Intrinsic lifetimes and anharmonic frequency shifts of long-wavelength optical phonons in polar crystals

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Quantitative calculations of phonon lifetimes due to anharmonic three-phonon processes require knowledge of cubic anharmonic coupling coefficients. In order to determine the temperature dependence of phonon frequencies, anharmonic force constants of up to fourth order are needed. In polar crystals, the macroscopic electric field gives rise to nonanalytic terms in these coefficients. It is shown how these non-analytic terms can be determined from other physical quantities including higher-order dipole moments, Raman coefficients, and nonlinear susceptibilities. The contribution of these terms to the intrinsic damping of the long-wavelength optical phonon modes in GaAs has been determined by an ab initio calculation.

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I. INTRODUCTION

In pure insulating crystals, the intrinsic lifetimes of phonons are due to anharmonic multi-phonon processes. If energy and momentum conservation allow for three-phonon processes to occur, these are usually the dominant ones. The finite lifetimes of long-wavelength optical phonons give rise to nonzero widths of the Raman lines and are relevant in other physical situations too. In polar semiconductors, the lifetimes of longitudinal optical (LO) phonons play an important role in the dynamics of highly excited free carriers. A precise knowledge of the decay efficiencies of long-wavelength optical phonons into acoustic phonons is also required for a quantitative interpretation of experiments carried out on nonequilibrium phonon dynamics in GaP.

For covalent semiconductors, the width of the Raman line has been calculated ab initio in very good agreement with experiment. The cubic anharmonic coupling coefficients needed for these calculations have been determined in two different ways: In their pioneering work, Debernardi et al. have applied the “2n + 1 theorem” by Gonze and Vigneron, to determine the cubic coefficients directly in the framework of density-functional perturbation theory (DFPT). Lang et al. have combined DFPT with the frozen phonon approach to calculate cubic coupling coefficients as numerical derivatives of dynamical matrices with respect to a frozen-in displacement pattern corresponding to an optical zone-center mode. This method was also used to determine lifetimes of vibrational adlayer modes. In this way, fourth-order anharmonic force constants have also been determined that are needed for a calculation of the temperature dependence of zone-center phonon frequencies. Debernardi has combined these two methods in his calculation of fourth-order coupling coefficients by taking numerically a first derivative of third-order force constants determined by DFPT for non-equilibrium configurations.

In the case of polar crystals, both approaches have to be modified to account for nonanalytic terms that occur in the anharmonic coupling coefficients due to the long-range Coulomb interactions giving rise to macroscopic electric fields. They are analogous to the term in the dynamical matrices of polar crystals that leads to the Lyddane-Sachs-Teller splitting. In the following section, we derive the form of these nonanalytic terms and relate them to other physical quantities. In the case of cubic anharmonic coupling coefficients, these are the dielectric tensor, the second-order nonlinear susceptibility tensor, the first-order and second-order dipole moments, and the first-order Raman tensor. Once these quantities are known, the cubic coupling coefficients relevant for the lifetimes of long-wavelength LO and TO phonons may be calculated using either of the two approaches. In Sec. III, we present ab initio data for the difference of LO and TO damping functions in GaAs. The influence of the macroscopic field on the temperature dependence of the zone-center optical frequencies is briefly discussed in Sec. IV, which is followed by concluding remarks.

II. CUBIC ANHARMONIC COUPLING COEFFICIENTS

The dynamical matrix of a polar crystal contains a contribution from the long-range Coulomb interaction of the ions, which is not analytic as a function of the wave vector at \( \mathbf{q} = \mathbf{0} \) (Ref. 9). As a consequence of this contribution, the limit \( \mathbf{q} \rightarrow \mathbf{0} \) is not unique and depends on the direction from which the center of the Brillouin zone is approached. Analogous terms exist in the Fourier-transformed anharmonic force constants. They are the subject of this work.

