Amplitudons and phasons in the triple-k incommensurate phase of quartz-type crystals

M. Vallade, V. Dvorak, J. Lajzerowicz

J. Physique **48** (1987) 1171-1179

Classification
Physics Abstracts
63.90 — 64.70K

Amplitudons and phasons in the triple-*k* incommensurate phase of quartz-type crystals

M. Vallade, V. Dvorak (*) and J. Lajzerowicz

Laboratoire de Spectrométrie Physique, B.P. 87, 38402 Saint-Martin-d'Hères Cedex, France

(*Reçu le 8 décembre 1986, révisé le 2 mars 1987, accepté le 4 mars 1987*)

Résumé. — Le spectre des amplitudons et des phasons a été calculé pour une structure incommensurable à 3-*k*, triangulaire, du type de celle observée dans les cristaux isomorphes au quartz, en utilisant un modèle phénoménologique. Deux excitations ont des courbes de dispersion du type acoustique (phasons sans « gap ») et quatre excitations sont du type optique, l'une de ces dernières correspondant aux fluctuations de la somme des phases des trois ondes de modulation. On discute la stabilité de la structure incommensurable 3-*k* par rapport à ces excitations et on montre en particulier la possibilité d'un amollissement de la vitesse de propagation d'un phason. Les règles de sélection concernant l'activité de ces excitations en absorption infrarouge et en diffusion Raman ont été établies.

Abstract. — The spectrum of amplitudons and phasons has been calculated for a 3-*k* triangular incommensurate structure (such as it is found in quartz-type crystals) using a phenomenological model. Two excitations have acoustic-like dispersion curves (gapless phasons) and four excitations are optic-like, one of the latter corresponding to fluctuations of the sum of the phases of the three modulation waves. The stability of the 3-*k* incommensurate structure with respect to these excitations is discussed and in particular a possible phason velocity softening is pointed out. The selection rules for infrared and Raman scattering activity of these excitations are derived.

1. Introduction

The elementary excitations of incommensurate (inc.) single-*k* systems have been shown to be of two different kinds : phasons and amplitudons [1-3]. The former ones have acoustic-like dispersion curves which go to zero frequency when the wave-vector $\mathbf{q}$ (taken from the modulation wave-vector $\mathbf{k}_0$) goes to zero. Such gapless excitations arise from the invariance of the system in a global shift of the phase of the modulation (Goldstone mode). Amplitudons have optic-like dispersion curves but their frequency at $\mathbf{k}_0$ goes to zero at a 2nd order phase transition point which separates the inc. and the parent (usually the high temperature) phases. The soft optic branch exhibits two parabolic minima at $\mathbf{k}_0$ and $-\mathbf{k}_0$, in the parent phase, so that excitations at $\mathbf{k}_0+\mathbf{q}$ and $-\mathbf{k}_0+\mathbf{q}$ are degenerate for sufficiently small $\mathbf{q}$ wave-vectors. This degeneracy is lifted in the inc. phase by the modulated potential created by the frozen-in inc. wave. The new elementary excitations, at small q, are found to be the symmetric and antisymmetric combinations of the normal coordinates $Q_{\mathbf{k}_0+\mathbf{q}}$ and $Q_{-\mathbf{k}_0+\mathbf{q}}$ of the parent phase

$$A_{\mathbf{q}} = \frac{1}{\sqrt{2}}\,(Q_{\mathbf{k}_0+\mathbf{q}} + Q_{-\mathbf{k}_0+\mathbf{q}})$$
$$\phi_{\mathbf{q}} = \frac{i}{\sqrt{2}}\,(Q_{\mathbf{k}_0+\mathbf{q}} - Q_{-\mathbf{k}_0+\mathbf{q}})\,. \tag{1}$$

The purpose of the present paper is to investigate how this simple picture is modified when a triple-*k* inc. structure is present, as is the case in quartz-type crystals. In these systems, the inc. structure results from the condensation of a soft mode at 6 symmetry equivalent points in the reciprocal space ($\pm\mathbf{k}_1$, $\pm\mathbf{k}_2$, $\pm\mathbf{k}_3$) near the Γ point. It is then clear that, for a given $\mathbf{q}$, six excitations at $\pm\mathbf{k}_i+\mathbf{q}$ are degenerate in the normal phase. The modulated potential couples these excitations, in the inc. phase, giving rise to three amplitudons and three phasons. Two phasons only, however, are gapless excitations at $\mathbf{q}=0$ because the inc. structure is left invariant by

(*) *Permanent address :* Institute of Physics of the Czechoslowak Academy of Sciences, Prague, Czechoslovakia.

translations within the plane of the modulation wave-vectors (the basal plane of the hexagonal structure). The phases of two modulation-waves can thus be chosen arbitrarily, but the third one is usually well defined with respect to the others. As a matter of fact the free energy can contain a cubic invariant :

$$(G\eta_{\mathbf{k}_1}\eta_{\mathbf{k}_2}\eta_{\mathbf{k}_3} + \text{c.c.}) = \\ = (G\rho_1\rho_2\rho_3 e^{i(\psi_1+\psi_2+\psi_3)} + \text{c.c.}) \quad (2)$$

where $\eta_{\mathbf{k}_i} = \rho_i e^{i\psi_i}$ is the inc. order parameter. The free-energy does depend upon the phase $\psi = \psi_1 + \psi_2 + \psi_3$ and the excitation which corresponds to changes in ψ will be a phason with a gap at $\mathbf{q} = 0$ while the excitations which change the ψ_i without modifying ψ (for example : $\delta\psi_1 = -\frac{1}{2}(\delta\psi_2 + \delta\psi_3)$ and $\delta\psi_2 = -\delta\psi_3$; $\delta\psi_1 = 0$) will correspond to the two gapless phasons.

In the present paper the spectrum of the inc. excitations is calculated using the phenomenological theory presented in reference [4] which has proved to be successful in explaining the most salient features of the static properties observed in the inc. phase of quartz-type crystals [5]. The role of the cubic invariant (Eq. (2)) — which is specific of a « triple-k » structure — will be particularly emphasized.

A brief summary of the present work was previously published as a short conference report [6]. We give here a thorough discussion of the problem and, in addition, the infrared and Raman activity of the excitations will be discussed in the last section. Walker *et al.* [7] have also discussed the dynamics of the inc. phase of quartz but they focussed their attention on the coupling between the phasons and the acoustic phonons and they did not consider the other (optic like) excitations.

We were also aware, during the course of this work, that Shionoya *et al.* [8] were also studying the same subject in connection with recent light scattering experiments. Their conclusions concerning the general picture of the excitation spectrum agree with the results published in [6], and therefore with those of the present paper. However those authors did not make a complete analysis of the wave-vector and temperature dependence of the mode frequencies and our present results are not in agreement with theirs concerning the Raman selection rules.

