Anharmonic coefficients in high symmetry directions for the diamond structure

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In this work, the cubic anharmonic coefficients are computed analytically in high symmetry directions considering central potential interactions up to fifth nearest neighbors for crystals with the diamond structure. It is found that certain channels of decay are forbidden. Furthermore particular relations between the different polarizations of the optical phonon for the cubic anharmonic coefficients are presented. Using these results, the validity of the so-called Peierls approximation is discussed.

Keywords: Peierls approximation; Fourier transformed anharmonic coefficients; diamond structure; optical-phonon channels of decay

En este artículo, se calculan de manera analítica los coeficientes anarmónicos cúbicos en direcciones de alta simetría considerando interacciones centrales de primeros a quintos vecinos para cristales con estructura de diamante. Se encuentra que ciertos canales de decaimiento están prohibidos. Además, se presentan relaciones entre los coeficientes anarmónicos cúbicos correspondientes a las diferentes polarizaciones del fonón óptico. A luz de estos resultados, se discute la validez de la aproximación de Peierls.

Descriptores: Aproximación de Peierls; la transformada de Fourier de los coeficientes anarmónicos; estructura de diamante; canales de decaimiento del fonón óptico

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1. Introduction

Many important experimental investigations of anharmonic processes in crystals with the diamond structure by Raman spectroscopy have been reported before [1-4]. In the past ten years, new results have been published on the anharmonic properties in silicon germanium alloys and heterostructures [5,6]. Anharmonicity is responsible for the interaction between phonons modifying phonon frequencies in two ways: first causing a phonon frequency shift, and secondly giving a determined lifetime because of the phonon-phonon interaction. These effects have been extensively studied both theoretically and experimentally. An essential ingredient for the theoretical models, developed in order to explain the experimental observations, are the Fourier transformed anharmonic coefficients that enter into the expressions of the phonon self-energy, the damping constant, and the frequency shift, among others. In many calculations of the properties of anharmonic crystals, it is necessary to evaluate sums over wave vector of the Fourier transformed anharmonic coefficients or its magnitude squared multiplied by various functions of the wave vector [7-12]. These computations are rather complex and frequently have been simplified by approximating the corresponding expressions by simpler ones. This is the case, for example, of the Peierls approximation [15], where the anharmonic coefficients are considered constant.

Previously, closed form expressions for the anharmonic coefficients within a central force model for a diatomic linear chain were obtained. The differences between these and other calculations, especially the Peierls approximation were discussed in Refs. 16 and 17. These results will be contrasted with our theoretical calculations in order to discuss the validity of the anharmonic coefficients obtained in this paper without doing any approximations.

In a previous work [12], we computed numerically the anharmonic coefficients and established that, when the optical phonon decay into two LA phonons along the [q00] direction, these coefficients were identical to 0, considering up to fourth-neighbor central interactions so that these channels of decay are forbidden, in contrast with previous results, for example Menéndez and Cardona [3]. To the best of our knowledge, however, analytical expressions for these anharmonic coefficients in a cubic crystal with diamond structure have never been obtained. In the present work, because of the lack of such calculation, we decided to study the cubic anharmonic coefficients in high symmetry directions considering central potential interactions up to the fifth nearest neighbors. We show that it is possible to give analytical expressions in several cases of interest. In addition, particular relationships between the expressions corresponding to different polarizations of the optical phonon are established.

2. Anharmonicity in crystals

For a system whose equilibrium positions are specified by:

$$\vec{R}(l,\kappa) = \vec{R}(1) + \vec{R}(\kappa) \tag{1}$$

where $\vec{R}(1) = 1_1\vec{\tau}_1 + 1_2\vec{\tau}_2 + 1_3\vec{\tau}_3$, τ_l are primitive translation vector, l_i are integers, and $\vec{R}(\kappa)$ is a vector of the basis; the

vibrational Hamiltonian can be written as:

$$H = \sum_{l\kappa\alpha} \frac{P_\alpha^2(l\kappa)}{2M} + \frac{1}{2}\sum_{l\kappa\alpha}\sum_{l'\kappa'\beta} \Phi_{\alpha\beta}(l\kappa|l'\kappa')u_\alpha(l\kappa)u_\beta(l'\kappa') + \frac{1}{6}\sum_{l\kappa\alpha}\sum_{l'\kappa'\beta}\sum_{l''\kappa''\gamma} \Phi_{\alpha\beta\gamma}(l\kappa|l'\kappa'|l''\kappa'')u_\alpha(l\kappa)u_\beta(l'\kappa')u_\gamma(l''\kappa'') + \frac{1}{24}\sum_{l\kappa\alpha}\cdots\sum_{l''\kappa''\delta} \Phi_{\alpha\beta\gamma\delta}(l\kappa|l'\kappa'|l''\kappa''|l'''\kappa''')u_\alpha(l\kappa)u_\beta(l'\kappa')u_\gamma(l''\kappa'')u_\delta(l'''\kappa'''), \quad (2)$$

where $u_\alpha(l\kappa)$ is the displacement component along a direction of atom $(l\kappa)$ from its equilibrium position and $\Phi_{\alpha\beta}$, $\Phi_{\alpha\beta\gamma}$ and $\Phi_{\alpha\beta\gamma\delta}$ are the second, third and fourth order harmonic force constants, respectively. The first two terms in Eq. (2) are the harmonic Hamiltonian H_0, and the remaining terms being the anharmonic Hamiltonian H_A. We diagonalize the harmonic Hamiltonian by means of the normal coordinate transformation:

$$\vec{u}(l\kappa) = \left(\frac{\hbar}{2M_\kappa N}\right)^{1/2}\sum_{qj}\frac{\vec{e}(\kappa|\vec{q}j)}{(\omega_{qj})^{1/2}}e^{i\vec{q}\circ\vec{R}(l)}A_{qj}. \quad (3)$$

$$\vec{P}(l\kappa) = -i\left(\frac{\hbar M_\kappa}{2N}\right)^{1/2}\sum_{qj}(\omega_{qj})^{1/2}\vec{e}(\kappa|\vec{q}j)e^{i\vec{q}\circ\vec{R}(l)}B_{qj}. \quad (4)$$