To identify these nonanalytic terms in the anharmonic coupling coefficients of polar crystals, we conveniently start with an expression for the potential energy of a crystal in a macroscopic electric field that contains the Fourier amplitudes \( E_\alpha(\mathbf{q}) \) of the macroscopic field \( \mathbf{E}(\mathbf{R}) \) as explicit variables in addition to the Fourier transforms \( u_{\alpha}(\mathbf{k}|\mathbf{q}) \) of the atomic displacement vectors \( \mathbf{u}(\mathbf{k}) \). Here, \( \alpha = x, y, z \) is a Cartesian index, \( \ell \) labels the unit cells, and \( \kappa \) the sublattices of the polar crystal. We adopt the definitions

\[
\mathbf{E}(\mathbf{R}) = \frac{1}{V} \sum_{\mathbf{q}} \mathbf{E}(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{R}},
\]

\[
\mathbf{u}(\mathbf{k}) = \frac{1}{N} \sum_{\mathbf{q}} \mathbf{u}(\mathbf{k}|\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{R}(\ell)},
\]

\( \ell = 1, 2, \ldots, N \) labels the unit cells, \( \kappa \) the sublattices, and \( \mathbf{R}(\ell) \) the position of the \( \ell \)th unit cell.
where $\mathbf{R}(\ell)$ is the position vector of the $\ell$th unit cell, $N$ is the number of unit cells, and $V$ the crystal volume. From the very beginning, we assume periodic boundary conditions and vanishing homogeneous macroscopic field $[\mathbf{E}(\mathbf{q}) = 0 \text{ for } \mathbf{q} = 0]$. This is in accordance with the treatment of the electronic system based on density-functional theory (see Ref. 10).

To simplify the notation, we invoke the summation convention for repeated Cartesian indices. Up to third order of the displacements and the macroscopic field the potential energy $\Phi$ is

$$\Phi = \sum_{\mathbf{q}} \left\{ \frac{1}{2} \sum_{\kappa, \kappa'} \tilde{C}_{\alpha\beta}(\mathbf{q}|\kappa\kappa') u_{\alpha}(\kappa|\mathbf{q}) u_{\beta}(\kappa'|-\mathbf{q}) - \right.$$

$$\left. \sum_{\kappa} Z_{\alpha\beta}(\kappa) u_{\alpha}(\kappa|\mathbf{q}) E_{\alpha}(-\mathbf{q}) - \frac{1}{2} \epsilon_{\alpha\beta\gamma} E_{\alpha}(\mathbf{q}) E_{\beta}(-\mathbf{q}) \right\}$$

$$+ \sum_{\mathbf{q}, \mathbf{q}'} \left\{ \frac{1}{6} \sum_{\kappa, \kappa', \kappa''} \tilde{C}_{\alpha\beta\gamma}(\mathbf{q}, \mathbf{q}'; -\mathbf{q} - \mathbf{q}'|\kappa\kappa'\kappa'') \right.$$

$$\times u_{\alpha}(\kappa|\mathbf{q}) u_{\beta}(\kappa'|\mathbf{q}') u_{\gamma}(\kappa''|-\mathbf{q}' - \mathbf{q}'')$$

$$- \frac{1}{2} \sum_{\kappa, \kappa'} M_{\alpha\beta\gamma}(\kappa'|\kappa\kappa') E_{\alpha}(\mathbf{q}) u_{\beta}(\kappa'|\mathbf{q}')$$

$$\times u_{\gamma}(\kappa'|-\mathbf{q} - \mathbf{q}'') - \frac{1}{2} \sum_{\kappa'} P_{\alpha\beta\gamma\delta}(\kappa) E_{\alpha}(\mathbf{q}) E_{\beta}(-\mathbf{q})$$

$$\times u_{\gamma}(\kappa'|-\mathbf{q} - \mathbf{q}'') - \frac{1}{6} \tilde{\chi}_{\alpha\beta\gamma}^{(2)} E_{\alpha}(\mathbf{q}) E_{\beta}(\mathbf{q}') E_{\gamma}(-\mathbf{q} - \mathbf{q}''). \right.$$

(2.2)

The above expansion, which we have truncated after cubic terms, is the Fourier-space version of Eqs. (6.5.1) and (6.5.2) in Ref. 9. It is understood that the wave vectors $\mathbf{q}$ and $\mathbf{q}'$ are in the neighborhood of the center of the Brillouin zone whenever they are associated with the macroscopic electric field. The coefficients occurring in (2.2) have the following meaning.