2. Amplitudons and phasons spectrum in the triple-*k* inc. phase of quartz.

The onset of an inc. phase in quartz-type crystals has been shown to arise from a coupling between a zone center soft optic mode (which induces the α-β structural phase transition) and acoustic phonons propagating in the (0, 0, 1) plane. After elimination of the elastic degrees of freedom the free energy takes on the general form :

$$F = \frac{1}{2}\sum_j A(\mathbf{k}_j)\,\eta_{\mathbf{k}_j}\eta_{-\mathbf{k}_j} + \frac{1}{3}\sum_{j,l,m} G(\mathbf{k}_j, \mathbf{k}_l, \mathbf{k}_m)\,\eta_{\mathbf{k}_j}\eta_{\mathbf{k}_l}\eta_{\mathbf{k}_m}\,\delta(\mathbf{k}_j + \mathbf{k}_l + \mathbf{k}_m) + \\ + \frac{1}{4}\sum_{j,l,m,n} B\eta_{\mathbf{k}_j}\eta_{\mathbf{k}_l}\eta_{\mathbf{k}_m}\eta_{\mathbf{k}_n}\,\delta(\mathbf{k}_j + \mathbf{k}_l + \mathbf{k}_m + \mathbf{k}_n) \quad (3)$$

the $\mathbf{k}$ dependence of the quartic term coefficient B will be neglected for the sake of simplicity.

Taking the hexagonal symmetry of the high-temperature phase, into account the coefficients A and G, when expanded as a function of $\mathbf{k}$, can be written [4] :

$$A(\mathbf{k}_j) = A(T - T_i) + h(k_j^2 - k_0^2)^2 + \\ + \Delta k_j^2 \cos^2(3\phi_j) \quad (4)$$

$$G(\mathbf{k}_j, \mathbf{k}_l, \mathbf{k}_m) = \\ = \sum_{i=j,l,m} \frac{i}{3}(Gk_i^3 + G'k_i)\cos(3\phi_i) \quad (5)$$

where $k_j = |\mathbf{k}_j|$ and ϕ_j is the angle between $\mathbf{k}_j$ and the 2-fold crystallographic axis Ox.

(A slightly different form of the cubic invariant was taken in [4] but it can be easily proved to be equivalent to (Eq. (5)) when the condition $\mathbf{k}_j + \mathbf{k}_l + \mathbf{k}_m = 0$ is taken into account.)

It has been shown in [4] that, for some values of the parameters, F exhibits a minimum for a state corresponding to a symmetric triangular triple-k structure, i.e. when the only non-zero Fourier components in equation (3) are $\eta_{\pm\mathbf{k}_1}$, $\eta_{\pm\mathbf{k}_2}$, $\eta_{\pm\mathbf{k}_3}$ with

$$\begin{cases} \rho_1 = \rho_2 = \rho_3 = \rho\ ; \\ \psi_1 + \psi_2 + \psi_3 = \psi = \pm\dfrac{\pi}{2} \\ k_1 = k_2 = k_3 = k\ ; \\ \cos(3\phi_1) = \cos(3\phi_2) = \\ \cos(3\phi_3) = \cos(3\phi) \end{cases} \quad (6)$$

When relations (6) are inserted into equation (3) one gets

$$F = 3(-t + (k^2-1)^2 + \Delta k^2\cos^2(3\phi))\,\rho^2 \pm \\ \pm 4(Gk^3 + G'k)\cos(3\phi)\,\rho^3 + \frac{45}{2}\rho^4 \quad (7)$$

where the following reduced coordinates have been used in order to simplify the notations :

$$\begin{cases} \dfrac{k}{k_0} \to k\,; \quad \rho \sqrt{\dfrac{B}{hk_0^4}} \to \rho\,; \\[2ex] F \dfrac{B}{(hk_0^4)^2} \to F\,; \quad \dfrac{A(T_i - T)}{hk_0^4} \to t\,; \\[2ex] \dfrac{\Delta k_0^2}{hk_0^4} \to \Delta\,; \quad \dfrac{Gk_0^3}{\sqrt{Bhk_0^4}} \to G\,; \quad \dfrac{G'\,k_0}{\sqrt{Bhk_0^4}} \to G' \end{cases} \tag{8}$$

The + and − signs in (7) correspond to the two possible values of $\sin\psi$. They explain the existence of « macro-domains » in the inc. phase. In the following we shall consider a single-domain state corresponding to $\sin\psi = -1$. In order to keep a symmetric form for the three modulation waves, we choose the origin of the phases such that at equilibrium :

$$\psi_1 = \psi_2 = \psi_3 = \frac{\pi}{2}$$

so that :

$$\eta_{\mathbf{k}_1} = \eta_{\mathbf{k}_2} = \eta_{\mathbf{k}_3} = i\rho\,.$$

The minimization of (7) with respect to ϕ and k leads to :

$$\begin{cases} \cos(3\phi) = \dfrac{2}{3}\left(\dfrac{Gk^2 + G'}{\Delta k}\right)\rho \\[2ex] k^2 = \left(1 + \dfrac{4}{9}\dfrac{GG'}{\Delta}\rho^2\right) \Big/ \left(1 - \dfrac{4}{9}\dfrac{G^2}{\Delta}\rho^2\right). \end{cases} \tag{9}$$

An explicit expression of ρ can only be obtained in the limit $t \to 0$:

$$\rho \simeq \left(\frac{t}{15 - p}\right)^{1/2}$$

with

$$p = \frac{8}{9}\frac{(G + G')^2}{\Delta}\,. \tag{10}$$

The elementary excitations at wave-vector $\mathbf{q}$ are found by calculating the excess free-energy ΔF associated to a change $\Delta\eta(\mathbf{r})$ of the modulated order parameter, of the form :

$$\Delta\eta(\mathbf{r}) = \sum_{j=1,3} (Q_j(\mathbf{q})\,\mathrm{e}^{i(\mathbf{k}_j + \mathbf{q})\cdot\mathbf{r}} + Q_{\bar{j}}(\mathbf{q})\,\mathrm{e}^{i(-\mathbf{k}_j + \mathbf{q})\cdot\mathbf{r}}) \tag{11}$$

the part of ΔF which is quadratic in Q_j, can be written as a matrix dot product :

$$\Delta F = \underset{\sim}{Q}^*(\mathbf{q})\,.\,\underset{\sim}{V}(\mathbf{q})\,.\,\underset{\sim}{Q}(\mathbf{q}) \tag{12}$$