Here $\omega_{\vec{q},j}$ is the normal-mode frequency for wave vector $\vec{q}$ and branch index j, $\vec{e}(\kappa|\vec{q},j)$ is the polarization vector for the normal mode, M_κ is the mass of atom κ, and N is the number of unit cells in the crystal. As usual, the field operators A_{qj} and B_{qj} are specified in terms of the phonon creation and annihilation operators,

$$A_{qj} = b_{qj} + b^\dagger_{-qj} \quad (5)$$

$$B_{qj} = b_{qj} - b^\dagger_{-qj} \quad (6)$$

After making the normal coordinate transformations, the Hamiltonian take the form

$$H_0 = \sum_{qj}\hbar\omega_{qj}\left(b^\dagger_{qj}b_{qj} + \tfrac{1}{2}\right) \quad (7)$$

$$H_A = \sum_{qj,q'j',q''j''} V\left(\vec{q}j|\vec{q}'j'|\vec{q}''j''\right)A_{qj}A_{q'j'}A_{q''j''} + \sum_{qj,\ldots,q'''j'''} V\left(\vec{q}j|\vec{q}'j'|\vec{q}''j''|\vec{q}'''j'''\right) \times A_{qj}A_{q'j'}A_{q''j''}A_{q'''j'''} + \cdots, \quad (8)$$

where H_0 and H_A stands for the harmonic and anharmonic parts of the vibrational Hamiltonian, and the anharmonic coefficients are given by:

$$V\left(\vec{q},j;\vec{q}',j';\vec{q}'',j''\right) = \frac{1}{6}\left(\frac{\hbar}{2N}\right)^{3/2}\left(\omega_{\vec{q},j}\omega_{\vec{q}',j'}\omega_{\vec{q}'',j''}\right)^{-1/2}N\Delta\left(\vec{q}+\vec{q}'+\vec{q}''\right) \times\sum_{\kappa,\alpha}\sum_{\bar{l}'\kappa',\beta}\sum_{\bar{l}'',\kappa'',\gamma}\Phi_{\alpha\beta\gamma}\left(0,\kappa;\bar{l}',\kappa';\bar{l}'',\kappa''\right)\frac{e_\alpha(\kappa|\vec{q},j)e_\beta(\kappa'|\vec{q}',j')e_\gamma(\kappa''|\vec{q}'',j'')}{(M_\kappa M_{\kappa'}M_{\kappa''})^{1/2}}e^{i[\vec{q}\cdot\vec{R}(\bar{l}')+\vec{q}''\cdot\vec{R}(\bar{l}'')]} \quad (9)$$

$$V\left(\vec{q},j;\vec{q}',j';\vec{q}''j,'';\vec{q}''',j'''\right) = \frac{N}{24}\left(\frac{\hbar}{2N}\right)^{3/2}\left(\omega_{\vec{q}j}\omega_{\vec{q}'j'}\omega_{\vec{q}''j''}\omega_{\vec{q}'''j'''}\right)^{-1/2}\Delta\left(\vec{q}+\vec{q}'+\vec{q}''+\vec{q}'''\right) \times\sum_{l\kappa\alpha}\sum_{l'\kappa'\beta}\sum_{l''\kappa''\gamma}\sum_{l'''\kappa'''\delta}\Phi_{\alpha\beta\gamma\delta}\left(0,\kappa;l'\kappa';l''\kappa'';l''',\kappa'''\right) \times\frac{e_\alpha\left(\kappa|\vec{q},j\right)e_\beta\left(\kappa'|\vec{q}',j'\right)e_\gamma\left(\kappa''|\vec{q}'',j''\right)e_\delta\left(\kappa|'''\vec{q}''',j'''\right)}{\left(M_\kappa M_{\kappa'}M_{\kappa''}M_{\kappa'''}\right)^{1/2}}e^{i\left[\vec{q}'\circ\vec{R}(l')+\vec{q}''\circ\vec{R}(l'')+\vec{q}'''\circ\vec{R}(l''')\right]}$$

with

$$\Delta(\vec{q}) = \begin{cases} 1 & \text{if} \quad \vec{q} = \vec{G} \\ 0 & \text{otherwise.} \end{cases} \quad (10)$$

3. Anharmonicity in crystals: central potential interactions

Let us now restrict our analysis to central potentials and consider only the cubic term in the vibrational Hamiltonian:

$$\Phi_{3c} = \frac{1}{12}\sum_{l,\kappa}\sum_{l',\kappa'}\sum_{\alpha\beta\gamma}\phi_{\alpha\beta\gamma}(l\kappa|l'\kappa')u_\alpha(l\kappa|l'\kappa')u_\beta(l\kappa|l'\kappa')u_\gamma(l\kappa|l'\kappa'), \quad (11)$$

where

$$\phi(l\kappa|l'\kappa') = \frac{x_\alpha x_\beta x_\gamma}{r^3}\left[\phi'''_{\kappa\kappa'}(r) - \frac{3\phi''_{\kappa\kappa'}(r)}{r} + \frac{3\phi'_{\kappa\kappa'}(r)}{r^2}\right] + \frac{(x_\alpha\delta_{\beta\gamma} + x_\beta\delta_{\alpha\gamma} + x_\gamma\delta_{\alpha\beta})}{r^2} \times \left(\phi''_{\kappa\kappa'}(r) - \frac{\phi'_{\kappa\kappa'}(r)}{r}\right)\Bigg|_{\vec{r}=\vec{x}(l\kappa|l'\kappa')} \quad (12)$$

with $\vec{r} = \sum_\alpha x_\alpha \hat{e}_\alpha$ and

$$\vec{R}(l\kappa|l'\kappa') = \vec{R}(l\kappa) - \vec{R}(l'\kappa') \quad (13)$$

and

$$\phi'(r)=\frac{d\phi(r)}{dr}, \quad \phi''(r)=\frac{d^2\phi(r)}{dr^2}, \quad \phi'''(r)=\frac{d^3\phi(r)}{dr^3}. \quad (14)$$

In this work, we are particularly interested in the disintegration of the optical phonon at the zone-center (Raman mode) into two phonons (cubic process). The zone-center phonon has a zero wave vector, so that the conservation laws of energy and momentum give in this case:

$$\omega(\vec{q}', j') + \omega(\vec{q}'', j'') = \omega(0, j)$$
$$\vec{q}' + \vec{q}'' \Rightarrow \vec{q}'' = -\vec{q}', \quad (15)$$

thus, the corresponding anharmonic coefficients are given by:

$$V^{(i)}(\vec{0}, j; \vec{q}, j'; -\vec{q}, j'') = \frac{N}{12}\left(\frac{\hbar}{2N}\right)^{3/2} \times (\omega_{\vec{0},j}\omega_{\vec{q},j'}\omega_{-\vec{q},j''})^{-1/2} \sum_{\alpha\beta\gamma}\sum_{\bar{l}'\kappa\kappa'} \Phi^{(i)}_{\alpha\beta\gamma}\left(0, \kappa|\bar{l}', \kappa'\right) \times \left[e_\alpha(\kappa|\vec{0}, j) - e_\alpha(\kappa'|\vec{0}, j)\right] \times \left[e_\beta(\kappa|\vec{0}, j) - e_\beta(\kappa'|\vec{0}, j)e^{-i[\vec{q}\cdot\vec{R}(\bar{l}')]}\right] \times \left[e_\gamma(\kappa| - \vec{q}, j'') - e_\gamma(\kappa'|\vec{0}, j'')e^{-i[\vec{q}\cdot\vec{R}(\bar{l}')]}\right] \quad (16)$$

4. Anharmonicity in crystals having the diamond structure

In the diamond structure, which has two atoms per unit cell, nearest neighbors of odd order belong to distinct sub-lattices, while even order neighbors belong to the same sub-lattice. Consider the expression (16) and particularly the factor $[e_\alpha(\kappa|\vec{0}j) - e_\alpha(\kappa'|\vec{0}j)]$. This term vanishes clearly for atoms belonging to the same sub-lattice, so that $V_c^{2n}(0j; q', j'; q'', j'') = 0$. This result can be generalized to higher order anharmonic processes thus $V_c^{2n}(0j; q', j'; q'', j''; \ldots) = 0$.

