction: This defines the superspace group $P^{Pmcn}_{ss\bar{1}}$ for the IC phase. In the first shell, the harmonic parameter was taken to be temperature dependent, $C_2=f(T)$, and changed to control the softening of the mode; this also produces small changes in the modulation vector. The critical value for f is $f_c=3.999$ for $\mathbf{q}=0.357\mathbf{c}^*$. Figure 1 shows dispersion curves for the normal phase, with $f<f_c$. Anharmonic terms were chosen arbitrarily, with reasonable orders of magnitude.

TABLE I. Parameters of the model. C_j's in arbitrary energy units.

Crystal parameters			
Cell parameters	$a=$ 3.7 Å	$b=4$ Å	$c=8$ Å
Atomic positions	$x=0.25$	$y=0.22$	$z=0.125$
Potential parameters			
$r\leqslant5.6$ Å	$C_2=f(T)$	$C_3=-4$	$C_4=10$
5.6 Å $\leqslant r\leqslant6.4$ Å	$C_2=-7.5$	$C_3=4$	$C_4=-10$
6.4 Å $\leqslant r\leqslant8.4$ Å	$C_2=5.3$	$C_3=-4$	$C_4=10$

The modes which participate in the distortion are $2Ag[y,z]$, with $\mathbf{k}=0$; $2\Sigma_2[x]$ for each $\mathbf{k}=(2m+1)$ $\mathbf{q}$; and $4\Sigma_1[y,z]$ for each $\mathbf{k}=2m\mathbf{q}$. We have minimized the interaction energy E, Eq. (2.3), for successive values of n up to $n=5$; the convergence is very fast, even for the largest distortion considered: For $n=1$ and 2, E is 58% and 99.98%, respectively, of its value at $n=5$. Truncating the series at $n=2$ we are left with eight relevant normal modes Q_s. Figure 2 shows the contribution of each Fourier term to the distortion (2.2), as a function of w_q^2, the eigenvalue corresponding to the principal mode which, as stated before, is directly related to the temperature. As predicted by Landau theory, the primary distortion is nearly linear in $|w_q|$, whereas the secondary ones are linear in w_q^2. We found that only one normal mode makes relevant contributions to each Fourier component.

We have calculated the elements of the dynamical matrix (2.4), for $\mathbf{k}=0$, and different values of the distortion; the problem was simplified using the coupling scheme of Table II. We are interested mainly in modes which are closely connected to those at $\mathbf{k}=0$, and as a first step we have included

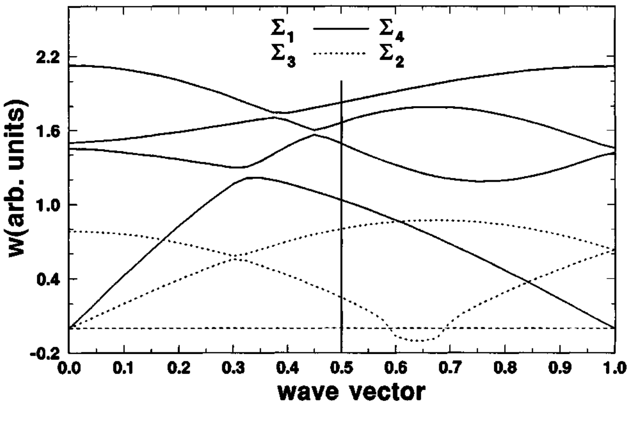

FIG. 1. Dispersion curves in an extended zone scheme for the normal phase crystal, with parameter $f=3.965$, showing the instability of the Σ_2 mode. For negative eigenvalues, $-|w|$ is represented.