and the (6×6) matrix $\underset{\sim}{V}(\mathbf{q})$ is given by

$$\underset{\sim}{V}(\mathbf{q}) = \begin{bmatrix} \alpha_1 & 2\beta & 2\beta & -\beta & \gamma_3 & \gamma_{\bar{2}} \\ 2\beta & \alpha_2 & 2\beta & \gamma_{\bar{3}} & -\beta & \gamma_1 \\ 2\beta & 2\beta & \alpha_3 & \gamma_2 & \gamma_{\bar{1}} & -\beta \\ -\beta & \gamma_{\bar{3}} & \gamma_2 & \alpha_{\bar{1}} & 2\beta & 2\beta \\ \gamma_3 & -\beta & \gamma_{\bar{1}} & 2\beta & \alpha_{\bar{2}} & 2\beta \\ \gamma_{\bar{2}} & \gamma_1 & -\beta & 2\beta & 2\beta & \alpha_{\bar{3}} \end{bmatrix} \tag{13}$$

with :

$$\begin{cases} \alpha_i(\mathbf{q}) = \alpha_{\bar{i}}(-\mathbf{q}) = A(\mathbf{k}_i + \mathbf{q}) + 18\,B\rho^2 \\ \beta = 3\,B\rho^2 \\ \gamma_i(\mathbf{q}) = \gamma_{\bar{i}}(-\mathbf{q}) \\ \qquad = -2\,i\rho\,G(\mathbf{k}_i, \mathbf{k}_j + \mathbf{q}, \mathbf{k}_l - \mathbf{q}) - 6\,B\rho^2\,. \end{cases} \tag{14}$$

The absence of any zero in $\underset{\sim}{V}(\mathbf{q})$ expresses the fact that the potential created by the frozen-in triple modulation couples together the 6 degenerate modes at $(\pm\,\mathbf{k}_j + \mathbf{q})$.

The eigenfrequencies squared $\omega_j^2(\mathbf{q})$ of the excitations are given by the eigenvalues of $\underset{\sim}{V}(\mathbf{q})$. Let us consider first the case $\mathbf{q} = 0$. Then, one has :

$$\begin{cases} \alpha_i(0) = \alpha_{\bar{i}}(0) = \alpha = -t + (k^2 - 1)^2 + \\ \qquad\qquad + \Delta k^2 \cos^2(3\phi) + 18\,\rho^2 \\ \gamma_i(0) = \gamma_{\bar{i}}(0) = \gamma = 2\,\rho\,(Gk^3 + G'\,k) - 6\,\rho^2 \end{cases} \tag{15}$$

where again the reduced parameters (8) have been used. The matrix $\underset{\sim}{V}(0)$ can be easily diagonalized using the unitary transformation

$$\underset{\sim}{Q}' = \underset{\sim}{P}\,.\,\underset{\sim}{Q}\,.$$

With

$$\underset{\sim}{P} = \frac{1}{\sqrt{6}} \begin{bmatrix} 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & \omega & \omega^* & 1 & \omega & \omega^* \\ 1 & \omega^* & \omega & 1 & \omega^* & \omega \\ 1 & 1 & 1 & -1 & -1 & -1 \\ 1 & \omega & \omega^* & -1 & -\omega & -\omega^* \\ 1 & \omega^* & \omega & -1 & -\omega^* & -\omega \end{bmatrix}; \qquad \omega = \mathrm{e}^{2i\pi/3}\,. \tag{16}$$

For $\mathbf{q} = 0$ excitations, the normal modes Q_j' which diagonalize $\underset{\sim}{V}(0)$, can be classified according to their transformation properties in the symmetry operation of the point group of the inc. structure. In the present case, one can easily establish [13] that this point group is C_6. The symmetry operations of this group send the wave-vectors k_j of the star into each other and the $Q_j'(0)$ normal modes are the linear combinations of the Q_j which transform according to the irreducible representations of this group. This result generalizes that obtained for single-k inc. structure, for which the group of $\mathbf{k}_0$ is C_2 and the normal modes are the symmetric and antisymmetric combinations of the Q_i, associated respectively to the even and to the odd irreducible representation of this group. The eigenvalues of $\underset{\sim}{V}(0)$ and their corresponding eigenvectors are found to be :

$$\omega_{A_1}^2(0) = \alpha + 5\beta - 2\gamma \to A_1 = \frac{1}{\sqrt{6}}(Q_1 + Q_2 + Q_3 - Q_{\bar{1}} - Q_{\bar{2}} - Q_{\bar{3}})$$

$$\omega_{A_2}^2(0) = \omega_{A_3}^2(0) = \alpha - \beta + \gamma \to \begin{cases} A_2 = \frac{1}{\sqrt{6}}(Q_1 + \omega Q_2 + \omega^* Q_3 - Q_{\bar{1}} - \omega Q_{\bar{2}} - \omega^* Q_{\bar{3}}) \\ A_3 = \frac{1}{\sqrt{6}}(Q_1 + \omega^* Q_2 + \omega Q_3 - Q_{\bar{1}} - \omega^* Q_{\bar{2}} - \omega Q_{\bar{3}}) \end{cases}$$

$$\omega_{\phi_1}^2(0) = \alpha + 3\beta + 2\gamma \to \phi_1 = \frac{1}{\sqrt{6}}(Q_1 + Q_2 + Q_3 + Q_{\bar{1}} + Q_{\bar{2}} + Q_{\bar{3}}) \tag{17}$$

$$\omega_{\phi_2}^2(0) = \omega_{\phi_3}^2(0) = \alpha - 3\beta - \gamma \to \begin{cases} \phi_2 = \frac{1}{\sqrt{6}}(Q_1 + \omega Q_2 + \omega^* Q_3 + Q_{\bar{1}} + \omega Q_{\bar{2}} + \omega^* Q_{\bar{3}}) \\ \phi_3 = \frac{1}{\sqrt{6}}(Q_1 + \omega^* Q_2 + \omega Q_3 + Q_{\bar{1}} + \omega^* Q_{\bar{2}} + \omega Q_{\bar{3}} \end{cases}$$

The last two frequencies vanish since :

$$\alpha - 3\beta - \gamma = (-t + (k^2 - 1)^2) + \Delta k^2 \cos^2(3\phi) - \\ - 2\rho k(Gk^2 + G')\cos(3\phi) + 15\rho^2$$

is proportional to $\partial F/\partial \rho$ (see Eq. (7)) and thus vanishes at equilibrium. The other frequencies can be calculated in the limit $t \to 0$:

$$\begin{cases} \omega_{A_1}^2(0) \simeq \frac{3t}{2}\frac{20-p}{15-p} \\ \omega_{A_2}^2(0) = \omega_{A_3}^2(0) \simeq 3t\left(\frac{p-2}{15-p}\right) \\ \omega_{\phi_1}^2 \simeq \frac{9pt}{2(15-p)} \end{cases} \tag{18}$$

(with p as defined in Eq. (10)).