Physically, the fact that neighboring atoms of even order do not contribute to the disintegration of the optical phonon can be seen by noting that optical branches are due exclusively to relative displacements of atoms belonging to distinct sub-lattices. In Fig. 1, the phonon dispersion curves are shown for the case of silicon; we have obtained this curves using the harmonic part of our model (consisting of central nearest neighbors, angle bending and dipole interactions) as described in Ref. 13. In this figure some possible channels of decay in high symmetry directions for the Raman phonon are indicated (dotted lines).

5. Cubic anharmonic coefficients in high symmetry directions

In high symmetry directions, it is possible to obtain simpler expressions for the cubic anharmonic coefficients. Let us label the phonon branches as follows: $j = 1, 2, 3$ for the TA_1, TA_2 and LA branches respectively; $j = 4, 5, 6$ for the TO_1, TO_2 and LO branches respectively. Furthermore we consider first nearest neighbor interactions only. The position vectors for this case are given in Table I.

The cubic anharmonic coefficients for this case can be written as:

$$V^{(i)}(\vec{0}, j; \vec{q}, j'; -\vec{q}, j'') = \frac{N}{6}\left(\frac{\hbar}{2NM}\right)^{3/2} \times (\omega_{\vec{0},j}\omega_{\vec{q},j'}\omega_{-\vec{q},j''})^{-1/2} \sum_{\alpha\beta\gamma}\sum_{l'\kappa\kappa'} \Phi^{(i)}_{\alpha\beta\gamma}(0, 0|\delta_i, 1) \times \left[e_\alpha(0|\vec{0}, j) - e_\alpha(1|\vec{0}, j)\right] \times \left[e_\beta(0|\vec{q}, j') - e_\beta(1|\vec{q}, j')e^{i(\vec{q}\cdot\vec{\delta}_i)}\right] \times \left[e_\gamma(0| - \vec{q}, j'') - e_\gamma(1| - \vec{q}, j'')e^{i(\vec{q}\cdot\vec{\delta}_i)}\right] \quad (17)$$

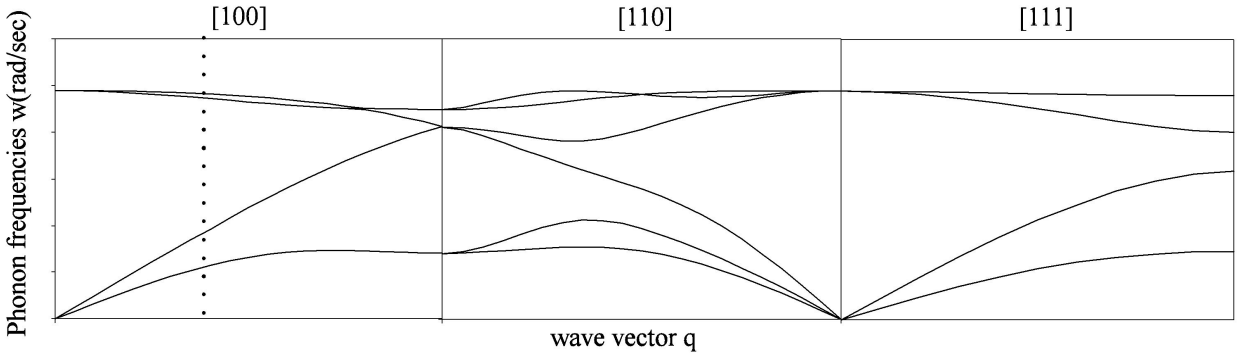

FIGURE 1. Phonon dispersion curves for silicon using Wanser model, the dotted lines indicate possible channels of decay.

TABLE I. Position vectors of the first, third and fifth nearest neighbors (NN).

