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COULOMB EFFECTS IN DYNAMICS OF POLAR LATTICES

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Zone-center phonon frequencies of polar lattices are calculated for uniaxial crystals from the symmetry arguments. Long-range Coulomb forces and crystal anisotropy are explicitly taken into account. Free-carrier contributions into the dielectric constant are included. The angular dispersion of optical-phonon modes is compared with data for hexagonal $6H$-SiC polytype.

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1. INTRODUCTION

Electrostatic dipole–dipole interactions play an important role in the theory of lattice vibrations. It is common knowledge [1] that the degeneracy of phonon modes at the Brillouin zone-center (e.g., in the cubic $3C$–SiC crystal) is removed if the atomic displacements are accompanied by the Coulomb field. Then the frequency of the longitudinal optical mode becomes larger than the frequencies of transverse modes. For noncubic crystals (e.g., for the hexagonal or rhombohedral SiC polytypes), the long-range Coulomb field also gives rise to an angular dependence of the zone-center modes: at $\mathbf{k} = 0$, *the optical-phonon frequencies depend on the propagation direction.*

Such a phenomenon is rather unusual from both the physical and mathematical standpoints: the eigenvalues of dynamical matrix calculated for $\mathbf{k} = 0$ depend on the $\mathbf{k}$-direction. This is caused by a nonanalytic $\mathbf{k}$-dependence of the dynamical matrix which results from a long-range dipole–dipole interaction. In polar cubic crystals, the Coulomb field splits the three-fold degeneracy of optical modes at the Brillouin zone-center, but the frequency dependence on the propagation direction also appears in uniaxial crystals due to the long-range electrostatic field.

The electrodynamic part of the problem was formulated by Loudon [2]. The Coulomb contributions in the dynamical matrix are usually calculated be means of an Evald summation [1]. The angular dispersion of optical modes is clearly demonstrated by the recent numerical calculations for the zone-center phonons [3] and for the entire Brillouin zone [4] in the case of A^3B^5 semiconductors with the wurtzite structure. The Coulomb field is also taken into account in the theory of phonon–plasmon coupled modes (polaritons) [5] when the effect of free carriers is studied.

The main purpose of this paper is i) to calculate the angular dispersion for the zone-center phonons in uniaxial crystals using the symmetry arguments and ii) to consider the effect of free carriers on these modes. For definiteness, we concentrate on the phonon modes of uniaxial SiC polytypes that are presently very popular in technical applications.

2. OPTICAL MODES AT THE ZONE-CENTER OF CUBIC CRYSTALS

Among the hexagonal and rhombohedral SiC polytypes, there is the cubic $3C$-SiC one with two atoms in the unit cell. First we consider the optical modes in this simplest case. For the nearest vicinity of the Brillouin zone-center, $k \ll \pi/d$, where d is the lattice parameter, the acoustic and optical modes can be divided using the series expansion in $\mathbf{k}$ of the dynamical matrix. As the result, in the zero approximation in $\mathbf{k}$ we obtain the system of three equations for the optical displacements u_i $(i = x, y, z)$:

$$(\phi - M^*\omega^2)\mathbf{u} = \mathbf{f}, \tag{1}$$

where M^* is the reduced mass of two atoms (Si and C) in the unit cell, ϕ is the diagonal element of the force-

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constant matrix (the only one diagonal element of the 3×3-matrixs exists in a cubic crystal). The value of ϕ can be calculated in the nearest-neighbor approximation, but the long-range Coulomb interaction cannot be considered in this way. The Coulomb effect is described by the force $\mathbf{f} = Ze\mathbf{E}$ acting on an effective charge Z, where the electric field $\mathbf{E}$ is found from Maxwell's equations. Eliminating the magnetic field from Maxwell's equations, we can express the electric field $\mathbf{E}$ in terms of polarization $\mathbf{P}$ as

$$\mathbf{E} = \frac{-4\pi\left[\mathbf{k}(\mathbf{k}\cdot\mathbf{P}) - \omega^2\mathbf{P}/c^2\right]}{k^2 - \omega^2/c^2}. \tag{2}$$

We are interested in the ω values of the order of optical mode frequencies, such that $\omega/c \approx 10^3$ cm^{-1}. If the phonon is excited by light, its wave vector has the value of the photon wave vector, i.e., of the order of 10^5 cm^{-1}. The condition $k \gg \omega/c$ is then satisfied and the terms involving c^2 must be omitted in Eq. (2), which then becomes

$$\mathbf{E} = -4\pi\mathbf{k}(\mathbf{k}\cdot\mathbf{P})/k^2. \tag{3}$$

In the long-wave limit ($k \ll \pi/d$), the polarization is related to the phonon displacement and the electric field by the macroscopic equation

$$\mathbf{P} = NZe\mathbf{u} + \chi\mathbf{E}, \tag{4}$$

where χ is the atomic permittivity and N is the number of unit cells in 1 cm^3. Sometimes, the local field is used in equations similar to (4) instead of the macroscopic field $\mathbf{E}$. For cubic crystals (for which only the simple Lorentz relationship exists), the local field can be eliminated by renormalizing the force constant ϕ.