One can note that, owing to the degeneracies of $\omega_{A_2}^2$ and $\omega_{A_3}^2$, the matrix $\underset{\sim}{V}$ can also be diagonalized using a real transformation (associated with the « physically » irreducible representation of C_6). The eigenvectors are in this case :

$$\begin{cases} A_\pm = \frac{1}{\sqrt{2}}(A_2 \pm A_3) \\ \phi_\pm = \frac{1}{\sqrt{2}}(\phi_2 \pm \phi_3). \end{cases} \tag{19}$$

The apparent antisymmetric form of the amplitudon as a function of Q_i, which contrasts with its usual symmetric form in single-k inc. systems, arises from the fact that the equilibrium amplitudes have been taken pure imaginary.

The physical meaning of these eigenvectors is readily pointed out by noting that for $q \to 0$ the complex amplitudes Q_j are related to small uniform changes of η

$$Q_j(0) = \Delta\rho_j e^{i\psi_j} + i\rho_j e^{i\psi_j}\Delta\psi_j \tag{20}$$

so that :

$$\begin{cases} A_1 \propto \Delta\rho_1 + \Delta\rho_2 + \Delta\rho_3 \\ A_+ \propto 2\Delta\rho_1 - \Delta\rho_2 - \Delta\rho_3 \\ A_- \propto \Delta\rho_2 - \Delta\rho_3 \\ \phi_1 \propto (\Delta\psi_1 + \Delta\psi_2 + \Delta\psi_3) \\ \phi_+ \propto \rho(2\Delta\psi_1 - \Delta\psi_2 - \Delta\psi_3) \\ \phi_- \propto \rho(\Delta\psi_2 - \Delta\psi_3) \end{cases} \tag{21}$$

ϕ_+ and ϕ_- correspond to translations of the inc. modulation in the basal plane (along the Ox and Oy axes respectively) and are the gapless phasons. ϕ_1 is the phason associated with a change $\Delta\psi$ and is thus an optic-like excitation.

The A_i are the amplitudon modes. All these modes are illustrated in figure 1. Let us now consider the case $\mathbf{q} \neq 0$. The matrix $\underset{\sim}{V}(\mathbf{q})$ can no longer be easily diagonalized. For sufficiently small q and not too small t the eigenfrequencies can be calculated using a perturbation technique. The matrix $\delta V = \underset{\sim}{V}(q) - \underset{\sim}{V}(0)$ has diagonal terms proportional to q^2, but some of the non-diagonal terms are proportional to q so that a perturbation calculation up to second order is necessary to get the $\omega_j^2(q)$ to lowest order in q. Unfortunately this perturbation method is of limited interest because it is invalid when t goe to zero, since the 6 eigenvalues become degenerate.

Therefore the diagonalization has to be performed numerically in order to determine the behaviour of the eigenfrequencies near the phase transition temperature T_i. Such a calculation has been performed for various sets of the parameters Δ, G and G'. The dispersion curves obtained for $\Delta = 9$, $G = 2$, $G' = 10$ are shown in figure 3 for various temperatures and for two different orientations of the wave-vector $\mathbf{q}$. This particular set of parameters has been chosen because it leads to a temperature dependence of k and ϕ (cf. Fig. 2) in qualitative agreement with those observed in quartz [10, 11]. (A detailed comparison between the phenomenological

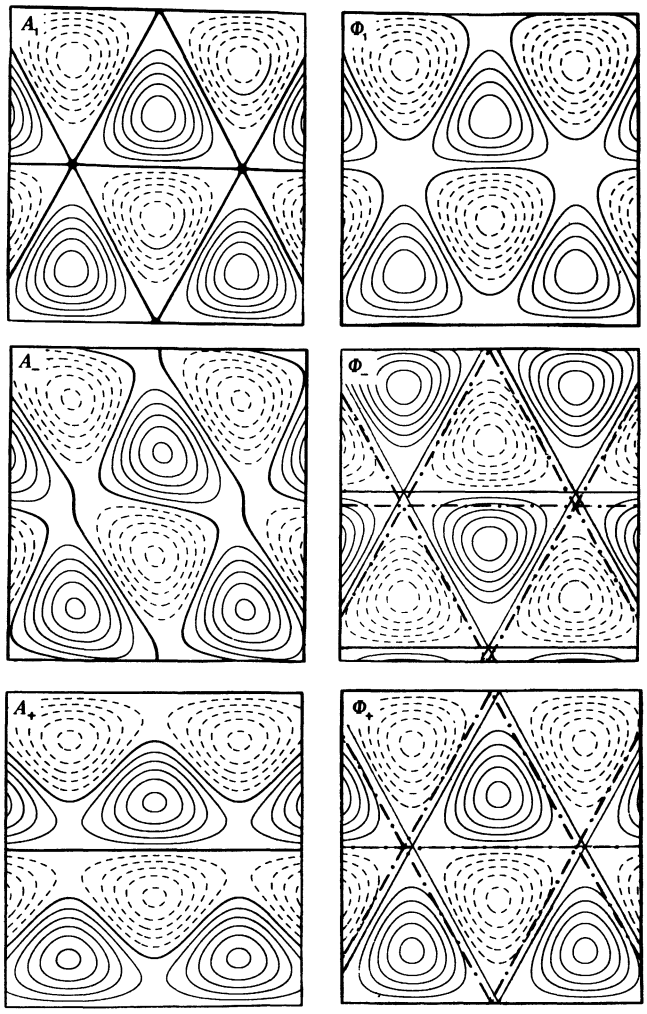

Fig. 1. — Constant amplitude curves for the inc. modulation $\eta(\mathbf{r}) = \eta_0(\mathbf{r}) + \Delta\eta_j(\mathbf{r})$ where $\eta_0(\mathbf{r})$ is the equilibrium value of η and $\Delta\eta_j(\mathbf{r})$ corresponds to each of the six $q = 0$ normal mode excitations.
The dashed curves correspond to $\eta < 0$, the full curves correspond to $\eta \geqslant 0$. The dashed-dotted lines correspond to $\eta_0 = 0$.