(i) $M_{\alpha\beta\gamma}(\kappa'|\kappa\kappa')$ are the second-order dipole moments. These quantities have been calculated from first principles for polar semiconductors very recently.11

(ii) $P_{\alpha\beta\gamma\delta}(\kappa)$ are the first-order Raman coefficients, for which ab initio calculations were performed earlier.12,13

(iii) $\tilde{\chi}_{\alpha\beta\gamma}^{(2)}$ are the second-order nonlinear susceptibilities. They have been determined ab initio using DFPT by Dal Corso et al.14

We now introduce the Lagrangian

$$L = \frac{1}{2} \sum_{\mathbf{q}} \sum_{\kappa} m_{\alpha} \ddot{u}_{\alpha}(\kappa|\mathbf{q}) - \Phi$$

(2.3)

and consider $\Phi$ as being a function of the displacement amplitudes $u_{\alpha}(\kappa|\mathbf{q})$ and the Fourier amplitudes of the scalar potential, $\phi(\mathbf{q})$, rather than of the electric field, with $E_{\alpha}(\mathbf{q}) = -iq_{\alpha}\phi(\mathbf{q})$. The Euler-Lagrange equations obtained from Eq. (2.3) are the equations of motion for the atomic displacements,

$$m_{\alpha} \ddot{u}_{\alpha}(\kappa|\mathbf{q}) = -\frac{1}{2} \frac{\partial \Phi}{\partial u_{\alpha}(\kappa|-\mathbf{q})}.$$  

(2.4)

coupled to the equation

$$\frac{\partial \Phi}{\partial \phi(-\mathbf{q})} = 0.$$  

(2.5)

The latter is merely Maxwell’s equation $\nabla \cdot \mathbf{D} = 0$, where $\mathbf{D}$ is the dielectric displacement field. Equation (2.5) can be solved for $\phi(\mathbf{q})$ iteratively to second order in $u$ to yield

$$\phi(\mathbf{q}) = S(\mathbf{q}) \left[ -iq_{\alpha} \sum_{\kappa} Z_{\alpha\beta}(\kappa) u_{\beta}(\kappa|\mathbf{q}) \right.$$  

$$+ \sum_{\mathbf{q}'} \sum_{\kappa, \kappa'} \left[ q_{\alpha}(\mathbf{q} - \mathbf{q}') P_{\alpha\beta\gamma\delta}(\kappa) S(\mathbf{q} - \mathbf{q}') \right.$$  

$$\times (q_{\gamma} - q_{\gamma}') Z_{\alpha\beta\gamma\delta}(\kappa') + \frac{1}{2} \chi_{\alpha\beta\gamma}^{(2)} q_{\alpha} q_{\beta} (q_{\gamma} - q_{\gamma}')$$  

$$\times S(\mathbf{q}') \sum_{\kappa'\kappa''} \left( \frac{1}{2} \sum_{\kappa''} \chi_{\alpha\beta\gamma}^{(2)} q_{\alpha} q_{\beta} \right) Z_{\alpha\beta\gamma\delta}(\kappa')$$  

$$\times u_{\gamma}(\kappa'|-\mathbf{q} - \mathbf{q}') \right] u_{\delta}(\kappa|\mathbf{q}') u_{\gamma}(\kappa''|-\mathbf{q}' - \mathbf{q}''). \right.$$  

(2.6)

For convenience, we have defined $S(\mathbf{q}) = 1/[q_{\alpha} \epsilon_{\alpha\beta\gamma} q_{\beta} q_{\gamma}]$.

