Coulomb effects in dynamics of polar lattices

L. A. Falkovsky *

Landau Institute for Theoretical Physics, 117337 Moscow, Russia

Abstract

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 a dielectric constant are included. The angular dispersion of optical-phonon modes is compared with data for hexagonal 6H-SiC politype.

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I. 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 gives rise also 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 point of view: the eigenvalues of dynamical matrix calculated for \(\mathbf{k} = 0\) depend on the \(\mathbf{k}\)-direction. This is caused by the nonanalytic \(\mathbf{k}\)-dependence of the dynamical matrix which results from the 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 as well 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 of the zone-center phonons \[3\] and for the whole Brillouin zone \[4\] in the case of semiconductors \(A^3B^5\) 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.

*e-mail: falk@itp.ac.ru
The main aim 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 the sake of definiteness, we are interested in the phonon modes of uniaxial SiC polytypes which are very popular now in technical applications.

II. 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 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 \( k \) of the dynamical matrix. As the result, we obtain in the zero approximation in \( k \) for the optical displacements \( u_i \ (i = x, y, z) \) the system of three equations

\[
(\phi - M^\star \omega^2)u = f, \tag{1}
\]

where \( M^\star \) is the reduced mass of two atoms (Si and C) in the unit cell, \( \phi \) is the diagonal element of the force-constant matrix (the only one diagonal element of the \( 3 \times 3 \)-matrix exist in a cubic crystal). The value of \( \phi \) can be calculated in the nearest-neighbor approximation. As for the long-range Coulomb interaction, it can not be considered in such a way. The Coulomb effect is described by a force \( f = Z e E \) acting on an effective charge \( Z \), where the electric field \( E \) is found from Maxwell’s equations. Eliminating the magnetic field from Maxwell’s equations, one can express the electric field from Maxwell’s equations, one can express the electric field \( E \) in terms of polarization \( P \):

\[
E = -\frac{4\pi k(kP) - \omega^2 P/c^2}{k^2 - \omega^2/c^2}. \tag{2}
\]

We are interested in \( \omega \) of the order of optical mode frequencies, i.e., \( \omega/c \sim 10^3 \text{ cm}^{-1} \). If the phonon is exited by light, its wave vector has the value of the photon wave vector, i.e., of the order of \( 10^5 \text{ cm}^{-1} \). Then the condition \( k \gg \omega/c \) is fulfilled, and the terms with \( c^2 \) have to be omitted in Eq. (2) which becomes:

\[
E = -\frac{4\pi k(kP)}{k^2}. \tag{3}
\]

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

\[
P = NZe u + \chi E \tag{4}
\]

where \( \chi \) is the atomic permittivity and \( N \) is the number of unit cells in 1 cm\(^3\). Sometimes, the local field is used in equations like (4) instead of the macroscopic field \( E \). But for cubic crystals (when the simple Lorentz relationship exists only), the local field can be eliminated renorming the force constant \( \phi \).

Using Eqs. (2) and (4), the electric field \( E \) can be expressed in terms of \( u \). Then Eq. (4) gives the frequencies of transverse and longitudinal optical modes in the cubic crystal

\[
\omega^2_{TO} = \frac{\phi}{M^\star} \quad \text{and} \quad \omega^2_{LO} = \frac{\phi}{M^\star} + \rho \tag{5}
\]
where
\[ \rho = Z^2 e^2 N/\varepsilon^\infty \quad \text{and} \quad \varepsilon^\infty = 1 + 4\pi\chi. \tag{6} \]

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

### III. 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 conserve the cubic symmetry. Let us introduce the strain tensor \( e_{ij} \) which describes a small difference between the dynamic matrices for the noncubic polytype and the cubic one. Then the phonon spectrum of the noncubic polytype can be obtained in the following way. In 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 the expansion of the dynamic matrix in the strain \( e_{ij} \).

In 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 giving additional weak modes. The weak-mode intensity in optics and Raman scattering was calculated in [7]. Therefore in the present paper, we consider only strong modes.