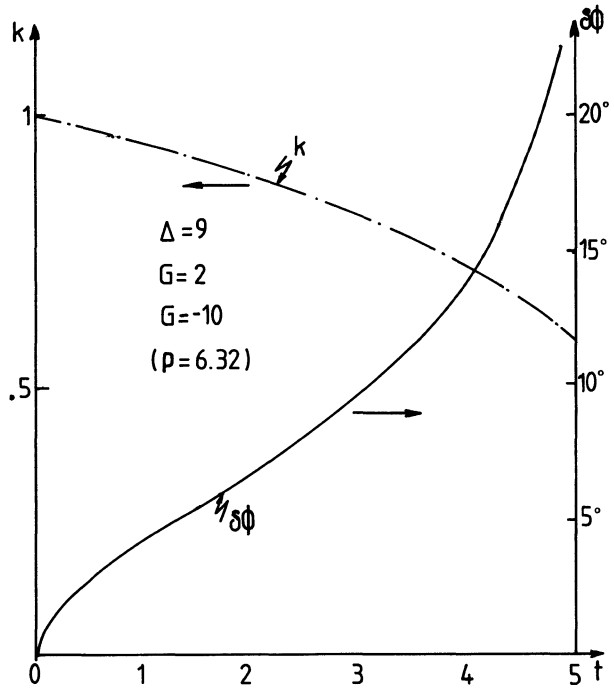

Fig. 2. — Reduced modulation wave-vector k and tilt angle $\delta\phi$ of the equilibrium « 3-k » inc. structure as a function of the reduced temperature t. They are obtained from minimization of the free energy (Eq. (7)) with $\Delta = 9$, $G = 2$ and $G' = -10$.

theory and experimental observations will be given in a forthcoming paper).

When considering the dispersion curves of figures 3 and 4 some points of special interest can be noted :

i) The slopes of the acoustic-like phasons at $\mathbf{q} = 0$, just below T_i are different from the slopes of the soft-mode at $T = T_i$, in the vicinity of the modulation wave-vector k_i.

This phenomenon is analogous to the discontinuity of the sound velocity observed at a 2nd order transition point. This discontinuity of the phason velocity arises in the present case from the dependence of the phason frequency upon the parameters G and G', for $T < T_i$.

ii) The anisotropy of the dispersion curves changes drastically with t and/or q. For small q and sufficiently large t, the dispersion curves are isotropic in the (001) plane. This is in agreement with the point group symmetry of the inc. phase (C_6 for the triangular structure) : when the q dependence of $\omega_j^2(q)$ is dominated by the quadratic terms ($\propto q^2$), the dispersion curves are expected to be isotropic in this plane. On the contrary for large q (or sufficiently small t) one recovers the anisotropy of the uncoupled excitations, characterized by the parameter Δ (quite large in the present case).

iii) The eigenvectors of the amplitudons A_2, A_3 and of the phasons ϕ_2 and ϕ_3 exhibit a strong wave-vector dependence associated with « anticrossing » effects quite visible in figure 3. The smaller t is, the narrower the range of wave-vector over which the excitations keep their pure phason or amplitudon character.

These effects are also a consequence of the existence of the cubic terms (Eq. (2)).

3. Possibility of a phase transition induced by a phason instability.

As discussed in (4) several types of inc. structures can be found according to the values of the parameters in the free energy (Eq. (3)). In order to be a possible equilibrium state, the « triple-k » triangular state defined by (Eq. (6)) has to correspond to a local minimum of the free energy F considered as a

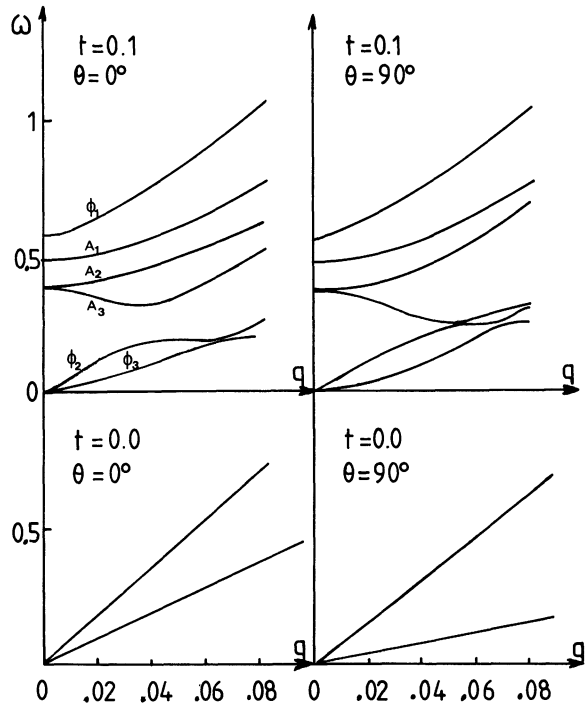

Fig. 3. — Dispersion curves of the 6 excitations of the inc. phase at small q wave-vectors. t is the reduced temperature measured from T_i and θ is the angle between q and the Ox cristallographic axis. $t = 0.0$ curves correspond to the set of dispersion curves of the soft mode at $T = T_i$, in the vicinity of the 6 modulation wave-vectors k_i.

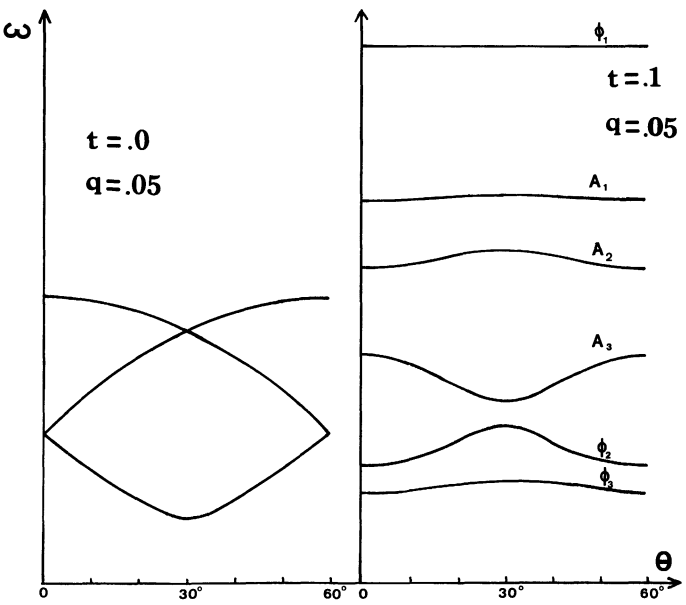

Fig. 4. — Same dispersion curves as in figure 3 plotted as a function of θ at constant q, in order to show the temperature dependence of the anisotropy.