	1^{st} NN	3^{rd} NN	5^{th} NN
$\mathbf{R}(\delta_1,1\|0,0)$	$\mathbf{e}_1+\mathbf{e}_2+\mathbf{e}_3$		
$\mathbf{R}(\delta_2,1\|0,0)$	$-\mathbf{e}_1-\mathbf{e}_2+\mathbf{e}_3$		
$\mathbf{R}(\delta_3,1\|0,0)$	$\mathbf{e}_1-\mathbf{e}_2-\mathbf{e}_3$		
$\mathbf{R}(\delta_4,1\|0,0)$	$-\mathbf{e}_1+\mathbf{e}_2-\mathbf{e}_3$		
$\mathbf{R}(\tau_1,1\|0,0)$		$\mathbf{e}_1-\mathbf{e}_2+3\mathbf{e}_3$	
$\mathbf{R}(\tau_2,1\|0,0)$		$\mathbf{e}_1-3\mathbf{e}_2+\mathbf{e}_3$	
$\mathbf{R}(\tau_3,1\|0,0)$		$3\mathbf{e}_1-\mathbf{e}_2+\mathbf{e}_3$	
$\mathbf{R}(\tau_4,1\|0,0)$		$-\mathbf{e}_1+\mathbf{e}_2+3\mathbf{e}_3$	
$\mathbf{R}(\tau_5,1\|0,0)$		$-\mathbf{e}_1+3\mathbf{e}_2+\mathbf{e}_3$	
$\mathbf{R}(\tau_6,1\|0,0)$		$-3\mathbf{e}_1+\mathbf{e}_2+\mathbf{e}_3$	
$\mathbf{R}(\tau_7,1\|0,0)$		$\mathbf{e}_1+\mathbf{e}_2-3\mathbf{e}_3$	
$\mathbf{R}(\tau_8,1\|0,0)$		$3\mathbf{e}_1+\mathbf{e}_2-\mathbf{e}_3$	
$\mathbf{R}(\tau_9,1\|0,0)$		$\mathbf{e}_1+3\mathbf{e}_2-\mathbf{e}_3$	
$\mathbf{R}(\tau_{10},1\|0,0)$		$-\mathbf{e}_1-\mathbf{e}_2-3\mathbf{e}_3$	
$\mathbf{R}(\tau_{11},1\|0,0)$		$-3\mathbf{e}_1-\mathbf{e}_2-\mathbf{e}_3$	
$\mathbf{R}(\tau_{12},1\|0,0)$		$-\mathbf{e}_1-3\mathbf{e}_2-\mathbf{e}_3$	
$\mathbf{R}(\rho_1,1\|0,0)$			$3\mathbf{e}_1+3\mathbf{e}_2+\mathbf{e}_3$
$\mathbf{R}(\rho_2,1\|0,0)$			$\mathbf{e}_1+3\mathbf{e}_2+3\mathbf{e}_3$
$\mathbf{R}(\rho_3,1\|0,0)$			$3\mathbf{e}_1+\mathbf{e}_2+3\mathbf{e}_3$
$\mathbf{R}(\rho_4,1\|0,0)$			$-3\mathbf{e}_1-3\mathbf{e}_2+\mathbf{e}_3$
$\mathbf{R}(\rho_5,1\|0,0)$			$\mathbf{e}_1-3\mathbf{e}_2-3\mathbf{e}_3$
$\mathbf{R}(\rho_6,1\|0,0)$			$-3\mathbf{e}_1+\mathbf{e}_2-3\mathbf{e}_3$
$\mathbf{R}(\rho_7,1\|0,0)$			$3\mathbf{e}_1-\mathbf{e}_2-3\mathbf{e}_3$
$\mathbf{R}(\rho_8,1\|0,0)$			$-\mathbf{e}_1+3\mathbf{e}_2-3\mathbf{e}_3$
$\mathbf{R}(\rho_9,1\|0,0)$			$-3\mathbf{e}_1-\mathbf{e}_2+3\mathbf{e}_3$
$\mathbf{R}(\rho_{10},1\|0,0)$			$-\mathbf{e}_1-3\mathbf{e}_2+3\mathbf{e}_3$
$\mathbf{R}(\rho_{11},1\|0,0)$			$-3\mathbf{e}_1+3\mathbf{e}_2-\mathbf{e}_3$
$\mathbf{R}(\rho_{12},1\|0,0)$			$3\mathbf{e}_1-3\mathbf{e}_2-\mathbf{e}_3$

For higher order neighbors the expressions are analogous. Special care must be taken in considering the corresponding position vectors as it will be shown later. In the next sections, we calculate analytical expressions for the cubic anharmonic coefficients along high symmetry directions. All of the eigenvectors appearing in these calculations have been obtained previously applying symmetry operations and theory of groups [22].

5.1. Decay of the optical phonon into two LA phonons in the [100] direction

In this direction: $\vec{q}=q\hat{e}_1$, and the eigenvectors are given by:

$$e_\alpha(0|\vec{q},3)=b\delta_{\alpha 1}=\frac{\delta_{\alpha 1}}{\sqrt{2}},$$

$$e_\alpha(1|\vec{q},3)=be^{iq(a/4)}\delta_{\alpha 1}=e^{iq(a/4)}\frac{\delta_{\alpha 1}}{\sqrt{2}},$$

where we have used the so-called normalization condition. The cubic anharmonic coefficients can then be written as:

$$V^1(\vec{0},j;\vec{q},3;-\vec{q},3)=\frac{N}{8}\left(\frac{\hbar}{2NM}\right)^{3/2}\times\frac{\sin^2(qa)}{3}(\omega_{\vec{0},j}\omega_{\vec{q},LA})^{-1/2}\times\sum_i\sum_\alpha\Phi_{\alpha ll}(0,0|\delta_i,1)\left[e_\alpha(0|\vec{0}j)-e_\alpha(1|\vec{0}j)\right]. \quad (18)$$

In fact, this is the 3D generalization of Eq. (20) from the Held and Pfeiffer article [17], where these authors, discussed the problem of anharmonicity in a linear diatomic chain. Now, using the results given in Tables I and II it is easy to show that:

$$\sum_i\Phi_{\alpha ll}(0,0|\delta_i,1)$$

thus

$$V^1(0j;q,3;-q,3)=0 \qquad \text{for} \qquad j=4,5,6$$

Therefore, this channel of decay is forbidden, in full agreement with the diatomic linear chain case (see Eqs. (20) and (21) from Ref. 17). In order to compute the corresponding anharmonic coefficients for higher order neighbors, 3rd and 5th nearest neighbors, we use the information given in tables I to IV. In this way, we obtain for the cubic anharmonic coefficients along this channel of decay that:

$$V^i(0j;q,3;-q3)=0 \quad \text{for} \quad j=4,5,6 \quad \text{and} \quad i=1,3,5. \quad (19)$$

5.2. Decay of the optical phonon into one LA and one TA phonon in the [100] direction

The eigenvectors for the LA branch in the [100] direction were given in the previous paragraph, meanwhile for a TA branch in the [100] direction we have:

$$e_\alpha(0|\vec{q},2)=a(\delta_{\alpha 2}-\delta_{\alpha 3})$$

$$e_\alpha(1|\vec{q},2)=b(\delta_{\alpha 2}-\delta_{\alpha 3})e^{iq(a/4)} \quad (20)$$

TABLE II. Cubic harmonic force constants for first nearest neighbors with $\alpha_1=c_1A_1+3d_1B_1$, $\alpha_2=c_1A_1+d_1B_1$, $\alpha_3=-c_1A_1$, $\Phi^{(i)}_{112}=\Phi^{(i)}_{332}$; $\Phi^{(i)}_{113}=\Phi^{(i)}_{223}$; $\Phi^{(i)}_{221}=\Phi^{(i)}_{331}$ for $i=1,2,3,4$, and

$A_1=\Phi_1'''(r_1)-3\Phi_1''(r_1)/r_1+3\Phi_1'(r_1)/r_1^2$

$B_1=\Phi_1''(r_1)-\Phi_1'(r_1)/r_1$ and $r_1=(\sqrt{3}/4)a$

$c_1=(a/4)^3/r_1^3$, $d_1=(a/4)/r_1^2$.