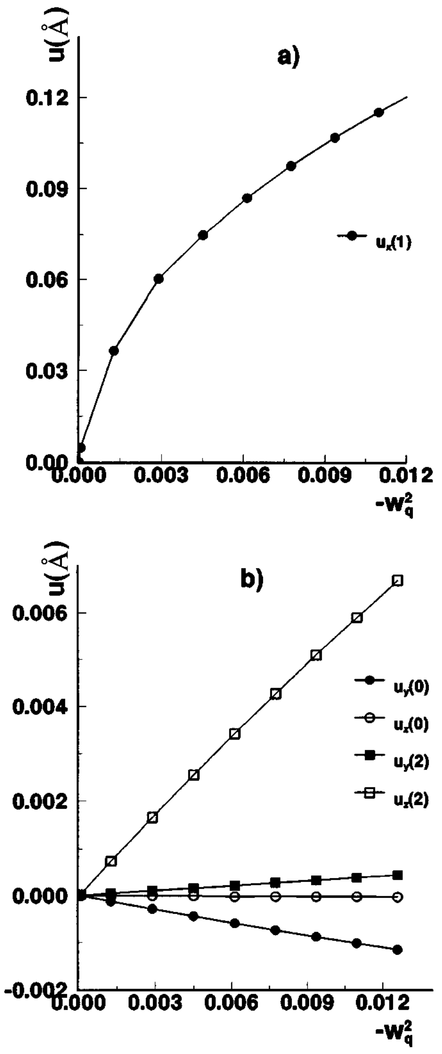

FIG. 2. Calculated IC distortion as a function of w_q^2 (a) $n=1$ Fourier component, containing the principal mode. (b) $n=0$ and $n=2$ Fourier components.

only modes at $\mathbf{k}=m\mathbf{q}$, with $m=0,\pm1$, and ±2. Figure 3 shows the behavior of the A_g and B_{1u} calculated frequencies as a function of w_q^2, including the two characteristic excitations of the IC phase: the phase and amplitude modes. From the physical point of view, it is crucial for any calculation to produce a phason with zero frequency and an eigenvector corresponding to a change in the phase of the distortion; for this to happen it is necessary to be consistent in the expansions of the interaction energy and the dynamical matrix. Furthermore, the maximum order m in the dynamical matrix and that of the interaction energy n must coincide: If this is not so, the eigenvector of the phason will not contain the same Fourier components as the distortion. The internal consistency of the calculation may be checked by adding terms and verifying their negligible effect; we found that, in our example, the addition of modes with $m=\pm3$ and ±4 does not affect appreciably our results.

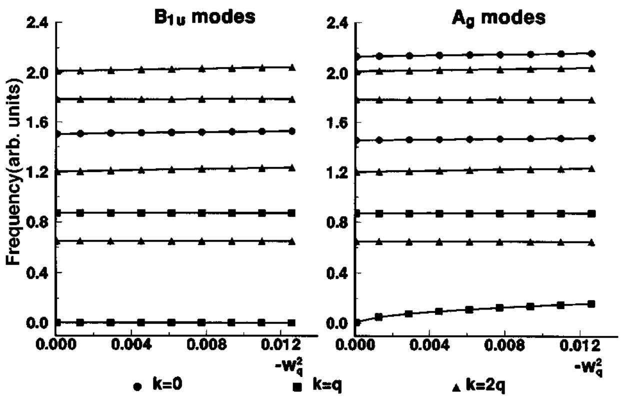

FIG. 3. Calculated frequencies of B_{1u} and A_g IC phase modes as functions of w_q^2.

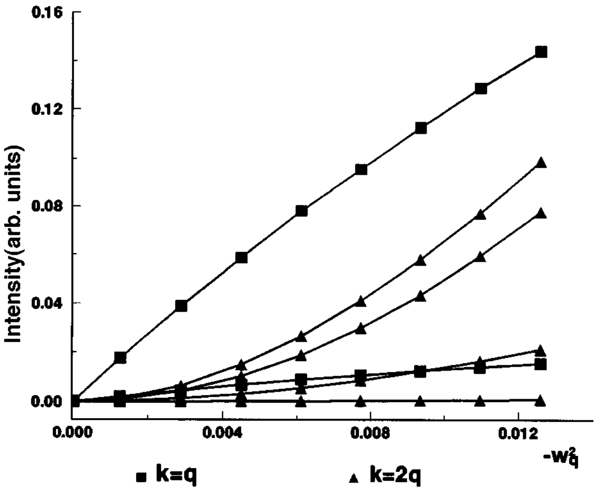

FIG. 4. Intensities of the folded A_g modes, calculated assuming an intensity of 10 for the two normal phase modes.

The amplitudon of A_{1g} symmetry does not seem to deserve its name: Its more noteworthy feature is that, due to the coupling of the principal mode with secondary ones, its eigenvector does not correspond in general to a global change of the modulation amplitude, although it is true that for temperatures barely under T_I this coupling is very weak. The other normal modes increase their frequencies from negligibly to about 4–5 % with decreasing temperature; the growth and its order of magnitude are compatible with experimental observations.[10] Finally, we observe that except for the amplitudon, the gaps which appear at points $n\mathbf{q}$ are in general small compared to the normal mode frequencies, and depend both on third- and fourth-order anharmonic terms; the amplitudon frequency grows linearly with the amplitude of the principal mode, indicating that third-order terms dominate the amplitudon dynamics.

