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Ionic Raman Effect. III. First- and Second-Order Ionic Raman Effects*

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The modulation of the ionic, rather than the electronic, contribution to the crystal polarizability by the atomic displacements is the dominant mechanism for scattering light when the incident light is in the infrared, and it is the ionic Raman effect that is studied in this paper. The problem considered is the effect of the second-order dipole moment on one- and two-phonon scattering spectra, in addition to the effect of the first-order dipole moment. An expression for the scattering efficiency is obtained and an order-of-magnitude estimate is included for the case of one-phonon scattering and for the case of two-phonon scattering in a crystal that possesses no first-order dipole moment. In the case of a crystal which also possesses a first-order dipole moment, there are additional contributions to the scattering efficiency, but these contributions are discussed qualitatively.

I. INTRODUCTION

The Raman scattering of light by the phonons in a crystal arises from the modulation of both the electronic and ionic contributions to the crystal polarizability by the displacements of the atoms from their equilibrium positions. For incident light in the visible region, the dominant scattering mechanism is the electronic one because the frequency of the incident light is large compared with the transition frequencies between vibrational states of the crystal corresponding to the electronic ground state.[1] However, a previous study[2] indicates that for incident light in the infrared region, the ionic mechanism is the dominant one, and as we now have available infrared lasers which emit at frequencies comparable with the vibrational transition frequencies, the observation of the ionic Raman effect should be possible.

The reason for this is that the scattering efficiency is proportional to the fourth power of the scattered frequency. In going from the region of visible frequencies to the infrared this factor can decrease by as much as five orders of magnitude. The electronic contribution to the Raman tensor is largely independent of frequency for frequencies of the incident (and scattered) light well below the frequency of the lowest electronic transition. Thus the intensity of infrared radiation scattered by the electronic mechanism will be as much as five orders of magnitude lower than the intensity of visible light scattered by this mechanism. However, in the ionic Raman effect, this fourth-power proportionality can be overcome due to the existence of resonances in the Raman tensor for frequencies of the incident light close to the frequencies of the optical vibration modes.

In a recent paper, Wallis and Maradudin[3] considered the contribution to the ionic Raman effect from the first-order dipole moment. In this paper we supplement their results by including the effect of the second-order dipole moment on one-phonon scattering spectra. In addition, we consider the case of two-phonon, or second-order, processes both in crystals which lack a first-order dipole moment and in crystals which possess a first-order dipole moment. We present expressions for the scattering efficiency for one-phonon and two-phonon scattering processes in the case of crystals which lack a first-order dipole moment.

II. EQUATIONS OF MOTION FOR SECOND-ORDER DIPOLE MOMENT

The scattering efficiency per unit solid angle, per unit frequency interval for scattering by the ionic Raman effect is given by

$$\mathcal{S} = \frac{1}{A}\left(\frac{\omega_s}{c}\right)^4 \sum_{\alpha\beta\gamma\lambda} n_\alpha n_\beta i_{\alpha\gamma\beta\lambda}(\Omega) n_{0\gamma} n_{0\lambda} \ . \tag{2.1}$$

In this expression, A is the cross-sectional area of the incident beam; ω_s is the frequency of the scattered light; $\Omega = \omega_s - \omega_0$ is the shift in the frequency of the incident light on scattering, where ω_0 is the frequency of the incident light; $\vec{n}_0$ and $\vec{n}$ are unit vectors which specify the polarization in the incident and scattered light, respectively; and c is the speed of light. The tensor $i_{\alpha\gamma\beta\lambda}(\Omega)$ can be expressed as[3]

$$i_{\alpha\gamma\beta\lambda}(\Omega) = (1/2\pi)\int_{-\infty}^{\infty} ds\, e^{-is\Omega}\langle P_{\lambda\beta}(s\,|\,\omega_0)\, P^\dagger_{\gamma\alpha}(0\,|\,\omega_0)\rangle \ , \tag{2.2}$$

where the angular brackets denote an average with respect to the canonical ensemble described by the vibrational Hamiltonian of the crystal, and the operator $P_{\lambda\beta}(s\,|\,\omega_0)$ is defined by

$$P_{\lambda\beta}(s\,|\,\omega_0) = \int_0^\infty e^{-i\omega_0 t - \eta t} P_{\lambda\beta}(s\,|\,t) \ , \tag{2.3a}$$

where

$$P_{\lambda\beta}(s\,|\,t) = (1/\hbar)\,[M_\lambda(s-t), M_\beta(s)] \ . \tag{2.3b}$$