function of the 12 parameters: ρ_i, ψ_i, k_i, ϕ_i ($i = 1$ to 3). Among these 12 parameters, 8 only are relevant, since F depends on ψ_i only through $\psi = \sum_i \psi_i$ and the δ function in equation (3) implies that $\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 = 0$. The stability of the state requires that the (8×8) matrix of the second derivatives $(\partial^2 F \backslash \partial x_i \, \partial x_j)$ be definite positive. The calculations can be most easily performed when using as independent variables ($\bar{\rho}$, ρ', ρ'', $\bar{\phi}$, ϕ', ϕ'', $\bar{k}$, $\bar{\psi}$) defined by:

$$\begin{cases} \bar{x} = \dfrac{1}{\sqrt{3}} (x_1 + x_2 + x_3) \\ x' = \dfrac{1}{\sqrt{6}} (2 x_1 - x_2 - x_3) \\ x'' = \dfrac{1}{\sqrt{2}} (x_2 - x_3) \\ (x = \rho, \phi, k, \psi) . \end{cases} \tag{22}$$

The matrix $(\partial^2 F / \partial x_i \, \partial x_j)$ can then be decomposed into three block diagonal matrices which involve respectively the second derivatives with respect to ($\bar{\rho}$, $\bar{\phi}$, $\bar{k}$), to $\bar{\psi}$ and to (ρ', ρ'', ϕ', ϕ'').

In the limit $t \to 0$, the stability condition can be simply written:

$$15 > p > p_0 = 6 \left(\frac{\Delta + 4/9}{\Delta + 4/3} \right) . \tag{23}$$

The upper bound for p corresponds to the fact that higher order terms are required to stabilize F for $t < 0$ and $p > 15$. (First order transition above T_i). The lower bound p_0 lies (for $\Delta > 0$) between 2 and 6. For $p < 6$ it has been shown in [4] that the « single-k » state is more stable than the « triple-k » state. For $p_0 < p < 6$, however, the « triple-k » state remains « locally » stable and one can readily check that the squared eigenfrequencies (Eq. (18)) are actually all positive. A question then arises: what kind of instability occurs near $p = p_0$? Numerical calculations show that the slope of the lowest phason branch becomes negative for $p < p_0$. The situation is then similar to that found for a ferroelastic phase transition, for which the instability of the lattice against a homogeneous strain is accompanied by the vanishing of a sound wave velocity (12). The analog of the strains are in our case the gradients of the phases $\nabla_j \psi_i(\mathbf{r})$, i.e. the wave-vectors $\mathbf{k}_i$ in the plane-wave approximation and $\mathbf{q} = 0$ limit. The distorted inc. phase corresponds to changes in the wave-vectors k_j, both in length and in orientation and the inc. structure is a homogeneously strained triangular lattice. Numerical calculations show that for $\Delta = 9$, $G = 2$, $G' = -8.7$ ($p = 4.43 < p_0$), the ferroelastic-like transition occurs when varying the temperature (see Fig. 5). It seems that the cubic terms (G and G') act as a « piezoelectric-like » coupling between the amplitudons (A_2, A_3) and the phason (ϕ_2, ϕ_3) and the decrease of the frequency ω_{A_2} when t goes to zero induces the phason instability (the stability limit

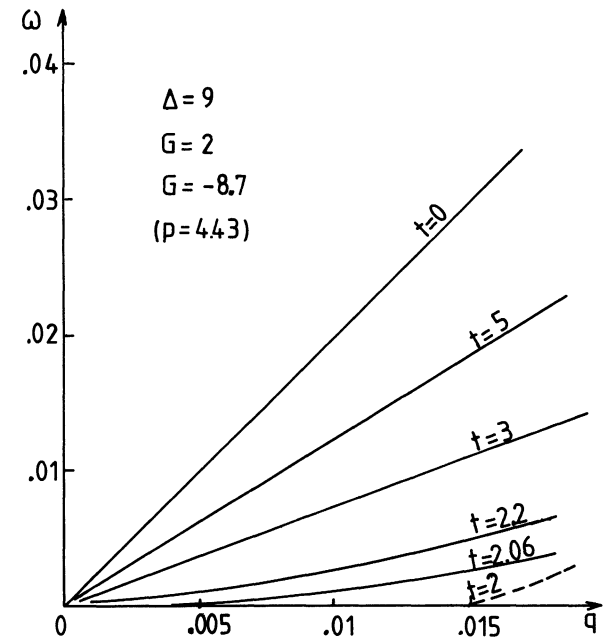

Fig. 5. — Temperature dependence of the lowest phason dispersion branch indicating a « ferroelastic » like instability of the incommensurate structure for the values of the parameters $\Delta = 9$, $G = 2$ and $G' = -8.7$.

p_0, given in equation (23) for $t = 0$, is then a decreasing function of t).

The present discussion is probably not relevant for quartz since the triple-k structure seems to be stable in this material. One can guess, however, that a phase transition between two different triple-k inc. phases, induced by a phason instability could well be found in other systems.

4. Infrared and Raman activity of phasons and amplitudons.

The optical activity of excitations can be discussed by assuming that the optical wavelength is far larger than the modulation wavelength. The selection rules can then be established by classifying these excitations according to the irreducible representations of the point group of the inc. phase. This point group can be defined as the group of symmetry elements which leave the system invariant, except for an irrelevant phase shift [13]. One can thus easily see that the triple-k triangular inc. structure of quartz belongs to the point group C_6. The way the amplitudons A_i and the phasons ϕ_i transform, can be derived by expressing $\Delta\eta(\mathbf{r})$ as a function of these coordinates (using Eqs. (11) and (17)) :

$$\Delta\eta(\mathbf{r}) = \sum_{i=1 \text{ to } 3} (A_i(0)\, C_i(\mathbf{r}) + \phi_i(0)\, d_i(\mathbf{r})) \quad (24)$$

The functions $C_i(\mathbf{r})$ and $d_i(\mathbf{r})$ are simple combinations of the $\exp(\pm i\mathbf{K}\cdot\mathbf{r})$ which transform as irreducible representations of C_6 and one can thus deduce the transformation properties of A_i and ϕ_i. The results are summarized in table I.

The infrared and Raman activity selection rules can then be established as for phonons. One must distinguish the case of optic-like excitations (A_1, A_2, A_3, ϕ_1) and that of acoustic-like excitations (ϕ_2, ϕ_3) [3, 14]. For the former ones, the mode is infrared (respectively Raman) active if it transforms as a vector component P_i (resp.) a symmetric 2nd rank tensor component α_{ij}. For the gapless phasons, one must consider the transformation properties of $(q_i\, \phi_j)$, associated with the gradient of the phases and analogous to the strain tensor. The results are summarized in table I. It is noticeable that the excitation ϕ_1 is silent (infrared and Raman inactive).

Table I. — *Infrared and Raman activity of the amplitudons and phasons, deduced from their symmetry properties in the point group of the* 3-k *inc. phase of quartz* (C_6). *The upper part of the table indicates the selection rules for the optic-like excitations and the lower part for the acoustic-like excitations* (*gapless phasons*).