Equation (2.6) may now be used to eliminate the electrical potential $\phi(\mathbf{q})$ in the equation of motion (2.4) for the displacement amplitudes $u_{\beta}(\kappa|\mathbf{q}')$, which then takes the form

$$m_{\alpha} \ddot{u}_{\alpha}(\kappa|\mathbf{q}) = - \sum_{\kappa'} C_{\alpha\beta}(\mathbf{q}|-\mathbf{q}\kappa\kappa') u_{\beta}(\kappa'|\mathbf{q})$$  

$$- \frac{1}{2} \sum_{\mathbf{q}'} \sum_{\kappa, \kappa''} C_{\alpha\beta\gamma}(\mathbf{q}|-\mathbf{q}\kappa\kappa') u_{\gamma}(\kappa''|-\mathbf{q}' - \mathbf{q}''). \right.$$  

(2.7)

where $\mathbf{q}$ is a wave vector near the center of the Brillouin zone.

The Fourier-transformed harmonic force constants have the well-known form

$$C_{\alpha\beta}(\mathbf{q}|\kappa\kappa') = \tilde{C}_{\alpha\beta}(\mathbf{q}|\kappa\kappa') + q_{\mu} Z_{\alpha\mu}(\kappa) S(\mathbf{q}) q_{\nu} Z_{\nu\beta}(\kappa').$$  

(2.8)

For the cubic anharmonic Fourier-transformed force constants, we first consider the case of $\mathbf{q}$ and $\mathbf{q}'$ being both wave vectors near the center of the Brillouin zone. One then obtains
\[ C_{\alpha\beta\gamma}(-q, q', q - q' | \kappa \kappa' \kappa'') = \bar{C}_{\alpha\beta\gamma}(-q, q', q - q' | \kappa \kappa' \kappa'') + \frac{1}{2} Z_{\alpha\beta}(0 | \kappa \kappa) M_{\kappa\gamma}(0 | \kappa' \kappa') q_{\mu} S(q) q_{\nu} + \frac{1}{2} M_{\alpha\beta}(0 | \kappa \kappa') Z_{\gamma\mu}(0 | \kappa' \kappa') q_{\mu} S(q') q_{\nu}' + \frac{1}{2} P_{\alpha\beta}(0 | \kappa \kappa') Z_{\gamma\kappa'}(0 | \kappa' \kappa') q_{\mu} S(q) q_{\nu} q_{\nu}' (q - q') \]

These expressions can be simplified by making use of the symmetry of the crystal under consideration. In particular, the \( T_{q} \) symmetry of the III-V semiconductors implies that \( S(q) = 1/(q^2 \varepsilon_{\omega}) \) with \( \varepsilon_{\omega} \) being the high-frequency dielectric constant, and the tensors \( [Z_{\alpha\beta}(\kappa)], [P_{\alpha\beta}(\kappa)], \) and \( [\chi^{(2)}_{\alpha\beta\gamma}] \) have only one independent component.

If in \( C_{\alpha\beta\gamma}(-q, q', q - q' | \kappa \kappa' \kappa'') \) the wave vector \( q' \) is not situated in the neighborhood of the Brillouin-zone center, only the first two terms in Eq. (2.9) have to be kept.

In applications of DFPT for the calculation of anharmonic force constants via the 2n + 1 theorem, the coefficients \( C_{\alpha\beta\gamma}(-q, q', q - q' | \kappa \kappa' \kappa'') \) are calculated on a grid of wave vectors in the first Brillouin zone. By subtracting the nonanalytic terms in Eq. (2.9) from these coefficients and transforming the remaining term \( \bar{C}_{\alpha\beta\gamma}(-q, q', q - q' | \kappa \kappa' \kappa'') \) into real space, one obtains force constants, which may be expected to be of sufficiently short range to lend themselves to Fourier interpolation. (The spatial range of the third-order force constants may be further reduced by subtracting the rigid-ion part with effective charges that are chosen appropriately.) To obtain the complete Fourier-transformed force constants for a given pair of wave vectors \( q, q' \), one has to add the nonanalytic terms for this combination of wave vectors.