Using Eqs. (3) and (4), we can express the electric field $\mathbf{E}$ in terms of $\mathbf{u}$. Equation (1) then gives the frequencies of transverse and longitudinal optical modes in the cubic crystal as

$$\omega_{TO}^2 = \phi/M^* \quad \text{and} \quad \omega_{LO}^2 = \phi/M^* + \rho, \tag{5}$$

where

$$\rho = 4\pi Z^2 e^2 N/M^*\varepsilon^\infty \quad \text{and} \quad \varepsilon^\infty = 1 + 4\pi\chi. \tag{6}$$

Although relation (3) between $\mathbf{E}$ and $\mathbf{P}$ involves the $\mathbf{k}$-direction explicitly, the frequencies of optical modes (5) are independent of the propagation direction as it must be for a cubic crystal.

3. OPTICAL MODES AT THE ZONE-CENTER OF UNIAXIAL CRYSTALS

The crystal anisotropy of the noncubic SiC polytypes is known to be small because the nearest neighbors of any given atom preserve the cubic symmetry. Let us introduce the strain tensor e_{ij} describing a small difference between the dynamic matrices for the noncubic polytype and the cubic one. The phonon spectrum of the noncubic polytype can then be obtained in the following way. At the first step, we transform the Brillouin zone of the cubic polytype («the large zone») using the strain e_{ij}. Hence, we find the frequencies of the so-called strong modes. For the zone-center, they can be obtained by expanding the dynamic matrix in the strain e_{ij}.

At the second step, we take into account that noncubic polytypes have more than two atoms in the unit cell and the additional optic modes appear. Phonon branches of the large zone are folded [6] into the Brillouin zone of the noncubic polytype, thereby producing additional weak modes. The weak-mode intensity in both optics and Raman scattering was calculated in [7]. In the present paper, we thus consider only strong modes.

The dynamic matrix can contain only the e_{ij} components that are invariant under the symmetry transformations of the crystal. There are two first-order invariants, e_{zz} and $e_{xx} + e_{yy}$, assuming that the z-axis is parallel to the c-axis. We can fix the crystal volume, i.e., impose the condition $e_{ii} = 0$. We then have only one invariant, for instance e_{zz}, which is involved only in the diagonal elements of the force-constant matrix in Eq. (1). The coefficients of the xx and yy elements are equal because of the rotation invariance around the c-axis. Finally, we can omit the common frequency shift. Instead of Eq. (1), we thus obtain

$$\begin{pmatrix} \beta+\rho n_x^2-\omega^2 & \rho n_x n_y & \rho n_x n_z \\ \rho n_x n_y & \beta+\rho n_y^2-\omega^2 & \rho n_y n_z \\ \rho n_x n_z & \rho n_y n_z & \alpha+\rho n_z^2-\omega^2 \end{pmatrix} \times \begin{pmatrix} u_x \\ u_y \\ u_z \end{pmatrix} = 0, \tag{7}$$

where $\mathbf{n} = \mathbf{k}/k$ and

$$\alpha = \phi/M^*, \quad \beta = \alpha + be_{zz}. \tag{8}$$

We take the vector $\mathbf{k}$ in the yz-plane and denote as θ the angle between $\mathbf{k}$ and the c-axis,

$$n_x = 0, \quad n_z = \cos\theta, \quad n_y = \sin\theta.$$

We then see from Eq. (7) that there are one transverse mode (TO_1) vibrating in the x-direction and two modes in the yz-plane with the frequencies

$$\omega^2_{TO_1} = \beta,$$
$$\omega^2_{y,z}(\theta) = \frac{1}{2}(\rho + \alpha + \beta) \pm \tag{9}$$
$$\pm\frac{1}{2}\left\{[\rho+(\alpha-\beta)\cos 2\theta]^2 + (\alpha-\beta)^2 \sin^2 2\theta\right\}^{1/2}.$$

We emphasize that Eqs. (9) give the phonon frequencies in the zone-center, but these frequences depend on the propagation direction θ. This dependence has its origin in the simultaneous effect of the Coulomb field (described by the constant ρ) and crystal anisotropy ($\beta \neq \alpha$). In absence of the Coulomb field ($\rho = 0$), we have $\omega_z^2 = \alpha$, $\omega_y^2 = \beta$, and there is no angular dispersion. For the isotropic case ($\alpha = \beta$), Eqs. (9) give the modes for the cubic crystal.

