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Amplitude-mode polaritons in the incommensurate phase of quartz

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The polar character of the *A*-symmetry amplitude mode in the incommensurate phase of quartz is emphasized, and the dispersion relation of the coupled electromagnetic field and amplitude-mode oscillations (i.e., the amplitude-mode polariton) is derived.

I. INTRODUCTION

Incommensurate crystals are expected to have special branches of vibrational excitations. The existence of a phason branch of the excitation spectrum was first suggested by Overhauser,[1] the existence of an amplitude-mode branch of the spectrum was suggested by Lee *et al.*,[2] and a number of authors have since studied the amplitudon-phason vibrational frequencies for various incommensurate models (e.g., see Refs. 3–7 and references therein).

It is known that in ordinary periodic crystals the zero-wave-vector normal modes of a crystal often contain modes which have a polar character, i.e., modes which transform like the x,y, or z components of a polar vector. A distortion of the crystal which is described by a polar normal mode is necessarily accompanied by the production of an electric dipole moment and an electric field. The description of the vibrations associated with polar modes must therefore take into account the coupling of the polar mode to the electric field (e.g., see Born and Huang,[8] or Hayes and Loudon[9]).

The fact that the phason or amplitude-mode vibrations of an incommensurate crystal can have polar character seems to have been ignored in the literature up to the present. The main purpose of this article is to emphasize that phasons and amplitude modes can have polar character, and when this is the case, the coupling of the polar mode to the electric field must be taken into account. These ideas are illustrated by studying in detail the particular case of the incommensurate phase of quartz.

Quartz has a high-temperature β phase and a low-temperature α phase, with the phase transition between these two phases occurring at approximately 845 K. The crystal structures of these two phases are illustrated schematically in Fig. 1. Relatively recently, it was discovered[10] that a triangular incommensurate phase exists over a relatively narrow temperature interval of about one degree of 845 K. Thus the phase transition from the β to the α phase as the temperature is lowered is not direct, but must proceed through the incommensurate phase. In the incommensurate phase, the order parameter η (defined[11] in Fig. 1) varies spatially and is given by

$$\eta(\mathbf{r})=\sum_{i=1}^{3} a_i \sin(\mathbf{q}_i\cdot\mathbf{r}+\psi_i) \;, \tag{1}$$

where the $\mathbf{q}_i$ are three wave vectors lying in the basal plane, making angles of 120° with one another and aligned approximately (but not exactly) along reciprocal lattice directions. The incommensurate phase of quartz has been studied extensively both theoretically and experimentally; a more detailed discussion and references to the literature can be found in Refs. 6, 7, and 10–12.

To study the amplitude-mode and phason vibrations of the incommensurate phase of quartz, one writes a_i and ψ_i of Eq. (1) in the form $a_i=a_i^0+\delta a_i$ and $\psi_i=\psi_i^0+\delta\psi_i$, where the a_i^0 and ψ_i^0 are the values appropriate to the equilibrium state, and the six quantities δa_i and $\delta\psi_i$ are small oscillating quantities. To proceed further, one introduces appropriate normal coordinates, i.e., coordinates which transform according to the irreducible representations of the point group[12] C_6 of the incommensurate phase. These coordinates are[7,13]

$$\begin{aligned}
&Q_A=\delta a_1+\delta a_2+\delta a_3 \;,\\
&Q_{E_1'}=2\delta a_1-\delta a_2-\delta a_3 \;,\\
&Q_{E_1''}=\delta a_2-\delta a_3 \;,\\
&Q_B=\delta\psi_1+\delta\psi_2+\delta\psi_3 \;,\\
&Q_{E_2'}=2\delta\psi_1-\delta\psi_2-\delta\psi_3 \;,\\
&Q_{E_2''}=\delta\psi_2-\delta\psi_3 \;,
\end{aligned} \tag{2}$$

and describe the vibrations of two nondegenerate (A and B) normal modes and two doubly-degenerate (E_1 and E_2) normal modes.