The dynamic matrix can contain only components \( e_{ij} \) invariant under the symmetry transformations of the crystal. There are two invariants of first order, \( e_{zz} \) and \( e_{xx} + e_{yy} \), the \( z \)-axis being parallel to the \( c \)-axis. We can fix the crystal volume, i.e., impose the condition \( e_{ii} = 0 \). Then we have only one invariant, for instance, \( e_{zz} \) which can be written only on the diagonal of the force-constant matrix of Eq. (1). The coefficients of the \( xx \) and \( yy \) elements are equal because of the rotation invariance around the \( c \)-axis. At last, we can omit the common frequency shift. Therefore instead of Eq. (1), we obtain

\[
\begin{pmatrix}
\beta + \rho n_x^2 - \omega^2 & \rho n_x n_y & \rho n_x n_z \\
\rho n_x n_y & \beta + \rho n_y^2 - \omega^2 & \rho n_y n_z \\
\rho n_x n_z & \rho n_y n_z & \alpha + \rho n_z^2 - \omega^2
\end{pmatrix}
\begin{pmatrix}
ux \\
uy \\
uz
\end{pmatrix}
= 0,
\tag{7}
\]

where \( n = k/k \) and
\[
\alpha = \phi/M^*, \quad \beta = \alpha + be_{zz}.
\tag{8}
\]

We take the vector \( k \) in the \( yz \)-plane and denote \( \theta \) the angle between \( k \) and the \( c \)-axis: \( n_x = 0, n_z = \cos \theta \) and \( n_y = \sin \theta \). Then we see from Eq. (7) that there are one transverse mode (TO1) vibrating in \( x \)-direction and two modes in the \( yz \)-plane with the frequencies

\[
\omega_{TO1}^2 = \beta,
\tag{9}
\]

\[
\omega_{y,z}^2(\theta) = \frac{1}{2}(\rho + \alpha + \beta) \pm \frac{1}{2} \left\{ [\rho + (\alpha - \beta) \cos 2\theta]^2 + (\alpha - \beta)^2 \sin^2 2\theta \right\}^{1/2}.
\]
Emphasize that Eq. (1) gives the phonon frequencies in the zone-center, but they depend on the propagation direction $\theta$. This dependence has its origin in the simultaneous effect of the Coulomb field (described by the constant $\rho$) 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 ($\alpha = \beta$), Eq. (1) gives the modes for the cubic crystal.

If the Coulomb effect is small in comparison with the crystal anisotropy ($\rho \ll |\alpha - \beta|$), we can omit the off-diagonal terms in the matrix (7). So there are 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, making in Eq. (7) the unitary transformation

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

Then we arrive to the diagonalization problem of 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 besides the TO$_1$ mode, in the case $|\alpha - \beta| \ll \rho$, there are another nearly transverse TO$_2$ mode and the nearly longitudinal LO mode with the frequencies

$$ \begin{align*}
\omega_{TO2}^2(\theta) &= \beta \cos^2 \theta + \alpha \sin^2 \theta, \\
\omega_{LO}^2(\theta) &= \rho + \beta \sin^2 \theta + \alpha \cos^2 \theta,
\end{align*} \tag{12} $$

which can be obtained also by the expansion of Eq. (1) with an accuracy to $(\alpha - \beta)^2/\rho^2$.

The dispersion curves (9), (12) are shown schematically in Fig. 1. The angular dispersions of the form (12) were obtained by Loudon [2].

One can see from Eq. (3) that a conservation law exists. Namely, the sum of the squared frequencies of the $yz$ 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 let us consider 6H-SiC polytippe. The angular dispersion of its optical modes is known from the experiment [3], [4]. For $\theta = 0$ (propagation parallel to the $c$-axis) the TO$_1$ and $y$ mode are degenerate, and their frequencies are equal to $\sqrt{\beta}$. The experimental value is 797 cm$^{-1}$ (with uncertainty about 1 cm$^{-1}$). The corresponding value for the longitudinal mode is $\omega_{LO}(\theta = 0) = \sqrt{\rho + \alpha}$. For $\theta = \pi/2$ (propagation perpendicular to the $c$-axis) $\omega_{TO2}(\theta = \pi/2) = \sqrt{\alpha}$ (experimental value is 788 cm$^{-1}$) and $\omega_{LO}(\theta = \pi/2) = \sqrt{\rho + \beta}$ (970 cm$^{-1}$). It immediately follows that: $\rho = 552.92$ cm$^{-2}$, $\alpha = 7882$ cm$^{-2}$ and $\beta = 7972$ cm$^{-2}$. Thus one calculates $\omega_{LO}(\theta = 0) = \sqrt{\rho + \alpha} = 962.6$ 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 following section.
IV. EFFECTS OF THE PERMITTIVITY ANISOTROPY AND FREE CARRIERS