	Φ_{111}	Φ_{222}	Φ_{333}	Φ_{112}	Φ_{113}	Φ_{221}	Φ_{123}
$i=1$	$-\alpha_1$	$-\alpha_1$	$-\alpha_1$	$-\alpha_2$	$-\alpha_2$	$-\alpha_2$	α_3
$i=2$	α_1	α_1	$-\alpha_1$	α_2	$-\alpha_2$	α_2	α_3
$i=3$	$-\alpha_1$	α_1	α_1	α_2	α_2	$-\alpha_2$	α_3
$i=4$	α_1	$-\alpha_1$	α_1	$-\alpha_2$	α_2	α_2	α_3

TABLE III. Cubic harmonic force constants for third nearest neighbors where $\beta_1 = c_3A_3 + 3d_3B_3$, $\beta_2 = 27c_3A_3 + 9d_3B_3$, $\beta_3 = c_3A_3 + d_3B_3$, $\beta_4 = 9c_3A_3 + d_3B_3$, $\beta_5 = 3c_3A_3$ and

$$A_3 = \Phi_3'''(r_3) - 3\Phi_3''(r_3)/r_3 + 3\Phi_3'(r_3)/r_3^2$$
$$B_3 = \Phi_3''(r_1) - \Phi_3'(r_3)/r_3 \quad \text{and} \quad r_3 = (\sqrt{3}/4)a$$
$$c_3 = (a/4)^3/r_3^3, \quad d_3 = (a/4)/r_3^2.$$

	Φ_{111}	Φ_{222}	Φ_{333}	Φ_{112}	Φ_{113}	Φ_{221}	Φ_{223}	Φ_{331}	Φ_{332}	Φ_{123}
$i=1$	$-\beta_1$	β_1	$-\beta_2$	β_3	$-3\beta_3$	$-\beta_3$	$-3\beta_3$	$-\beta_4$	β_4	β_5
$i=2$	$-\beta_1$	β_2	$-\beta_1$	$3\beta_3$	$-\beta_3$	$-\beta_4$	$-\beta_4$	$-\beta_3$	$3\beta_3$	β_5
$i=3$	$-\beta_2$	β_1	$-\beta_1$	β_4	$-\beta_4$	$-3\beta_3$	$-\beta_3$	$-3\beta_3$	β_3	β_5
$i=4$	β_1	$-\beta_1$	$-\beta_2$	$-\beta_3$	$-3\beta_3$	β_3	$-3\beta_3$	β_4	$-\beta_4$	β_5
$i=5$	β_1	$-\beta_2$	$-\beta_1$	$3\beta_3$	$-\beta_3$	β_4	$-\beta_4$	β_3	$-3\beta_3$	β_5
$i=6$	β_2	$-\beta_1$	$-\beta_1$	$-\beta_4$	$-\beta_4$	$3\beta_3$	$-\beta_3$	$3\beta_3$	$-\beta_3$	β_5
$i=7$	$-\beta_1$	$-\beta_1$	β_2	$-\beta_3$	$3\beta_3$	$-\beta_3$	$3\beta_3$	$-\beta_4$	$-\beta_4$	β_5
$i=8$	$-\beta_2$	$-\beta_1$	β_1	$-\beta_4$	β_4	$-3\beta_3$	β_3	$-3\beta_3$	$-\beta_3$	β_5
$i=9$	$-\beta_1$	$-\beta_2$	β_1	$-3\beta_3$	β_3	$-\beta_4$	β_4	$-\beta_3$	$-3\beta_3$	β_5
$i=10$	β_1	β_1	β_2	β_3	$3\beta_3$	$-\beta_3$	$3\beta_3$	β_4	β_4	β_5
$i=11$	β_2	β_1	β_1	β_4	β_4	$3\beta_3$	β_3	$3\beta_3$	β_3	β_5
$i=12$	β_1	β_2	β_1	$3\beta_3$	β_3	β_4	β_4	β_3	$3\beta_3$	β_5

TABLE IV. Cubic harmonic force constants for fifth nearest neighbors where $\gamma_1 = 27c_5A_5 + 9d_5B_5$, $\gamma_2 = c_5A_5 + 3d_5B_5$, γ_3=$27c_5A_5 + 3d_5B_5$, γ_4=$3c_5A_5 + 3d_5B_5$, γ_5=$9c_5A_5 + d_5B_5$, $\gamma_6 = -9c_5A_5$ and

$$A_5 = \Phi_5'''(r_5) - 3\Phi_5''(r_5)/r_5 + 3\Phi_5'(r_5)/r_5^2$$
$$B_5 = \Phi_5''(r_5) - \Phi_1'(r_5)/r_5 \quad \text{and} \quad r_5 = (\sqrt{3}/4)a$$
$$c_5 = (a/4)^3/r_5^3, \quad d_5 = (a/4)/r_5^2.$$

	Φ_{111}	Φ_{222}	Φ_{333}	Φ_{112}	Φ_{113}	Φ_{221}	Φ_{223}	Φ_{331}	Φ_{332}	Φ_{123}
$i=1$	$-\gamma_1$	$-\gamma_1$	$-\gamma_2$	$-\gamma_3$	$-\gamma_5$	$-\gamma_3$	$-\gamma_5$	$-\gamma_4$	$-\gamma_4$	γ_6
$i=2$	$-\gamma_2$	$-\gamma_1$	$-\gamma_1$	$-\gamma_4$	$-\gamma_4$	$-\gamma_5$	$-\gamma_3$	$-\gamma_5$	$-\gamma_3$	γ_6
$i=3$	$-\gamma_1$	$-\gamma_2$	$-\gamma_1$	$-\gamma_5$	$-\gamma_3$	$-\gamma_4$	$-\gamma_4$	$-\gamma_3$	$-\gamma_5$	γ_6
$i=4$	γ_1	γ_1	$-\gamma_2$	γ_3	$-\gamma_5$	γ_3	$-\gamma_5$	γ_4	γ_4	γ_6
$i=5$	$-\gamma_2$	γ_1	γ_1	γ_4	γ_4	$-\gamma_5$	γ_3	$-\gamma_5$	γ_3	γ_6
$i=6$	γ_1	$-\gamma_2$	γ_1	$-\gamma_5$	γ_3	γ_4	γ_4	γ_3	$-\gamma_5$	γ_6
$i=7$	$-\gamma_1$	γ_2	γ_1	γ_5	γ_3	$-\gamma_4$	γ_4	$-\gamma_3$	γ_5	γ_6
$i=8$	γ_2	$-\gamma_1$	γ_1	$-\gamma_4$	γ_4	γ_5	γ_3	γ_5	$-\gamma_3$	γ_6
$i=9$	γ_1	γ_2	$-\gamma_1$	γ_5	$-\gamma_3$	γ_4	$-\gamma_4$	γ_3	γ_5	γ_6
$i=10$	γ_2	γ_1	$-\gamma_1$	γ_4	$-\gamma_4$	γ_5	$-\gamma_3$	γ_5	γ_3	γ_6
$i=11$	γ_1	$-\gamma_1$	γ_2	$-\gamma_3$	γ_5	γ_3	γ_5	γ_4	$-\gamma_4$	γ_6
$i=12$	$-\gamma_1$	γ_1	γ_2	γ_3	γ_5	$-\gamma_3$	γ_5	$-\gamma_4$	γ_4	γ_6

where a and b are normalization constants. Next we choose for the optical phonon the following polarizations:

$$e_\alpha(0|\vec{0},4) = \frac{\delta_{\alpha1}}{\sqrt{2}}; \quad e_\beta(0|\vec{0},5) = \frac{\delta_{\beta2}}{\sqrt{2}};$$
$$e_\gamma(0|\vec{0},6) = \frac{\delta_{\gamma3}}{\sqrt{2}}; \quad e_\alpha(1|\vec{0},4) = \frac{\delta_{\alpha1}}{\sqrt{2}};$$
$$e_\beta(1|\vec{0},5) = \frac{\delta_{\beta2}}{\sqrt{2}}; \quad e_\gamma(1|\vec{0},6) = \frac{\delta_{\gamma3}}{\sqrt{2}}; \qquad (21)$$