For the calculation of Fourier-transformed anharmonic force constants involving an optical near-zone-center mode, one may proceed in the following way:

Let \( w_{a}(\kappa | qj) \) be the eigenvector of the dynamical matrix corresponding to wave vector \( q \) and branch \( j \), and let \( W_{a}(\kappa | q) = \lim_{\epsilon \rightarrow 0} w_{a}(\kappa | \epsilon qj) \). (Here, \( \hat{q} = q|q \) is the unit vector pointing into the direction of the wave vector \( q \).) Using DFPT, one may then calculate Fourier-transformed force constants \( C^{(A)}(\kappa \kappa | \kappa' \kappa'') \) for a crystal structure with a displacement pattern \( u_{a}(\kappa) = A W_{a}(\kappa | qj) \sqrt{m_{\kappa}} \) frozen in. Subtracting the nonanalytic term \( q_{\mu} C^{(A)}(\kappa | \kappa') S^{(A)}(q') q_{\mu} C^{(A)}(q' | \kappa' \kappa'') \) (Note that \( S^{(A)}(q') \) depends on \( A \) via the dielectric tensor) and also the analytic part of the rigid-ion contribution, and Fourier-transforming into real space, one obtains again short-ranged force constants depending on the amplitude \( A \) of the frozen-in displacement pattern. Consequently, one may take numerically the derivative of these force constants with respect to \( A \), transform into Fourier space and calculate \( [\partial C^{(A)}(q' \kappa \kappa' \kappa'') / \partial A]_{A=0} = \lim_{\epsilon \rightarrow 0} \bar{C}_{\alpha\beta\gamma}(-q, q', q - q' | \kappa \kappa' \kappa'') \) for any wave vector \( q' \). Adding now the rigid-ion part including the nonanalytic terms on the right-hand side of (2.9), the complete Fourier-transformed cubic coupling constants are obtained that are needed for the calculation of lifetimes of zone-center optical modes.

We emphasize that within a rigid-ion model of a polar crystal, there are no nonanalytic terms in the Fourier-transformed anharmonic coupling coefficients of any order, because the nonlinear dipole moments, the Raman tensor, and the nonlinear susceptibilities vanish in this model.

### III. LIFETIMES OF LONG-WAVELENGTH OPTICAL PHONONS

The lifetime \( \tau_{qj} \) of a phonon with wave vector \( q \) belonging to branch \( j \) is a well-defined quantity, if the self-energy of this phonon mode is a slowly varying function of frequency in the neighborhood of the phonon frequency \( \omega_{qj} \). \( \tau_{qj} \) may then be calculated from the imaginary part of the self-energy, \(- \Gamma_{qj}(\omega)\), via

\[ 1 / \tau_{qj} = 2 \Gamma_{qj}(\omega_{qj}) \]  

and to lowest order in the anharmonicity, the damping function \( \Gamma_{qj}(\omega) \) is obtained from

\[ \Gamma_{qj}(\omega) = \frac{\pi}{2} \sum_{q', j''} |V(3(-qj, q'j'', q - q'j''))|^2 \left[ 1 + n_{q'j''} \right] \delta(\omega_{q'j''} + \omega_{q - q'j''} - \omega) + 2 \left[ n_{q - q'j''} \right] \delta(\omega_{q - q'j''} - \omega) \].

Here, \( \omega_{qj} \) is the phonon frequency and \( n_{qj} \) the corresponding Bose factor. [In writing Eq. (3.1), it has been assumed that \( q \) is a wave vector close to the center of the Brillouin zone, and hence no umklapp processes occur.] The coefficients \( V_{3} \) in Eq. (3.2) are related to the Fourier-transformed cubic anharmonic force constants considered in the preceding section via

\[ V_{3}(-qj, q'j'', q - q'j'') = \left[ \frac{\hbar}{8 \omega_{qj} \omega_{q'j''} \omega_{q - q'j''} N} \right]^{1/2} \times \bar{V}_{3}(-qj, q'j'', q - q'j'') \]  

with
where \( w_a(\kappa | \mathbf{q}_i) \) is the eigenvector associated with the phonon mode \( \mathbf{q}_i \) normalized as \( \sum_{\alpha, \kappa} |w_a(\kappa | \mathbf{q}_i)|^2 = 1 \). In the expression (3.2) for the damping function, the sum over \( \mathbf{q}' \) has to be extended over the first Brillouin-zone. The immediate vicinity of the Brillouin-zone center yields a negligible contribution to this sum. Therefore, we do not pay special attention to the nonanalytic terms associated with \( \mathbf{q}' \) and \( \mathbf{q} - \mathbf{q}' \) in Eqs. (3.4) and (3.2).