Excitations	Irr. represent.	Infrared	Raman
A_1	A	P_z	$\alpha_{xx} + \alpha_{yy}$, α_{zz}
A_2	E_1'	—	$(\alpha_{xx} - \alpha_{yy}) - 2\, i\alpha_{xy}$
A_3	E_1''	—	$(\alpha_{xx} - \alpha_{yy}) + 2\, i\alpha_{xy}$
ϕ_1	B	—	—
ϕ_2	E_2'		
ϕ_3	E_2''		
$q_-\, \phi_2$	A	P_z	$\alpha_{xx} + \alpha_{yy}$, α_{zz}
$q_+\, \phi_3$	A	P_z	$\alpha_{xx} + \alpha_{yy}$, α_{zz}
$q_+\, \phi_2$	E_1''	—	$(\alpha_{xx} - \alpha_{yy}) + 2\, i\alpha_{xy}$
$q_-\, \phi_3$	E_1'	—	$(\alpha_{xx} - \alpha_{yy}) - 2\, i\alpha_{xy}$
$q_z\, \phi_2$	E_2'	$P_x + iP_y$	$\alpha_{xz} + i\alpha_{yz}$
$q_z\, \phi_3$	E_2''	$P_x - iP_y$	$\alpha_{xz} - i\alpha_{yz}$

$q_\pm = q_x \pm iq_y$

In the preceding sections we only considered the dispersion curves for wave-vectors lying in the (0, 0, 1) plane, nothing new being expected when they lie in the other planes. For the sake of completeness we give the selection rules for arbitrary direction of the wave-vector in table I.

An alternative way to establish the preceding selection-rules is to build the various invariants of the high-temperature phase, which involve a uniform polarization component P_i (or polarizability component α_{ij}) and powers of the order-parameter η and of its spatial derivatives [14, 15].

Discarding the invariants which are exact derivatives and which thus vanish after integrations, the other ones allow a determination of the kind of coupling which exists between P_i (or α_{ij}) and the excitation eigenvectors A_i or ϕ_i. Limiting ourselves

to lowest order terms, two types of invariants have to be considered :

$$\begin{cases} c(\mathbf{k}_i + \mathbf{q})\, \eta_{\mathbf{k}_i}\, \eta_{-\mathbf{k}_i+\mathbf{q}}\, X_{\mathbf{q}}^* \\ [c(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3 + \mathbf{q})\, \eta_{\mathbf{k}_1}\, \eta_{\mathbf{k}_2}\, \eta_{\mathbf{k}_3+\mathbf{q}}\, X_{\mathbf{q}}^* + \text{c.p.}] \end{cases} \tag{25}$$

(where X stands for P_i or α_{ij} and c.p. means « cyclic permutation » over the indices).

$\eta_{\mathbf{k}_i+\mathbf{q}}$ is then expressed as a function of $A_i(\mathbf{q})$ and $\phi_i(\mathbf{q})$ while $\eta_{\mathbf{k}_i}$ is taken at its equilibrium value $\eta_{\mathbf{k}_i} = i\rho$. For optic-like excitations it is sufficient to consider equation (22) for $q = 0$, but for acoustic-like excitations one has to keep terms linear in q. Since the infrared (or Raman) efficiency is proportional of the coupling terms (Eq. (25)), this method presents the advantage to provide information concerning the temperature dependence of this efficiency. The various invariants, expressed as a function of ρ (the order parameter amplitude), k_0 and δ (the tilt angle of the inc. wave vectors from their direction at $T = T_i$) are listed in table II. (let us recall that $\delta \propto \rho \propto (T_i - T)^{1/2}$).

The results are obviously in agreement with the selection rules derived by group-theory, but they disagree with those given in reference [8] concerning the phasons. The origin of the discrepancy could arise from the fact that Shinoya *et al.* implicitly assume that the cubic term coefficient (B with their notation) does not vanish at T_i whereas it contains a term $\cos 3\,\phi$ (see Eqs. (7), (9)).

5. Concluding remarks.

The whole analysis presented in this paper is based on the free energy (Eq. 3). This form of the free-energy has been obtained after elimination of the elastic degrees of freedom so that the coupling between the order parameter η and the strain field u_{ij} does not appear explicitly in our treatment. A more rigorous approach would consist in studying the dynamics of the acoustic phonons and of the phasons and amplitudons simultaneously (terms like $(\mathbf{q}\cdot\mathbf{U}_q)\, \eta^*_{-\mathbf{k}_i+\mathbf{q}}\, \eta_{\mathbf{k}_i}$ for example couple acoustic phonons near $q = 0$ bilinearly with the excitation coordinates Q_{ki}). This kind of coupling was previous-

Table II. — *List of the lowest order terms invariant in the symmetry operations of the β-phase of quartz, which couples a vector component P_i, or a symmetric 2nd peak tensor component α_{ij}, with the α-β order parameter η or its first derivatives ($\partial\eta/\partial x_j$). (Only terms which are not exact derivatives have been retained.) The column on the right hand side, indicates the corresponding invariants which involve the excitation coordinates and P_i or α_{ij}. ρ is the amplitude and k_0 wave-vector length of the inc. modulation wave. δ is the tilt angle of the wave vector from the $\langle 1, 0, 0 \rangle$ crystallographic directions.*