Here $M_\alpha(t)$ is the α Cartesian component of the crystal dipole-moment operator in the Heisenberg representation. From Eqs. (2.3) we find that the operator $P_{\lambda\beta}(s\,|\,\omega_0)$ obeys the relation

$$P^\dagger_{\lambda\beta}(s\,|\,\omega_0) = -P_{\lambda\beta}(s\,|\,-\omega_0) \ , \tag{2.4}$$

which serves as a useful check on the determinations of this operator in what follows.

Equation (2.1) is obtained from Eq. (1) of Ref. 4 on dividing it by the average rate of energy flow in the incident beam. The latter is given by

$$I_0 = (cA/2\pi)E^+E^- \ ,$$

where E^+ and E^- are defined in terms of the unit vector $\vec{n}_0$ by

$$\vec{E}^+ = \vec{n}_0 E^+ \ , \qquad \vec{E}^- = \vec{n}_0 E^- \ .$$

Equation (2.1) is a general expression applicable to all types of crystals and all scattering angles, subject to the qualifications concerning scattering by infrared-active modes discussed in Ref. 3. At the conclusion of Sec. III, we will specialize our results to the case of GaAs in order to obtain an estimate of the integrated scattering efficiency.

The expansion of the α component of the crystal dipole moment in powers of the displacements of the atoms from their equilibrium positions is given by

$$M_\alpha = \sum_{l\kappa\mu} M_{\alpha\mu}(l\kappa)u_\mu(l\kappa) + \tfrac{1}{2}\sum_{l\kappa\mu}\sum_{l'\kappa'\nu} M_{\alpha\mu\nu}(l\kappa;l'\kappa') \times u_\mu(l\kappa)u_\nu(l'\kappa') + \cdots \ . \tag{2.5}$$

In this expansion $u_\alpha(l\kappa)$ is the α component of the displacement of the κth atom in the lth unit cell. The coefficients $\{M_{\alpha\mu}(l\kappa)\}$ are the transverse effective-charge tensors of the atoms, and the $\{M_{\alpha\mu\nu}(l\kappa;\, l'\kappa')\}$ are the second-order dipole-moment coefficients. In addition to considering the first-order dipole-moment term, we are concerned with the second term in the expansion which describes the contribution of the second-order dipole moment to $i_{\alpha\gamma\beta\lambda}(\Omega)$.

It is advantageous to carry out the normal coordinate transformation from the atomic displacements and their conjugate momenta to the corresponding phonon operators:

$$u_\alpha(l\kappa) = \left(\frac{\hbar}{2NM_\kappa}\right)^{1/2}\sum_{\vec{k}j}\frac{e_\alpha(\kappa\,|\,\vec{k}j)}{[\omega_j(\vec{k})]^{1/2}}\,e^{i\vec{k}\cdot\vec{x}(l)}A_{\vec{k}j} \ , \tag{2.6a}$$

$$P_\alpha(l\kappa) = \frac{1}{i}\left(\frac{\hbar M_\kappa}{2N}\right)^{1/2}\sum_{\vec{k}j}[\omega_j(\vec{k})]^{1/2}e_\alpha(\kappa\,|\,\vec{k}j)\,e^{i\vec{k}\cdot\vec{x}(l)}B_{\vec{k}j} \ , \tag{2.6b}$$

where M_κ is the mass of the κth atom, $\vec{x}(l)$ is the position vector defining the location of the lth primitive unit cell, and N is the total number of primitive unit cells in the crystal. $\omega_j(\vec{k})$ is the frequency of the normal mode of vibration defined by the wave vector $\vec{k}$ and branch index j, and $e_\alpha(\kappa\,|\,\vec{k}_j)$ is the corresponding unit polarization vector. If periodic boundary conditions on the displacements are assumed, the permitted values of the wave vector $\vec{k}$ are distributed densely and uniformly throughout the first Brillouin zone of the crystal. The phonon field and momentum operators $A_{\vec{k}j}$ and $B_{\vec{k}j}$ are defined in terms of $b^\dagger_{\vec{k}j}$ and $b_{\vec{k}j}$, the creation and destruction operators for phonons in the mode $(\vec{k}j)$, by

$$A_{\vec{k}j} = b_{\vec{k}j} + b^\dagger_{-\vec{k}j} = A^\dagger_{-\vec{k}j} \ , \tag{2.7a}$$

$$B_{\vec{k}j} = b_{\vec{k}j} - b^\dagger_{-\vec{k}j} = -B^\dagger_{-\vec{k}j} \ . \tag{2.7b}$$