For this case the anharmonic coefficients can be written as:

$$V^1(\vec{0},j;\vec{q},2;-\vec{q},3) = \frac{N}{6}\left(\frac{\hbar}{2NM}\right)(\omega_{\vec{0},j}\omega_{\vec{q},TA}\omega_{-\vec{q},LA})^{1/2}$$
$$\times \sum_i \sum_{\alpha\beta\gamma} \Phi^{(i)}_{\alpha\beta\gamma}(0,0|\delta_i,1)\left[e_\alpha(0|\vec{0}j) - e_\alpha(0|\vec{0}j'')\right]$$
$$\times \left[(\delta_{\beta2}-\delta_{\beta3})a - (\delta_{\beta2}-\delta_{\beta3})e^{i\vec{q}\cdot\vec{\delta}_i}e^{iq(a/4)}\right]$$
$$\times \left[\frac{\delta_{\gamma1}}{\sqrt{2}}\left(1 - e^{-i\vec{q}\cdot\vec{\delta}_i}e^{-iq(a/4)}\right)\right]$$

after performing the summations one obtains the following relations between the cubic anharmonic coefficients:

$$V^i(\vec{0},4;\vec{q},2;-\vec{q}3) = 0$$
$$V^i(\vec{0},6;\vec{q},2;-\vec{q}3) = -V^i(\vec{0},5;\vec{q},2;-\vec{q}3) \qquad (22)$$

for $i = 1, 3, 5$ with

$$V^1(\vec{0},5;\vec{q},2;-\vec{q}3) = \frac{N}{6}\left(\frac{\hbar}{2NM}\right)^{3/2}(\omega_{\vec{0}5}\omega_{\vec{q}LA}\omega_{\vec{q},TA})^{-1/2}$$
$$\times \Big[\left(a - be^{iq(a/4)}\right)\left(1 - e^{iq(a/4)}\right)(-2d_1B_1)$$
$$+ \left(a - be^{-iq(a/4)}\right)\left(1 - e^{iq(a/4)}\right)(4c_1A_1 + 2d_1B_1)\Big]. \quad (23)$$

In a completely similar fashion, we found that, for the third nearest neighbors, the corresponding relation is:

$$V^3(\vec{0},5;\vec{q},2;-\vec{q}3) = \frac{N}{3\sqrt{2}}\left(\frac{\hbar}{2NM}\right)^{3/2}(\omega_{\vec{0}5}\omega_{\vec{q}LA}\omega_{\vec{q},TA})^{-1/2}$$
$$\Big[\left(a - be^{iq(a/4)}\right)\left(1 - e^{iq(a/4)}\right)(-32c_3A_3 - 4d_3B_3)$$
$$+ \left(a - be^{3iq(a/4)}\right)\left(1 - e^{-3iq(a/4)}\right)(-12c_3A_3 - 6d_3B_3)$$
$$+ \left(a - be^{-iq(a/4)}\right)\left(1 - e^{iq(a/4)}\right)(8c_3A_3 + 4d_3B_3)$$
$$+ \left(a - be^{-3iq(a/4)}\right)\left(1 - e^{3iq(a/4)}\right)(6d_3B_3)\Big]. \quad (24)$$

Finally for the fifth nearest neighbors we have:

$$V^5(\vec{0},5;\vec{q},2;-\vec{q}3)=\frac{N}{3}\left(\frac{\hbar}{2NM}\right)^{3/2}(\omega_{\vec{0}5}\omega_{\vec{q}LA}\omega_{\vec{q},TA})^{-1/2}$$
$$\Big[\left(a-be^{iq(a/4)}\right)\left(1-e^{-iq(a/4)}\right)(-d_5B_5)$$
$$+\left(a-be^{3iq(a/4)}\right)\left(1-e^{-3iq(a/4)}\right)(-12c_5A_5-6d_5B_5)$$
$$+\left(a-be^{-iq(a/4)}\right)\left(1-e^{iq(a/4)}\right)(18c_5A_5+d_5B_5)$$
$$+\left(a-be^{-3iq(a/4)}\right)\left(1-e^{3iq(a/4)}\right)$$
$$\times(48c_5A_5+6d_5B_5)\Big]. \quad (25)$$

where the coefficients A_1, A_3, A_5, B_1, B_3, B_5, c_1, c_3, c_5, d_1, d_3, d_5 are given in Tables II-IV, respectively.

5.3. Decay of the raman mode into two LA phonons in the [111] direction

In this direction: $\vec{q}=(q/\sqrt{3})(\vec{e}_1+\vec{e}_2+\vec{e}_3)$. Also, the eigenvectors are given by:

$$e_\alpha(0|\vec{q},3)=b(\delta_{\alpha1}+\delta_{\alpha2}+\delta_{\alpha3}),$$
$$e_\alpha(0|\vec{q},3)=c(\delta_{\alpha1}+\delta_{\alpha2}+\delta_{\alpha3})e^{i\sqrt{3}q(a/4)}.$$

Using the normalization condition we have: $b^2+c^2=1/3$; therefore, the cubic anharmonic coefficients can be written as:

$$V^1(\vec{0},5;\vec{q},2;-\vec{q}3)=\frac{N}{6}\left(\frac{\hbar}{2NM}\right)^{3/2}(\omega_{\vec{0},j}\omega_{\vec{q},LA}\omega_{\vec{q},LA})^{-1/2}$$
$$\times\sum_i\sum_{\alpha\beta\gamma}\Phi^{(i)}_{\alpha\beta\gamma}(0,0|\delta_i,1)\left[e_\alpha(0|\vec{0}j)-e_\alpha(1|\vec{0}j)\right]$$
$$\times(\delta_{\beta1}+\delta_{\beta2}+\delta_{\beta3})(\delta_{\gamma1}+\delta_{\gamma2}+\delta_{\gamma3})$$
$$\times\left[\frac{1}{3}-2bc\cos\left(\frac{\sqrt{3}qa}{4}+\vec{q}\cdot\vec{\delta}_i\right)\right].$$