$\left(\frac{\partial\eta}{\partial z}\right)\left[\frac{\partial\eta}{\partial y} P_x - \frac{\partial\eta}{\partial x} P_y\right]$	$\rho k_0[(P_x + iP_y)\, q_z\, \Phi_2\, e^{i\delta} + (P_x - iP_y)\, q_z\, \Phi_3\, e^{-i\delta}]$
$\left[\left(\frac{\partial\eta}{\partial y}\right)^3 - 3\left(\frac{\partial\eta}{\partial x}\right)^2\left(\frac{\partial\eta}{\partial y}\right)\right] P_z$	$\rho^2\, k_0^3\, P_z\, A_1\, \cos 3\,\delta$ $i\rho^2\, k_0^2\, P_z[q_-\, \Phi_2\, e^{2i\delta} - q_+\, \Phi_3\, e^{-2i\delta}]$
$\eta^2(\alpha_{xx} + \alpha_{yy})$ $\eta^2(\alpha_{zz})$	$\rho(\alpha_{xx} + \alpha_{yy})\, A_1$ $\rho\alpha_{zz}\, A_1$
$\left[\left(\frac{\partial\eta}{\partial x}\right)^2 + \left(\frac{\partial\eta}{\partial y}\right)^2\right](\alpha_{xx} + \alpha_{yy})$ $\left[\left(\frac{\partial\eta}{\partial x}\right)^2 + \left(\frac{\partial\eta}{\partial y}\right)^2\right]\alpha_{zz}$	$i\rho k_0 \left\{\begin{matrix} \alpha_{xx} + \alpha_{yy} \\ \alpha_{zz} \end{matrix}\right\} [q_-\, \Phi_2\, e^{i\delta} - q_+\, \Phi_3\, e^{-i\delta}]$
$\left[\left(\frac{\partial\eta}{\partial x}\right)^2 - \left(\frac{\partial\eta}{\partial y}\right)^2\right](\alpha_{xx} - \alpha_{yy}) + 4\left(\frac{\partial\eta}{\partial x}\right)\left(\frac{\partial\eta}{\partial y}\right)\alpha_{xy}$	$i\rho k_0^2[(\alpha_{xx} - \alpha_{yy} - 2\, i\alpha_{xy})\, A_2\, e^{2i\delta} -$ $- (\alpha_{xx} - \alpha_{yy} + 2\, i\alpha_{xy})\, A_3\, e^{-2i\delta}]$ $i\rho k_0[(\alpha_{xx} - \alpha_{yy} + 2\, i\alpha_{xy})\, q + \Phi_2\, e^{-i\delta} -$ $- (\alpha_{xx} - \alpha_{yy} - 2\, i\alpha_{xy})\, q_-\, \Phi_3\, e^{-i\delta}]$
$\left(\frac{\partial\eta}{\partial z}\right)\left[\frac{\partial\eta}{\partial x}\alpha_{xz} + \frac{\partial\eta}{\partial y}\alpha_{yz}\right]$	$i\rho k_0[(\alpha_{xz} + i\alpha_{yz})\, q_z\, \Phi_2\, e^{i\delta} -$ $- (\alpha_{xz} - i\alpha_{yz})\, q_z\, \Phi_3\, e^{-i\delta}]$

ly considered for amplitudons by Hirotsu *et al.* [15] and for phasons by Bruce *et al.* [2] and Poulet *et al.* [3]. In the case of quartz it has been discussed by Walker *et al.* [7]. These authors, on another hand, did not consider the optic-like excitations which play an important role in the shape of the dispersion curves of the phasons, as shown in section 2.

The damping of the excitations was also ignored in the present work. However, nothing qualitatively new is expected for « triple-k » inc. structures, compared to the usual « single-k » case. Phason and amplitudon damping is roughly given by that of the soft mode at k_i in the high temperature phase [14, 17]. In quartz-type crystals neutron scattering experiments [18] indicate that this damping is rather large ($\simeq$ 0.3 to 0.7 THz) so that the phasons and probably also the amplitudons are overdamped over the whole range of temperatures of the inc. phase. This makes a direct experimental observation of these modes quite difficult. It is likely that a large amount of the central component intensity observed in Raman and Brillouin scatterings [19] is related to these excitations, since this intensity shows a maximum in the inc. phase. The indirect effect of phasons and amplitudons on the sound wave velocity dispersion [7, 14, 20] could be another way to get information about the eigen frequencies of these excitations.

To conclude, we have shown that the spectrum of the low frequency excitations of the triple-k inc. phase of quartz-type crystals is composed of two gapless phasons and four optic-like other excitations, one of which corresponds to fluctuations of the sum of the phases of the 3 modulation waves. We have pointed out the special role played by the cubic invariant term on the shape of the dispersion curves and in particular our phenomenological model suggests the possibility of a phase transition between two triple-k inc. structures induced by a phason velocity softening which results from the presence of this cubic invariant. Such an instability, however, occurs when the triple-k structure is only metastable ; it would be interesting to look for other phenomenological models for which it would actually occur in the domain of stability of the triple-k structure.

Acknowledgment.

One of the authors (V.D.) expresses his thanks to members of Laboratoire de Spectrométrie Physique, in particular to all members of the group Transitions de phases structurales, for their warm hospitality extended to him during his stay there.

References

[1] AXE, J. D., Proc. Conf. neutron scattering, Gatlinburg, Tennessee (1976).

[2] BRUCE, A. D. and COWLEY, R., *J. Phys.* **C 11** (1978) 3609.

[3] POULET, H. and PICK, R. M., *J. Phys.* **C 14** (1981) 2675.

[4] ASLANYAN, T. A., LEVANYUK, A. P., VALLADE, M., LAJZEROWICZ, J., *J. Phys.* **C 16** (1983) 6705.

[5] DOLINO, G., in *Incommensurate phases in Dielectrics,* vol. 2, ch. 16, R. Blinc and A. P. Levanyuk ed. (North Holland) 1986.

[6] VALLADE, M., Proceedings of the 2nd International Conference on phonon physics, (Budapest 1985) p. 266, J. Kollar, N. Kroo, N. Menyhard, T. Siklos ed.

[7] WALKER, M. B. and GOODDING, R. J., *Phys. Rev.* **B 32** (1985) 7412.

[8] SHIONOYA, J., ABE, K. and SHIGENARI, T., *J. Phys.* **C 19** (1986) 4547.

[9] ASLANYAN, T. A. and LEVANYUK, A. P., *Solid State Commun.* **31** (1979) 547.

[10] BASTIE, P. and DOLINO, G., *Phys. Rev.* **B 31** (1985) 2857.

[11] GOUHARA, R. and KATO, N., *J. Phys. Soc. Jpn.* **53** (1984) 2177.

[12] AUBRY, S. and PICK, R., *J. Physique* **32** (1971) 657.

[13] DVORAK, V., JANOVEC, V. and ISHIBASHI, Y., *J. Phys. Soc. Jpn.* **52** (1983) 2053.

[14] GOLOVKO, V. A. and LEVANYUK, A. P., in *Light Scattering near phase transitions,* ch. 3, H. Z. Cummins and A. P. Levanyuk ed. (North Holland) 1983.

[15] HIROTSU, S., TOYOTA, K. and HAMANO, K., *J. Phys. Soc. Japan* **46** (1979) 1389.

[16] DVORAK, V. and PETZELT, J., *J. Phys.* **C 11** (1978) 4827.

[17] ZEYHER, R. and FINGER, N., *Phys. Rev. Lett.* **49** (1982) 1933.

[18] BERGE, B., BACHHEIMER, J. P., DOLINO, G., VALLADE, M. and ZEYEN, C. M. E., *Ferroelectrics* **66** (1986) 73.

[19] BERGE, B., VALLADE, M. and MARTINEZ, G., *J. Phys.* **C 17** (1984) L 167.

[20] SCOTT, J. F., *Ferroelectrics* **47** (1983) 33.