We proceed to substitute Eq. (2.6a) into Eq. (2.5), and obtain the expression

$$M_\mu = \sum_j M_\mu(j)A_{\vec{0}j} + \tfrac{1}{2}\sum_{\vec{k}j}\sum_{\vec{k}'j'} M_\mu(\vec{k}j;\vec{k}'j')A_{\vec{k}j}A_{\vec{k}'j'} \ , \tag{2.8}$$

where

$$M_\mu(j) = \left(\frac{\hbar N}{2\omega_j(\vec{0})}\right)^{1/2}\sum_{\kappa\alpha}M_{\mu\alpha}(\kappa)\,\frac{e_\alpha(\kappa\,|\,\vec{0}j)}{M_\kappa^{1/2}} \tag{2.9a}$$

and

$$M_\mu(\vec{k}j\,;\vec{k}'j') = \frac{\hbar}{2N}\;\frac{1}{[\omega_j(\vec{k})\omega_{j'}(\vec{k}')]^{1/2}} \times \sum_{l\kappa\alpha}\sum_{l'\kappa'\beta}M_{\mu\alpha\beta}(l\kappa\,;l'\kappa')\frac{e_\alpha(\kappa\,|\,\vec{k}j)\,e_\beta(\kappa'\,|\,\vec{k}'j')}{(M_\kappa)^{1/2}(M_{\kappa'})^{1/2}} \times \exp[i\vec{k}\cdot\vec{x}(l) + i\vec{k}'\cdot\vec{x}(l')] = M_\mu(\vec{k}'j';\vec{k}j) \ , \tag{2.9b}$$

because

$$M_{\mu\alpha\beta}(l\kappa;\,l'\kappa') = M_{\mu\beta\alpha}(l'\kappa';\,l\kappa) \ . \tag{2.10}$$

It should be noted that the coefficient $M_\mu(\vec{k}j;\vec{k}'j')$ vanishes unless $\vec{k}+\vec{k}'=0$.

Using Eq. (2.8), we find that the operator $P_{\lambda\beta}(s\,|\,t)$ is given by

$$P_{\lambda\beta}(s\,|\,t)=\frac{1}{\hbar}\sum_{jj'}M_\lambda(j)M_\beta(j')\,[A_{\vec{0}j}(s-t),A_{\vec{0}j'}(s)]+\frac{1}{2\hbar}\sum_{\substack{\vec{k}_1j_1\\ \vec{k}_2j_2}}\sum_{j}M_\lambda(j)M_\beta(\vec{k}_1j_1;\vec{k}_2j_2)\,[A_{\vec{0}j}(s-t),A_{\vec{k}_1j_1}(s)A_{\vec{k}_2j_2}(s)]$$

$$+\frac{1}{2\hbar}\sum_{\substack{\vec{k}_1j_1\\ \vec{k}_2j_2}}\sum_{j}M_\lambda(\vec{k}_1j_1;\vec{k}_2j_2)\,M_\beta(j)[A_{\vec{k}_1j_1}(s-t)A_{\vec{k}_2j_2}(s-t),A_{\vec{0}j}(s)]+\cdots\,. \tag{2.11}$$

All the terms given in this expression contribute to one-phonon or first-order ionic Raman scattering. The contribution to $P_{\lambda\beta}(s\,|\,t)$ from the first term has been obtained by Wallis and Maradudin,[3] who showed that it is necessary to evaluate the commutator to the first order in the cubic anharmonic force constants of the crystal to obtain a nonzero first-order ionic Raman effect. The second-order dipole moment contributes to the one-phonon spectrum in the harmonic approximation for lattice vibrations. However, in this section we will also determine the contributions to the commutators in the second and third terms of Eq. (2.11) linear in the cubic anharmonic force constants, since these will be needed in the discussion of two-phonon scattering in a later section.