If the Coulomb effect is small compared to the crystal anisotropy ($\rho \ll |\alpha - \beta|$), we can omit the off-diagonal terms in matrix (7). We then have one mode vibrating close to the c-direction with the frequency $\omega_z^2 = \alpha + \rho\cos^2\theta$ (with an accuracy to $\rho^2/(\alpha-\beta)^2$), and the other mode near the y-direction with the frequency $\omega_y^2 = \beta + \rho\sin^2\theta$.

In the opposite limiting case of the small crystal anisotropy, it is useful to pass to the coordinate system with the z'-axis along the $\mathbf{k}$-vector, subjecting Eq. (7) to the unitary transformation

$$U_{ij} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & \sin\theta \\ 0 & -\sin\theta & \cos\theta \end{pmatrix}. \tag{10}$$

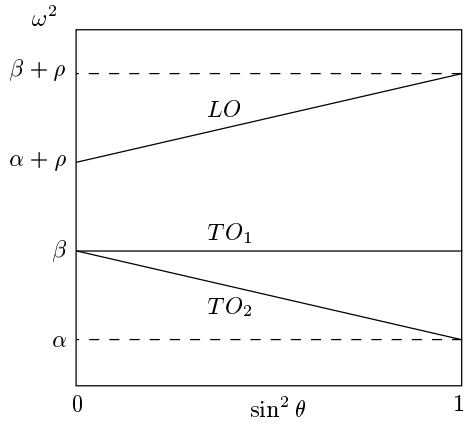
We must then diagonalize the matrix

$$\begin{pmatrix} \beta & 0 & 0 \\ 0 & \beta\cos^2\theta+\alpha\sin^2\theta & (\beta-\alpha)\sin\theta\cos\theta \\ 0 & (\beta-\alpha)\sin\theta\cos\theta & \beta\sin^2\theta+\alpha\cos^2\theta+\rho \end{pmatrix}. \tag{11}$$

We see that in addition to the TO_1 mode, in the case where $|\alpha - \beta| \ll \rho$, there are another nearly transverse TO_2 mode and nearly longitudinal LO mode with the frequencies

$$\omega^2_{TO_2}(\theta) = \beta\cos^2\theta + \alpha\sin^2\theta,$$
$$\omega^2_{LO}(\theta) = \rho + \beta\sin^2\theta + \alpha\cos^2\theta, \tag{12}$$

which can also be obtained by expanding Eq. (9) with an accuracy to $(\alpha-\beta)^2/\rho^2$. The dispersion curves corresponding to Eqs. (9) and (12) are shown schematically in figure. The angular dispersions of form (12) were obtained by Loudon [2].



Angular dispersion of optical-phonon modes in uniaxial crystals at the zone-center. The angle θ is the angle between the c-axis and the wave vector $\mathbf{k} \to 0$. The TO_1 mode is polarized perpendicularly to the c-$\mathbf{k}$ plane. The LO and TO_2 modes have a nearly longitudinal and transverse character, respectively, if the Coulomb force effects dominate over the crystal anisotropy

One can see from Eq. (9) that a conservation law exists. Namely, the sum of the squared frequencies of the y and z modes is independent of the propagation direction, e.g.,

$$\omega_y^2(\theta=0) + \omega_z^2(\theta=0) = \omega_y^2(\theta=\pi/2) + \omega_z^2(\theta=\pi/2). \tag{13}$$

As an example, we consider $6H$-SiC polytype. The angular dispersion of its optical modes is known from the experiment [5,6]. For $\theta = 0$ (propagation parallel to the c-axis), the TO_1 and y modes are degenerate and their frequencies are equal to $\sqrt{\beta}$. The experimental value is 797 cm^{-1} (with the uncertainty about 1 cm^{-1}). The corresponding value of the longitudinal mode is

$$\omega_{LO}(\theta=0) = \sqrt{\rho+\alpha}.$$

For $\theta = \pi/2$ (propagation perpendicular to the c-axis),

$$\omega_{TO_2}(\theta=\pi/2) = \sqrt{\alpha}$$

(the experimental value is 788 cm^{-1}) and

$$\omega_{LO}(\theta=\pi/2) = \sqrt{\rho+\beta}$$

(the experimental value is 970 cm^{-1}). It immediately follows that $\rho = 552.9^2$ cm^{-2}, $\alpha = 788^2$ cm^{-2}, and $\beta = 797^2$ cm^{-2}.

We then find

$$\omega_{LO}(\theta=0) = \sqrt{\rho+\alpha} = 962.6 \text{ cm}^{-1},$$

which should be compared with the experimental value 964 cm^{-1}. The small difference between these two values can be attributed to the anisotropy in the atomic permittivity, which is considered in the next section.