Although the doubly-degenerate mode described by the coordinates $Q_{E_2'}$ and $Q_{E_2''}$ has a polar character (since the coordinates transform like the spatial coordinates x,y under operations of the point group C_6 of the incommensurate phase—throughout the article the z axis is assumed to be the axis of hexagonal symmetry), they are phason branches of the excitation spectrum which have zero frequency (at infinite wavelength). Thus they require special treatment, which has already been given,[14] and will not be described further in this article. The coordinate Q_A, on the other hand is an amplitude mode with a nonzero frequency; it transforms like the spatial coordinate z and is the only other coordinate which is polar. The remainder of the article will focus on a description of the vibrations associated with the coordinate Q_A.

As mentioned above, a polar mode in a crystal produces a lattice polarization which in turn generates an electric field. Coupled polar-mode and electromagnetic field vibrations have become known as polaritons. The polariton dispersion relation for cubic crystals was first derived by Huang[8,15] and the first observation of light scattering from polaritons was by Henry and Hopfield[16] on GaP. The experimental and theoretical study of polaritons has been extensive (e.g., see the reviews by Mills and Burstein[17] and by Claus *et al.*[18]).

The polariton behavior of the Q_A mode (see above) of the incommensurate phase of quartz can be fully investigated by adapting the results for uniaxial crystals described in the reviews[17,18] just mentioned. In our case, the analysis is particularly simple, as only one polar mode, Q_A, need be considered: The other polar modes, which also occur in the normal phase of quartz (these are the usual infrared-active zone-center normal modes), occur at much higher frequencies than the Q_A mode and can hence be ignored.

II. THE AMPLITUDE-MODE POLARITON DISPERSION RELATION

Electromagnetic radiation in matter is described by Maxwell's equations, which, for a wave with frequency ω and wave vector $\mathbf{q}$, become

$$\mathbf{q}\times(\mathbf{q}\times\mathbf{E})+\frac{\omega^2}{c^2}\epsilon(\omega)\cdot\mathbf{E}=0 \ . \tag{3}$$

In writing Eq. (3) we have assumed a small amplitude of propagation for which the medium will respond linearly to the incident fields. The magnetic permeability has been set equal to unity, for we are dealing with a dielectric crystal, and the effects of spatial dispersion have been ignored. In the frequency range of interest ($\omega \sim 10$ cm^{-1}) the electromagnetic waves that couple strongly to the amplitude mode have very long wavelengths compared with the lattice spacing and we can confine ourselves to the form of the dielectric tensor in the limit $\mathbf{q}\rightarrow 0$.

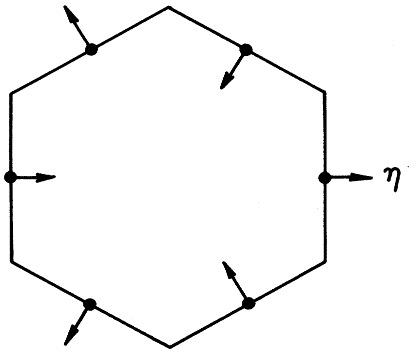

FIG. 1. Projection onto the basal plane of the positions of the silicon ions in a Wigner-Seitz unit cell of the quartz crystal structure. The solid circles represent the positions of the ions in the high temperature β-phase and the arrows show the directions of the displacements which these ions undergo in the transition to the α-phase. An order parameter η describing the β to α phase transition can be defined as having a magnitude equal to the displacement of one of the silicon ions, and a sign which is positive if the displacement is in the direction shown, and negative if the displacement is in the opposite direction.

For uniaxial crystals, the dielectric functions are identical for two principal directions which describe the optically isotropic plane, i.e., $\epsilon_x(\omega)=\epsilon_y(\omega)=\epsilon_\perp(\omega)$; for the third principal direction, which is perpendicular to this plane, the dielectric function is $\epsilon_z(\omega)=\epsilon_\parallel(\omega)$. Here $\perp$ and $\parallel$ denote directions perpendicular and parallel to the optic axis.

In developing a description of the polariton behavior in the incommensurate phase of quartz, we follow the harmonic approximation of the potential energy approach described by Cochran and Cowley.[19] In the frequency region of interest, the amplitude mode Q_A is the only polar mode, and it transforms as the z component of the polarization with the z axis being the axis of hexagonal symmetry. The free energy is therefore

$$F=\tfrac{1}{2}b_1Q_A^2+b_2Q_AE_z+\frac{1}{8\pi}[\epsilon_{ij}(\infty)-\delta_{ij}]E_iE_j \ . \tag{4}$$

Here $\epsilon_{ij}(\infty)$ represents the contribution to the dielectric function from sources of polarization other than the incommensurate excitations.