After performing the sums one finds:

$$V^i(0,4;q,3;-q,3)=V^i(0,5;q,3;-q,3)$$
$$=V^i(0,6;q,3;-q,3), \quad (26)$$

for $i=1,3,5$. So that the three anharmonic coefficients are equal in this case for the three distinct polarizations of the optical phonon:

$$V^1(\vec{0},j;\vec{q},3;-\vec{q}3)=\frac{N}{\sqrt{2}}\left(\frac{\hbar}{2NM}\right)^{3/2}(\omega_{\vec{0},j}\omega^2_{\vec{q},LA})^{-1/2}$$
$$\times\left[\left(\frac{1}{3}-2bc\cos\frac{\sqrt{3}qa}{4}\right)(-3c_1A_1-3d_1B_1)\right.$$
$$\left.+\left(\frac{1}{3}-2bc\cos\frac{\sqrt{3}qa}{12}\right)(\tfrac{1}{3}c_1A_1-3d_1B_1)\right], \quad (27)$$

with $j=4,5,6$, and where A_1 and B_1 are given in Table I. For the third nearest neighbors the corresponding expression is given by:

$$V^3(\vec{0},j;\vec{q},3;-\vec{q}3)=\frac{N}{3\sqrt{2}}\left(\frac{\hbar}{2NM}\right)^{3/2}(\omega_{\vec{0},j}\omega^2_{\vec{q},LA})^{-1/2}$$
$$\times\left[\left(\frac{1}{3}-2bc\cos\frac{\sqrt{3}qa}{4}\right)(-54c_3A_3-54d_3B_3)\right.$$
$$+\left(\frac{1}{3}-2bc\cos\frac{\sqrt{3}qa}{12}\right)(c_3A_3+9d_3B_3)$$
$$\left.+\left(\frac{1}{3}-2bc\cos\frac{5\sqrt{3}qa}{12}\right)(125c_3A_3+45d_3B_3)\right], \quad (28)$$

and for the fifth nearest neighbors we have:

$$V^5(\vec{0},j;\vec{q},3;-\vec{q}3)=\frac{2N}{3\sqrt{2}}\left(\frac{\hbar}{2NM}\right)^{3/2}(\omega_{\vec{0},j}\omega^2_{\vec{q},LA})^{-1/2}$$
$$\times\left[\left(\frac{1}{3}-2bc\cos\frac{\sqrt{3}qa}{12}\right)(c_5A_5+9d_5B_5)\right.$$
$$\left.-\left(\frac{1}{3}-2bc\cos\frac{7\sqrt{3}qa}{12}\right)(109c_5A_5+9d_5B_5)\right]. \quad (29)$$

5.4. Decay of the optical phonon into one ta and one la phonon in the [111] direction

For a TA phonon in the [111] direction we have:

$$e_\alpha(0|\vec{q},2)=a(\delta_{\gamma1}+\delta_{\gamma2},$$
$$e_\alpha(1|\vec{q},2)=d(\delta_{\gamma1}+\delta_{\gamma2})e^{i\sqrt{3}q(a/4)},$$

with: $a^2+d^2=1/2$ from the normalization condition. The eigenvectors for the LA mode in the [100] direction are given by the expression (20). The corresponding formula for the cubic anharmonic coefficients is:

$$V^1(\vec{0},j;\vec{q},2;-\vec{q}3)=\frac{N}{6}\left(\frac{\hbar}{2NM}\right)^{3/2}(\omega_{\vec{0},j}\omega^2_{\vec{q},TA})^{-1/2}$$
$$\times\sum_i\sum_{\alpha\beta\gamma}\Phi^{(i)}_{\alpha\beta\gamma}(0,0|\delta_i,1)\left[e_\alpha(0|\vec{0}j)-e_\alpha(1|\vec{0}j)\right]$$
$$\times(\delta_{\beta1}-\delta_{\beta2})\left(a-de^{i\sqrt{3}q(a/4)}e^{i\vec{q}\cdot\vec{\delta}_i}\right)$$
$$\times(\delta_{\gamma1}+\delta_{\gamma2}+\delta_{\gamma3})\left(b-ce^{i\sqrt{3}q(a/4)}e^{-i\vec{q}\cdot\vec{\delta}_i}\right).$$

Evaluating the sums leads to the following relations:

$$V^i(0,4;q,2;-q,3)=-V^i(0,5;q,2;-q,3)$$
$$V^i(0,6;q,2;-q,3)=0, \quad (30)$$

for $i = 1, 3, 5$, with:

$$V^1(\vec{0},5;\vec{q},2;-\vec{q}3) = \frac{N}{2\sqrt{3}}\left(\frac{\hbar}{2NM}\right)^{3/2}(\omega_{\vec{0},j}\omega_{\vec{q},TA}\omega_{-\vec{q},LA})^{-1/2}$$
$$\times\left[\left(ab+cd-ace^{-i\sqrt{3}(aq/4)}-bde^{i\sqrt{3}(aq/4)}\right)(-3d_1B_1)\right.$$
$$\left.+\left(ab+cd-ace^{-i\sqrt{3}(aq/12)}-bde^{i\sqrt{3}(aq/12)}\right)(4c_1A_1+3d_1B_1)\right], \quad (31)$$

for the third nearest neighbors we have:

$$V^3(\vec{0},5;\vec{q},2;-\vec{q}3) = \frac{N}{2\sqrt{3}}\left(\frac{\hbar}{2NM}\right)^{3/2}(\omega_{\vec{0},j}\omega_{\vec{q},TA}\omega_{-\vec{q},LA})^{-1/2}$$
$$\left[\left(ab+cd-ace^{-i\sqrt{3}(aq/4)}+bde^{-i\sqrt{3}(aq/4)}\right)(72c_3A_3+18d_3B_3)\right.$$
$$+\left(ab+cd+ace^{-i\sqrt{3}(aq/12)}+bde^{i\sqrt{3}(aq/12)}\right)(-16c_3A_3-3d_3B_3)$$
$$\left.+\left(ab+cd+ace^{-i5\sqrt{3}(aq/12)}+bde^{i5\sqrt{3}(aq/12)}\right)(-20c_3A_3-15d_3B_3)\right]. \quad (32)$$

Finally, for the fifth nearest neighbors the expression is given by:

$$V^5(\vec{0},5;\vec{q},2;-\vec{q}3) = \frac{N}{3\sqrt{2}}\left(\frac{\hbar}{2NM}\right)^{3/2}(\omega_{\vec{0}j}\omega_{\vec{q}TA}\omega_{-\vec{q}LA})^{-1/2}$$
$$\left[\left(ab+cd+ace^{-i7\sqrt{3}(aq/4)}+bde^{-i7\sqrt{3}(aq/4)}\right)(28c_5A_5+21d_5B_5)\right.$$
$$+\left(ab+cd+ace^{-i7\sqrt{3}(aq/12)}+bde^{i7\sqrt{3}(aq/12)}\right)(-80c_5A_5-24d_5B_5)$$
$$\left.+\left(ab+cd+ace^{-i\sqrt{3}(aq/12)}+bde^{i\sqrt{3}(aq/12)}\right)(-56c_5A_5-6d_5B_5)\right]. \quad (33)$$