4. EFFECTS OF THE PERMITTIVITY ANISOTROPY AND FREE CARRIERS

In the previous section, we assumed that the uniaxial anisotropy affects only the short-range contribution to the force-constant matrix. But in uniaxial crystals, the atomic permittivity χ is a tensor with two independent components, $\chi_\parallel$ and $\chi_\perp$, corresponding to the crystal axes. This effect is small because each atom has nearly cubic surroundings, but it must be included for a careful comparison with experiments. In a similar way, free carriers contribute to the angular dispersion of the longitudinal optical mode.

Taking into account both the anisotropy of atomic permittivity and the conductivity of free carriers σ, we replace Eq. (4) with

$$\begin{aligned} P_\parallel &= NZeu_\parallel + \left(\chi_\parallel + i\frac{\sigma_\parallel}{\omega}\right) E_\parallel, \\ P_\perp &= NZeu_\perp + \left(\chi_\perp + i\frac{\sigma_\perp}{\omega}\right) E_\perp. \end{aligned} \tag{14}$$

Using Eqs. (3) and (14), we obtain the equation of motion in form (7) and phonon frequencies (9), but the conservation law (13) does not apply now because ρ becomes a function of θ,

$$\rho(\theta) = 4\pi Z^2 e^2 N/M^* \left[\left(\varepsilon_\parallel^\infty + 4\pi i\frac{\sigma_\parallel}{\omega}\right)\cos^2\theta + \left(\varepsilon_\perp^\infty + 4\pi i\frac{\sigma_\perp}{\omega}\right)\sin^2\theta\right], \tag{15}$$

where $\varepsilon_\parallel^\infty = 1 + 4\pi\chi_\parallel$ and $\varepsilon_\perp^\infty = 1 + 4\pi\chi_\perp$. We note that the vibration modes acquire some damping due to conductivity. In addition, the optical phonon has a natural width Γ given by its probability to decay into lower energy phonons, and the term $i\Gamma/2$ must be added to ω in Eq. (7).

We can then use transformation (10) and obtain matrix (11) with the function $\rho(\theta)$ instead of constant ρ. We see that in the limiting case of the weak anisotropy, $|\alpha - \beta| \ll \rho(\theta)$, the Coulomb field (and therefore the carriers) affects only the longitudinal mode. Its frequency is determined by the equation

$$R(\omega) \equiv \rho(\theta) + \beta\sin^2\theta + \alpha\cos^2\theta - i\omega\Gamma - \omega^2 = 0, \tag{16}$$

where $\rho(\theta)$ given by Eq. (15) depends on ω explicitly and through the conductivity σ.

Equation (16) gives the frequency of the LO-phonon–plasmon coupled mode in uniaxial semiconductors. Notice that in the isotropic case, Eq. (16) coincides with the condition $\varepsilon(\omega) = 0$, where the dielectric function $\varepsilon(\omega)$ is given by the well-known expression

$$\varepsilon(\omega) = \varepsilon^\infty\left[1 + \frac{\omega_{LO}^2 - \omega_{TO}^2}{\omega_{TO}^2 - \omega^2 - i\omega\Gamma} - \frac{\omega_p^2}{\omega(\omega + i\gamma)}\right],$$

and the plasmon frequency is

$$\omega_p^2 = \frac{4\pi ne^2}{\varepsilon^\infty m}.$$

In this case, Eqs. (5), (6), and (8) give

$$\omega_{TO}^2 = \alpha = \beta, \quad \omega_{LO}^2 = \omega_{TO}^2 + \frac{4\pi Z^2 e^2 N}{M^*\varepsilon^\infty},$$

and the Drude formula for the conductivity reads

$$\sigma = \frac{ne^2}{m(-i\omega + \gamma)}.$$

The function $R(\omega)$ in Eq. (16) is measured in Raman experiments. Namely, the Raman intensity considered as a function of frequency transfer ω is

$$I(\omega, \theta) \approx \mathrm{Im}\,\frac{1}{R(\omega)} \tag{17}$$

for the LO mode excitation with the propagation direction θ. If the incident or scattered light has a finite aperture, Eq. (17) must be integrated over the allowed range of θ.

Equation (17) can be used in experimental studying the effect of carriers on the Raman scattering in uniaxial semiconductors. The conductivity tensor in Eq. (15) is given by the Drude-like formula with the diagonal components $m_{\parallel,\perp}$ and $\gamma_{\parallel,\perp}$, for instance, $\sigma_\parallel = ne^2/m_\parallel(-i\omega + \gamma_\parallel)$.

Let us summarize the main result of the paper: the effects of crystal anisotropy ($\alpha \neq \beta$) and Coulomb field $\rho(\theta)$ on the phonon dispersion are explicitly separated as one can see in Eqs. (9) and (16).

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