One may now distinguish three causes for the difference between the lifetimes of longitudinal and transverse optical zone-center phonons.

(i) The difference of the frequencies \( \omega_{\text{LO}} \) and \( \omega_{\text{TO}} \), at which the damping function has to be evaluated.

(ii) The factor \( 1/\sqrt{\omega_{\text{q}_i}} \) in Eq. (3.3).

(iii) The nonanalytic part of the Fourier-transformed cubic anharmonic coupling coefficients in Eq. (3.4).

In the analytic part of the Fourier-transformed cubic coupling constants, the limit \( \mathbf{q} \to \mathbf{0} \) is unique, and if there were no nonanalytic parts, its contribution to the inverse lifetime would not depend on the direction of the eigenvector \( [w_a(\kappa | \mathbf{q}_i)] \) in the degenerate subspace of the optical zone-center modes. The nonanalytic part, however, leads to a difference of lifetimes for different optical modes even if their frequencies were the same. This is due to the term

\[
\delta V_3(-q_j, q'_j, q - q'_j) = \frac{1}{2} g_{\mu} S(\mathbf{q}) \sum_{\nu, \kappa} Z_{\mu \nu \kappa} w_a(\kappa | \mathbf{q}_i) \frac{|w_a(\kappa | \mathbf{q}_i)|}{\sqrt{m_\kappa}} \times M_{\nu}(\mathbf{q}' | q'_j, -q'_j),
\]

where we have again used the notation \( \hat{q} = q/|q| \) for the unit vector, and

\[
M_{\nu}(\mathbf{q}' | q'_j, -q'_j) = \sum_{\kappa, \kappa'} M_{\nu | \beta \gamma}(\mathbf{q}' | \kappa \kappa') \frac{w_{\beta}(\kappa | \mathbf{q}_j') w_{\gamma}(\kappa' | -q'_j)}{\sqrt{m_\kappa}} \sqrt{m_{\kappa'}.}
\]

in the same way as in the theory of two-phonon infrared absorption. In the case of cubic diatomic crystals with one Born effective charge \( Z \), such as the III-V semiconductors, this simplifies to

\[
\delta V_3(-q_{\text{LO}}, q'_j, q - q'_j) = \pm \frac{Z}{2 \sqrt{m_{\text{R}} e_a}} \hat{q}_{\mu} M_{\mu}(\mathbf{q}' | q'_j, -q'_j),
\]

while

\[
\delta V_3(-q_{\text{TO}}, q'_j, q - q'_j) = 0.
\]
mode from the nonanalytic terms is 0.009 64 cm\(^{-1}\). These numbers show that the nonanalytic parts of the cubic anharmonic coupling constants lead to a contribution to the inverse lifetime of zone-center LO phonons in the case of GaAs which is negligible in comparison to the difference between the TO and LO widths. It is even smaller than the accuracy to which the inverse lifetimes or Raman widths can be determined experimentally at present. A compilation of corresponding experimental data can be found in Ref. 16. The partly considerable deviations between various experimental low-temperature values can partly be explained by the presence of defects and especially of free carriers that influence the Raman line as well as the lifetimes of coherently excited phonon modes in coherent anti-Stokes Raman scattering experiments. However, in highly polar materials with a Lyddane-Sachs-Teller split much larger than the one of GaAs, the contribution of the nonanalytic terms to the inverse lifetime of LO phonons may be of a detectable magnitude.