Another point of interest is the optical intensity of the modes, since it refers to valuable experimental information. At the lowest order, the modes at $\mathbf{k}=\mathbf{q}$ and $2\mathbf{q}$ which are folded into $\mathbf{k}=0$ obtain their optical intensities by borrowing from the parent phase active modes;[16,17] the intensities can be calculated directly from the participation of these in the normal modes of the IC phase, i.e., the corresponding eigenvectors; the selection rules are a direct consequence. In Fig. 4 we show the intensities of the folded A_g modes, assuming a value of 10 for the intensity of each of the two A_g normal phase modes; the mode which develops the largest intensity is the amplitudon; other models[3] give the same result. It is

TABLE II. Coupling scheme, in the $P_{ss\bar{1}}^{Pmcn}$ superspace group, between modes at Γ, $\mathbf{k}=\mathbf{q}$ and $\mathbf{k}=2\mathbf{q}$. Σ_i refer to the classification of the modes in the group of $\mathbf{k}$ of the normal phase; plus and minus superscripts refer to symmetric and antisymmetric linear combinations of modes at $\mathbf{k}$ and $-\mathbf{k}$.

Γ	$\mathbf{k}=\mathbf{q}$	$\mathbf{k}=2\mathbf{q}$
A_g	Σ_2^+	Σ_1^+
B_{1g}	Σ_1^+	Σ_2^+
B_{2g}	Σ_4^+	Σ_3^+
B_{3g}	Σ_3^+	Σ_4^+
A_u	Σ_1^-	Σ_2^-
B_{1u}	Σ_2^-	Σ_1^-
B_{3u}	Σ_4^-	Σ_3^-
B_{2u}	Σ_3^-	Σ_4^-

noteworthy that modes which stem from $\mathbf{k}=2\mathbf{q}$ have intensities comparable to others from $\mathbf{k}=\mathbf{q}$. The growth of the respective intensities with temperature is quadratic and linear, as predicted by Landau theory.[16]

IV. CONCLUSIONS

The example above is just a first approach to a consistent calculation of the dynamics of a very simple three-dimensional incommensurate crystal, and some of its features may well be peculiar to our model; it is intended to show how such a calculation can actually be performed, and give some general indication of results to be expected.

The equations used in our calculations have the general form of those appearing in the Landau formulation, and both results coincide qualitatively in many cases; however, we wish to stress the quantitative character of our formulation, which allows us to relate directly the distortion and the coupling coefficients between modes with concrete physical quantities i.e., anharmonic terms, keeping all relevant terms without *a priori* simplifications. The expression for the distortion is completely general; the nature of the phase transition and crystallographic evidence are linked to the magnitude of the anharmonic terms involved. Frequency shifts may also yield valuable information: Their magnitude is determined by the anharmonic coefficients. Similar considerations apply to optical intensities, which also have a direct relation to the coupling coefficients.

The example we have presented in the previous section is found to be in the sinusoidal regime, and no trace of discommensuration has been observed. This is a result of the calculation, and not a previous hypothesis; it is due to the fact that the modulation vector is not close enough to a simple commensurate value for resonances to be relevant, and to the low expansion order adopted for the interaction potential.

The coupling with optical modes is important for the analysis of the optical activities of folded modes; the forementioned fact that, against intuition, modes which stem from $\mathbf{k}=2\mathbf{q}$ may have intensities larger than others from $\mathbf{k}=\mathbf{q}$, deserves to be taken into account when experimental results are analyzed. The explanation is quite simple: If the soft mode is not total symmetric in the group of $\mathbf{q}$, the direct coupling between modes differing by $\mathbf{q}$ occurs among different branches, whereas modes differing by $2\mathbf{q}$ couple if they belong to the same branch; in the case of a relatively flat branch, the latter may develop a considerable intensity. The appearance of a band close to one already active in the normal phase, as has been observed,[10] may also be attributed to a folded $2\mathbf{q}$ mode; a definitive answer could be obtained by observing the behavior of its intensity with temperature. Another consequence of the coupling scheme described above is that gaps may open in the dispersion curves at points $n\mathbf{q}$ but not at $(2n+1)\mathbf{q}/2$.

An interesting result of our example regards the amplitudon: We find that the growth of its frequency is determined mainly by couplings due to third-order anharmonic coefficients, consistently with the behavior of the optical intensity discussed above: This is important since these terms are often neglected in simplified treatments.[3,12]

Besides optical experiments, in the last years a good deal of effort has been devoted to the study of dynamical properties of IC phases using inelastic neutron scattering,[18] NMR,[19] and Debye-Waller factors in diffraction experiments.[20] Real crystals undergoing IC phase transition tend to be quite complicated: We believe that the main advantage of the procedure outlined above is that it gives us tools to gain quantitative information on their interatomic interactions, taking into account all available experimental evidence in a unified way.

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