The equations of motion and the macroscopic polarization are derived from Eq. (4) as

$$\ddot{Q}_A=\frac{\partial F}{\partial Q_A}=b_1Q_A+b_2E_z \ , \tag{5a}$$

$$P_i=\frac{\partial F}{\partial E_i}=\delta_{i3}b_2Q_A+\frac{1}{4\pi}[\epsilon_i(\infty)-1]E_i \ . \tag{5b}$$

By assuming a harmonic time dependence eliminating Q_A in favor of E_z and taking into account the constitutive relation $\epsilon(\omega)\cdot\mathbf{E}=\mathbf{E}+4\pi\mathbf{P}$, one obtains

$$\epsilon_\parallel(\omega)=\epsilon_\parallel(\infty)+\frac{4\pi b_2^2}{\omega_A^2-\omega^2}=\epsilon_\parallel(\infty)\frac{\omega_{\parallel L}^2-\omega^2}{\omega_A^2-\omega^2} \tag{6}$$

where $\omega_{\parallel L}^2=[\epsilon_\parallel(0)/\epsilon_\parallel(\infty)]\omega_A^2$ is the longitudinal optic (LO) frequency and $\omega_A^2=-b_1$ is the infrared dispersion frequency. Also $\epsilon_\perp(\omega)=\epsilon_\perp$, which is independent of frequency.

The dependence of the frequency on the wave vector can be obtained from Eqs. (3) and (6). To this end, we can assume without loss of generality, that $\mathbf{q}$ lies in the xz plane (a plane containing the optic axis). Due to the invariance of the dielectric tensor with respect to rotations about the z axis the frequency can depend only on the angle between the wave vector and the optic axis. Let this angle be θ and note that

$$q_x=q\sin\theta, \quad q_z=q\cos\theta \ . \tag{7}$$

From Eq. (3) one obtains[17]

$$\left[\frac{\omega^2}{c^2q^2}\epsilon_\perp-\cos^2\theta\right]E_x+\sin\theta\cos\theta\,E_z=0 \ , \tag{8a}$$

$$\left[\frac{\omega^2}{c^2q^2}\epsilon_\perp-1\right]E_y=0 \ , \tag{8b}$$

$$\sin\theta\cos\theta\,E_x+\left[\frac{\omega^2}{c^2q^2}\epsilon_\parallel(\omega)-\sin^2\theta\right]E_z=0 \ . \tag{8c}$$

Equation (8b) shows that for the incommensurate phase of quartz, an ordinary wave whose phase velocity is nondispersive and independent of the orientation of the wave vector propagates in the medium with its electric field polarized perpendicular to the plane formed by the wave vector and the optic axis. In this case there is no contribution to the polarization from the lattice motion; the wave is a purely electromagnetic wave in a dielectric medium.

When the electric field lies in the xz plane, one obtains the extraordinary amplitude-mode polariton dispersion law, for which the phase velocity is a function of the frequency and of the orientation of the wave vector with respect to the optic axis. The dispersion law which follows from (8a) and (8c) is

$$\omega^4-\omega^2\left[c^2q^2\left[\frac{\sin^2\theta}{\epsilon_{\parallel}(\infty)}+\frac{\cos^2\theta}{\epsilon_{\perp}}\right]+\omega_{\parallel L}^2\right]+c^2q^2\omega_{\parallel L}^2\left[\frac{\sin^2\theta}{\epsilon_{\parallel}(0)}+\frac{\cos^2\theta}{\epsilon_{\perp}}\right]=0\ . \qquad (9)$$