IV. ANHARMONIC FREQUENCY SHIFTS

At lowest order of the anharmonic terms in the lattice potential, perturbation theory yields three contributions to the anharmonic shifts of phonon frequencies that are expected to be of comparable magnitude at low temperatures:

\[ V_4(-\mathbf{q}, \mathbf{q}, -\mathbf{q}', \mathbf{q}'') = \frac{\hbar}{4N\omega_{\mathbf{q}}\omega_{\mathbf{q}' \mathbf{q}'}} \times \sum_{\kappa_1, \kappa_2, \kappa_3, \kappa_4} C_{\alpha\beta\mu\nu}(-\mathbf{q}, -\mathbf{q}', \mathbf{q}'', |\kappa_1\kappa_2\kappa_3\kappa_4|) \times \frac{w_\alpha(\kappa_1 - \mathbf{q})}{\sqrt{m_{\kappa_1}}} \frac{w_\beta(\kappa_2 |\mathbf{q}|)}{\sqrt{m_{\kappa_2}}} \frac{w_\mu(\kappa_3 - \mathbf{q}'')}{\sqrt{m_{\kappa_3}}} \frac{w_\nu(\kappa_4 |\mathbf{q}'|)}{\sqrt{m_{\kappa_4}}}. \]

When identifying the nonanalytic terms in the Fourier-transformed quartic force constants \( C_{\alpha\beta\mu\nu}(-\mathbf{q}, \mathbf{q}, -\mathbf{q}', \mathbf{q}'') |\kappa_1\kappa_2\kappa_3\kappa_4| \), we account only for cases of the wave vector \( \mathbf{q}' \) not being near the center of the Brillouin zone, since only those are relevant for the sum over the Brillouin zone in Eq. (4.3). The following additional terms have to be considered in the expansion (2.2) of the potential energy:

\[
\Delta \omega_{\mathbf{q}} = -\omega_{\mathbf{q}} c \Delta V/V, \tag{4.1}
\]

where \( \Delta V \) is the change of crystal volume due to quantum and thermal fluctuations of the atomic positions and \( c \) is the Grüneisen constant of mode \( \mathbf{q} \). From the derivative of the Lyddane-Sachs-Teller relation for a diatomic crystal with respect to the crystal volume we obtain

\[
\lim_{\mathbf{q} \to 0} \left[ \gamma(\mathbf{q} \mathbf{q} \mathbf{TO}) - \gamma(\mathbf{q} \mathbf{q} \mathbf{LO}) \right] = \frac{V}{2} \left[ \frac{1}{\varepsilon_0} \frac{\partial \varepsilon_0}{\partial V} - \frac{1}{\varepsilon_\infty} \frac{\partial \varepsilon_\infty}{\partial V} \right] \tag{4.2}
\]

involving elasto-optic coefficients and volume-derivatives of the Born effective charge. In Eq. (4.2) \( \varepsilon_0 \) is the static dielectric constant.

The third contribution to the anharmonic frequency shift involves quartic anharmonicity,

\[
\delta \omega_{\mathbf{q}} = \frac{1}{2} \sum_{\mathbf{q}', \mathbf{q}''} V_4(-\mathbf{q}, \mathbf{q}, -\mathbf{q}', \mathbf{q}'')(2n_{\mathbf{q}' \mathbf{q}''} + 1). \tag{4.3}
\]

The coefficients \( V_4 \) are related to the Fourier-transformed quartic anharmonic force constants in a way analogous to Eqs. (3.3) and (3.4):
These terms involve the second-order Raman coefficients \( P_{a\beta\mu}(q^\mu|\kappa\kappa') \), for which \textit{ab initio} data exist for covalent semiconductors. The coefficients \( M_{a\beta\mu}(q^\mu|\kappa\kappa') \) correspond to third-order dipole moments. We are not aware of any quantitative evaluation of these quantities so far.