5.5. Decay of the optical phonon into two TA phonons in the [110] direction

In this direction the eigenvectors for the TA phonons which are orthogonally polarized both the z axis and the direction of propagation are given by:

$$e_\alpha(0|\vec{q},2) = b(\delta_{\alpha1}+\delta_{\alpha2}),$$
$$e_\alpha(1|\vec{q},2) = b(\delta_{\gamma1}+\delta_{\gamma2})e^{i\sqrt{3}q(a/4)}, \quad (34)$$

the corresponding anharmonic coefficients can be written as:

$$V^1(\vec{0},j;\vec{q},2;-\vec{q},2) = \frac{N}{6}\left(\frac{\hbar}{2NM}\right)^{3/2}(\omega_{\vec{0},j}\omega^2_{\vec{q},TA})^{-1/2}$$
$$\times\sum_i\sum_{\alpha\beta\gamma}\Phi^{(i)}_{\alpha\beta\gamma}(0,0|\delta_i,1)\left[e_\alpha(0|\vec{0}j)-e_\alpha(1|\vec{0}j)\right]$$
$$\times b(\delta_{\beta1}-\delta_{\beta2})\left(1-e^{i\sqrt{2}q(a/4)}e^{i\vec{q}\cdot\vec{\delta}_i}\right)$$
$$\times b(\delta_{\gamma1}-\delta_{\gamma2})\left(1-e^{-i\sqrt{2}q(a/4)}e^{-i\vec{q}\cdot\vec{\delta}_i}\right),$$

carrying out the sums one obtains:

$$V^1(\vec{0},6;\vec{q},2;-\vec{q},2) = \frac{16N}{3}\frac{b^2}{\sqrt{2}}\left(\frac{\hbar}{2NM}\right)^{3/2}$$
$$(\omega_{\vec{0},j}\omega^2_{\vec{q},TA})^{-1/2}d_1B_1\sin^2\left(\frac{qa}{4\sqrt{2}}\right). \quad (35)$$

The preceding results can be extended to the third nearest neighbor interactions giving:

$$V^3(\vec{0},6;\vec{q},2;-\vec{q},2)=\frac{2N}{3}\frac{b^2}{\sqrt{2}}\left(\frac{\hbar}{2NM}\right)^{3/2}(\omega_{\vec{0},j}\omega^2_{\vec{q},TA})^{-1/2}$$
$$\times\left[(-64c_3A_3+4d_3B_3)\sin^2\left(\frac{qa}{4\sqrt{2}}\right)\right.$$
$$\left.+(16c_3A_3+8d_3B_3)\sin^2\left(\frac{qa}{4\sqrt{2}}\right)\right], \quad (36)$$

and for the fifth nearest neighbor we obtains:

$$V^5(\vec{0},6;\vec{q},2;-\vec{q},2)=\frac{2N}{3}\frac{b^2}{\sqrt{2}}\left(\frac{\hbar}{2NM}\right)^{3/2}(\omega_{\vec{0},j}\omega^2_{\vec{q},TA})^{-1/2}$$
$$\times\left[(-48c_5A_5-24d_5B_5)\sin^2\left(\frac{qa}{2\sqrt{2}}\right)\right.$$
$$\left.+(192c_5A_5+24d_5B_5)\sin^2\left(\frac{qa}{4\sqrt{2}}\right)\right], \quad (37)$$

finally we have for the remaining coefficients the relations:

$$V^i(0,4;q,2;-q,3)=V^i(0,5;q,2;-q,3)=0 \qquad (38)$$

for $i=1,3,5$.

6. Discussion and conclusions

In this work, we have computed analytically the cubic anharmonic coefficients for the diamond structure in high symmetry directions. This has been done considering central potential interactions from first to fifth nearest neighbors. These calculations lead to the following relations between different channels of decay:

6.1. [100] Direction

2 LA phonons

This channel of decay (the so-called Klemens channel) is forbidden, as it is shown from the following expression

$$V^{(i)}(\vec{0}j|\vec{q}3|-\vec{q}3)=0 \quad j=4,5,6; \quad i=1,3,5.$$

The former result is remarkable, because of the fact that previous calculations [3,16] considered to this channel of decay the fundamental disintegration process for the Raman phonon. Mention must be done to the work of Held and Pfeiffer [17], where the effect of anharmonicity in the absorption spectrum of a diatomic linear chain is discussed. Among other things, these authors discuss the validity of the Peierls approximation; in particular, as well as we have obtained through all these exact calculations for a three dimensional lattice, the Peierls approximation is found to be a very rough estimation, and its validity is strongly questioned in almost every relevant channel of decay like the Klemens one, that as Held et al have obtained in full agreement with our calculation for this direction, is completely forbidden.

LA-TA phonons

We must remember that the squared magnitude of the anharmonic coefficients is proportional to the probability of disintegration. So that, for this case, one phonon polarized along the y or z axis have equal probability of decaying into the pair $\{LA,TA\}$; an x-polarized phonon, instead, cannot decay into one phonon LA and other TA. In fact, as we have shown in a previous paper, this channel of decay is the most important because of its contribution of about 90% percent to the linewidth in silicon and germanium [13].

6.2. [111] Direction

2 LA phonons

For this case, every allowed polarization of the Raman phonon had the same probability of decaying into the pair $\{LA,LA\}$. Considering silicon, for example, we can understand this selection rule because the flattening of LA branches, especially near the boundary zone, eventually allows that the addition of two LA phonon frequencies could be equal to ω_{RA}.

LA-TA phonons

With a similar reasoning like we stated above, this channel of decay can be explained; two polarizations are equally feasible (x and y) and the other (z) completely forbidden.

6.3. [110] Direction

$TA_{\perp z}$ phonons

Finally, for this channel of decay, only phonons perpendicularly polarized both along the z-axis and to the direction of propagation contributes for this selection rule. So that, it is not surprising that the only allowed polarizations (with the same probability) are the x and y axis; therefore z-axis polarization is forbidden.

Bearing in mind that these Fourier transformed anharmonic coefficients are of primordial importance in many calculations like phonon dispersion curves, phonon line widths, specific heats, and frequency shifts we also strongly believe that computational efforts needed to carry out these calculations can be dramatically reduced by using the results we have obtained in this paper in combination with the symmetry properties of the diamond structure.

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