Unlike the general case for an uniaxial crystal for which $\epsilon_{\perp}$ is a function of frequency, a closed analytic expression for the dispersion relation results in the particular case studied here. Fig. 2 shows this dispersion relation for the extraordinary amplitude-mode polariton for several angles. This dispersion relation possesses two branches. For $q \rightarrow 0$, the frequency of the upper branch approaches the value $\omega=\omega_{\parallel L}$ whatever the orientation of $\mathbf{q}$ relative to the optic axis. The frequency of the lower branch goes to zero as q goes to zero with slope $c/n_e(0)$, where

$$n_e^{-2}(0)=\frac{\sin^2\theta}{\epsilon_{\parallel}(0)}+\frac{\cos^2\theta}{\epsilon_{\perp}}\ . \qquad (10)$$

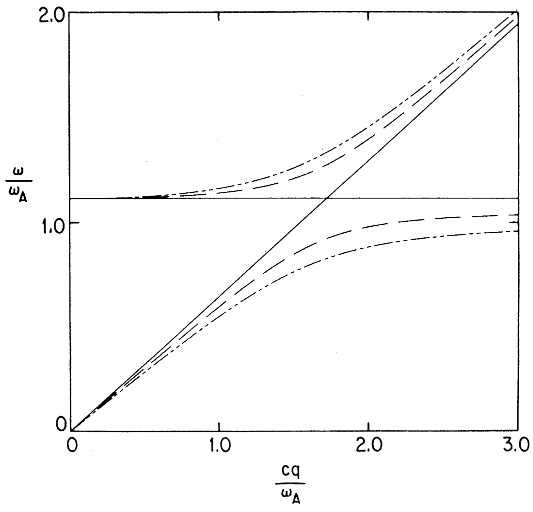

FIG. 2. Dispersion relation for the amplitudon-polariton for different values of θ, the angle between the wave vector and the optic axis. The solid lines correspond to $\theta=0$, the dashed lines to $\theta=45°$ and the dashed dotted lines to $\theta=90°$, for the values $\epsilon_{\perp}=2.3839$, $\epsilon_{\parallel}(\infty)=2.4118$, $\epsilon_{\parallel}(0)=3.00$.

For $q \rightarrow \infty$, the upper branch exhibits a linear variation of frequency with wave vector which is characterized by the phase velocity $c/n_e(\infty)$ where

$$n_e^{-2}(\infty)=\frac{\sin^2\theta}{\epsilon_{\parallel}(\infty)}+\frac{\cos^2\theta}{\epsilon_{\perp}}\ . \qquad (11)$$

On the other hand, the lower branch at large wave vectors has a frequency which is independent of the magnitude of the wave vector, and which is given by

$$\omega=\omega_{\parallel L}\frac{n_e(\infty)}{n_e(0)}\ . \qquad (12)$$

Another aspect of the dispersion relation of Fig. 2 is that for $\theta=0$, the electric displacement vector is perpendicular to the optic axis and does not couple to the amplitude-mode; under these conditions the amplitude-mode and the electromagnetic wave are independent and their dispersion relations cross. As soon as θ moves away from zero, however, the amplitude-mode and the electromagnetic wave interact and there can be no crossing of the two branches of the dispersion relation.

III. RAMAN SCATTERING

Polaritons can be observed by Raman scattering provided the Raman tensor of the polar modes does not vanish, or by infrared reflexion when the mode is Raman inactive.[18] The Raman tensor describing light scattering from the polar amplitude mode in quartz has nonzero elements $\alpha_{xx}=\alpha_{yy}$ and α_{zz}.

The amplitude-mode polariton in quartz can in principle be observed using the $x(zz)y$ scattering geometry employed in Refs. 7 and 20. In both these references scattering from relatively low-frequency excitations (≈ 10 cm^{-1}) was observed. Unfortunately, the observation of the temperature dependence of these features led to different conclusions in the two references. Shionoya *et al.*[7] concluded that the mode which they observed at 7 cm^{-1} was the amplitude mode, whereas Berge *et al.*[20] concluded that the similar features observed by them were probably not the amplitude mode. In view of these differences in interpretation, it would be worth while looking at the low-frequency features observed in the scattering from other points of view. One way of doing this would be to use other scattering geometries, to be discussed below, to investigate the polar character of this mode.