Eliminating the macroscopic field, we finally obtain the following for \( q \) being a wave vector close to the center of the Brillouin zone and \( q' \) corresponding to a short wavelength:

\[
C_{a\beta\mu}(q,q',q'')\left|\kappa_1\kappa_2\kappa_3\kappa_4\right.
= \sum_{\lambda} \delta_{a\beta\mu}(q,q',q'')\left|\kappa_1\kappa_2\kappa_3\kappa_4\right.
+ q\sum_{\lambda\lambda'}\mathcal{Z}(q)q_{\lambda\lambda'}M_{a\beta\mu}(0,q',q''|\kappa_1\kappa_2\kappa_3\kappa_4)
+ q\sum_{\lambda\lambda'}\mathcal{Z}(q)q_{\lambda\lambda'}M_{a\beta\mu}(0,q',q''|\kappa_2\kappa_3\kappa_4)
- q\sum_{\lambda\lambda'}\mathcal{Z}(q)q_{\lambda\lambda'}Z_{\gamma\beta}(q)S(q)
× q_{\lambda\lambda'}P_{a\beta\mu}(q',q'')\left|\kappa_1\kappa_2\kappa_4\right.
\]

In deriving Eq. (4.6), we have made explicit use of the condition that the homogeneous part of the macroscopic field vanishes. Applying these expressions to crystals with zinc blende structure, we find that the nonanalytic terms [the last three terms on the right-hand side of Eq. (4.6)] do not contribute to \( V_4(-q_{TO},q_{TO},-q_{LO},-q_{LO},-q_{TO},q_{LO}) \), while their contribution to \( V_4(-q_{LO},q_{LO},-q_{LO},-q_{LO},-q_{LO},q_{LO}) \) is

\[
\delta V_4(-\epsilon q_{LO},\epsilon q_{LO},-q_{j'j'},q_{j'j'})
= \frac{\hbar}{4N\omega_0\omega_0q_{q_{j'j'}}} \pm 2 \frac{Z}{\sqrt{m_R\epsilon_\infty}} \hat{q}_{q_{j'j'}}M_\gamma(-\epsilon q_{LO},-q_{j'j'},q_{j'j'})
- \left( \frac{Z}{\sqrt{m_R\epsilon_\infty}} \right)^2 \hat{q}_{a\beta}P_{a\beta}(q_{j'j'},-q_{j'j'}).
\]

The quantities \( M_\gamma(-q_{j'j'},q_{j'j'}) \) and \( P_{a\beta}(q_{j'j'},-q_{j'j'}) \) are defined in direct analogy to Eq. (3.5).

V. CONCLUSIONS

Differences between the lifetimes of longitudinal and transverse optical near zone-center phonons in polar crystals do not only result from the two-phonon density of states, but also from differences in the matrix elements. In particular, the matrix elements contain nonanalytic terms as functions of the wave vector of the near zone-center phonons that have been identified and related to other physical quantities.

Although the lifetime of the LO-phonon mode at the center of the Brillouin zone in polar semiconductors is a quantity of fundamental importance, also in view of electronic transport processes in semiconductor devices, a theoretical treatment that would fully include the macroscopic field has not yet been given, to our knowledge. Our direct interpretations of the nonanalytic contributions to the damping function using \textit{ab initio} second-order dipole moments have shown that these contributions are negligibly small for GaAs. This is not surprising given the good agreement of experimental data for the Raman line shape and temperature-dependent Raman frequency of the LO mode on the one hand and calculations that do not account for the effect of the macroscopic field in the anharmonic coupling constants on the other. However, the differences may be more significant in highly polar materials that have a larger Lyddane-Sachs-Teller splitting than GaAs.

For the calculation of the effects of thermal and zero-point motion of the atoms on the frequencies of optical zone-center modes, one also has to account for quartic anharmonicity. The contributions of the macroscopic field to the quartic coupling constants involve the second-order Raman coefficients and the third-order dipole moments. Reliable \textit{ab initio} data for the prior quantities are not available yet for polar materials, while no data at all are known to us for the latter. Since both quantities are not accessible via linear electronic density response \((2\pi \pm 1)\) theorem, it is unlikely that a complete evaluation of the quartic nonanalytic terms will be possible in the near future.

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