We assumed in the previous section that the uniaxial anisotropy affects only the short-range contribution to the force-constant matrix. But in uniaxial crystals the atomic permittivity $\chi$ 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 should be included for a careful comparison with experiments. In a similar way, free carriers make a contribution to the angular dispersion of the longitudinal optical mode.

To take into account both the anisotropy of atomic permittivity and the conductivity of free carriers $\sigma$, we write instead of Eq. (4) the following

$$
P_{\parallel} = NZ e u_{\parallel} + \left( \chi_{\parallel} + i \frac{\sigma_{\parallel}}{\omega} \right) E_{\parallel},$$
$$
P_{\perp} = NZ e u_{\perp} + \left( \chi_{\perp} + i \frac{\sigma_{\perp}}{\omega} \right) E_{\perp}.
$$

(14)

Using Eqs. (3) and (14), we obtain the equation of motion in the form (7) and the phonon frequencies (9), but the conservation law (13) does not work now because $\rho$ becomes the function of $\theta$:

$$
\rho(\theta) = Z^2 e^2 N \left[ \left( \varepsilon_{\parallel}^\infty + 4 \pi i \frac{\sigma_{\parallel}}{\omega} \right) \cos^2 \theta + \left( \varepsilon_{\perp}^\infty + 4 \pi i \frac{\sigma_{\perp}}{\omega} \right) \sin^2 \theta \right]^{-1},
$$

(15)

where $\varepsilon_{\parallel}^\infty = 1 + 4 \pi \chi_{\parallel}$, $\varepsilon_{\perp}^\infty = 1 + 4 \pi \chi_{\perp}$. Notice, that the vibration modes obtain same damping due to conductivity. In addition, the optical phonon has a natural width $\Gamma$ given by its probability to decay into phonons of lower energy, and the term $i \Gamma$ should be added to $\omega$ in Eq. (7).

Then we can use transformation (10) and obtain matrix (11) with the function $\rho(\theta)$ instead of constant $\rho$. 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

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

(16)

where $\rho(\theta)$ given by Eq. (13) depends on $\omega$ explicitly and by means of the conductivity $\sigma$.

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

$$
\omega_p^2 = 4 \pi n e^2 / \varepsilon^\infty m.
$$

In this case, Eqs. (5), (6), and (8) give $\omega_{TO}^2 = \alpha = \beta$, $\omega_{LO}^2 = \omega_{TO}^2 + Z^2 e^2 N / \varepsilon^\infty$, and the Drude formula for conductivity reads $\sigma = ne^2 / m(-i \omega + \gamma)$.

The function $R(\omega)$ from Eq. (16) is measured in Raman experiments. Namely, the Raman intensity as a function of frequency transfer $\omega$ is
I(\omega, \theta) \simeq \text{Im} \frac{1}{R(\omega)} \tag{17}

for the LO mode excitation with the propagation direction \( \theta \). If the incident or scattered light has a finite aperture, Eq. (17) should be integrated over allowed \( \theta \).

Eq. (17) can be used in experimental studying the effect of carriers on the Raman scattering in uniaxial semiconductors. Then 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 emphasize 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), (16).

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**Figure caption** Angular dispersion of optical-phonon modes in uniaxial crystals at the zone-center. The angle $\theta$ is the angle between the c-axis and the wave vector $\mathbf{k} \rightarrow 0$. The TO$_1$ mode is polarized perpendicular 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.