Raman scattering is usually observed in the right-angle scattering geometry, i.e., a geometry in which the incident and scattered rays are at right angles. Unfortunately a right angle scattering geometry allows only the large wave-vector limit of the polariton frequency to be measured. To investigate the polariton dispersion relation more fully the $x(z\zeta)\xi$ scattering geometry (see Fig. 3) can be used. In this case, by observing scattering which is close to the forward direction (i.e., by making the angle ϕ of Fig. 3 small) one can observe the polariton frequency at smaller wave vectors,[16–18] i.e., one can observe the lower branch of the dispersion relation shown in Fig. 2 in a region where the wave vector is relatively

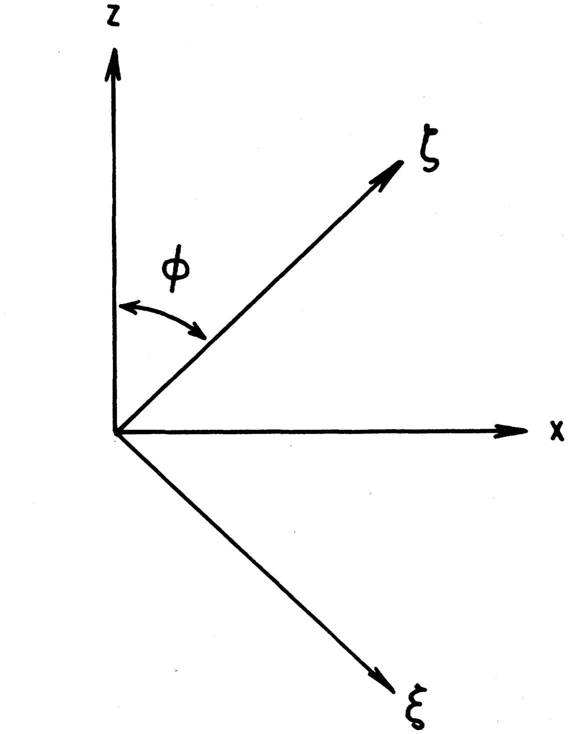

FIG. 3. Scattering geometry $x(z\zeta)\xi$. The incident beam propagates in the x direction and is polarized in the z direction while the scattered beam propagates in the ξ direction and is polarized in the ζ direction.

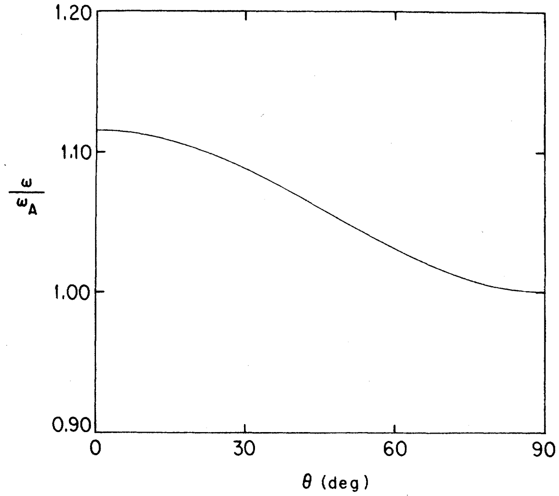

FIG. 4. Directional dispersion. The parameters used are the same as in Fig. 2.

small and the frequency begins to decrease below the large-wave-vector limit.

Now note in Fig. 2 that the large-wave-vector limit of the amplitude-mode vibrational frequency depends on the orientation of the wave vector of this mode relative to the optic axis. In Fig. 4, this dependence is shown more explicitly. This dependence of the mode frequency on the direction of the wave vector is called directional dispersion. The directional dispersion of the ordinary zone-center polar phonons in quartz has been observed by Shapiro and Axe.[21] A similar scattering geometry could be used to study the directional dispersion of the polar amplitude mode in quartz.

IV. CONCLUSIONS

The A-symmetry amplitude mode in quartz is a polar mode and its coupling to the electromagnetic field should be considered when calculating its vibrational frequency. This coupling leads to a characteristic polariton type dispersion relation as shown in Fig. 2. Similarly, the polar characteristics of the amplitude modes and phasons in any incommensurate crystal should be taken into account when calculating their frequencies.

The investigation in the manner described above of a possible polariton-type behavior and directional dispersion of the features observed at frequency shifts of the order of 10 cm^{-1} in Raman scattering from quartz[7,20] could help to clarify the nature of these features.

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