The operators $A_{\vec{k}j}(s-t)$ and $A_{\vec{k}_1j_1}(s-t)A_{\vec{k}_2j_2}(s-t)$ can be expanded in Taylor series in powers of t. These expansions have the advantage that they enable us to evaluate equal time commutators only in Eq. (2.11).

The Hamiltonian of the crystal through cubic anharmonic terms is given by

$$H=\sum_{\vec{p}s}\hbar\omega_s b^\dagger_{\vec{p}s}b_{\vec{p}s}+\sum_{\vec{p}_1s_1}\sum_{\vec{p}_2s_2}\sum_{\vec{p}_3s_3}V(\vec{p}_1s_1;\vec{p}_2s_2;\vec{p}_3s_3)\times A_{\vec{p}_1s_1}A_{\vec{p}_2s_2}A_{\vec{p}_3s_3}\,. \tag{2.12}$$

Using the Heisenberg equations of motion

$$i\hbar\frac{d}{dt}A_{\vec{k}_1j_1}=[A_{\vec{k}_1j_1},H]=\hbar\omega_{j_1}(\vec{k}_1)B_{\vec{k}_1j_1}\,, \tag{2.13}$$

$$i\hbar\frac{d}{dt}B_{\vec{k}_1j_1}=[B_{\vec{k}_1j_1},H]=\hbar\omega_{j_1}(\vec{k}_1)A_{\vec{k}_1j_1}+6\sum_{\vec{p}_3s_3}\sum_{\vec{p}_4s_4}V(-\vec{k}_1j_1;\vec{p}_3s_3;\vec{p}_4s_4)A_{\vec{p}_3s_3}A_{\vec{p}_4s_4}\,, \tag{2.14}$$

we proceed to calculate the derivatives of the operator $A_{\vec{k}_1j_1}(s)A_{\vec{k}_2j_2}(s)$:

$$\frac{d^0}{ds^0}A_{\vec{k}_1j_1}A_{\vec{k}_2j_2}=A_{\vec{k}_1j_1}A_{\vec{k}_2j_2}\,, \tag{2.15a}$$

$$\frac{d}{ds}A_{\vec{k}_1j_1}A_{\vec{k}_2j_2}=-i\omega_{j_1}(\vec{k}_1)B_{\vec{k}_1j_1}A_{\vec{k}_2j_2}-i\omega_{j_2}(\vec{k}_2)A_{\vec{k}_1j_1}B_{\vec{k}_2j_2}\,, \tag{2.15b}$$

$$\frac{d^2}{ds^2}A_{\vec{k}_1j_1}A_{\vec{k}_2j_2}=-[\omega_{j_1}(\vec{k}_1)+\omega_{j_2}(\vec{k}_2)]A_{\vec{k}_1j_1}A_{\vec{k}_2j_2}-2\omega_{j_1}(\vec{k}_1)\omega_{j_2}(\vec{k}_2)B_{\vec{k}_1j_1}B_{\vec{k}_2j_2}-\frac{6\omega_{j_1}(\vec{k}_1)}{\hbar}\sum_{\substack{\vec{p}_3s_3\\ \vec{p}_4s_4}}V(-\vec{k}_1j_1;\vec{p}_3s_3;\vec{p}_4s_4)$$

$$\times A_{\vec{p}_3s_3}A_{\vec{p}_4s_4}A_{\vec{k}_2j_2}-\frac{6\omega_{j_2}(\vec{k}_2)}{\hbar}\sum_{\substack{\vec{p}_3s_3\\ \vec{p}_4s_4}}V(-\vec{k}_2j_2;\vec{p}_3s_3;\vec{p}_4s_4)\,A_{\vec{k}_1j_1}A_{\vec{p}_3s_3}A_{\vec{p}_4s_4}\cdots\,. \tag{2.15c}$$

In arriving at these results, we have made use of the fact that the Fourier-transformed cubic anharmonic force constant $V(\vec{k}j;\vec{k}'j';\vec{k}''j'')$ is completely symmetric in the indices $(\vec{k}j)$, $(\vec{k}'j')$, and $(\vec{k}'',j'')$. If we retain the terms linear in $V(-\vec{k}_1j_1;\vec{p}_3s_3;\vec{p}_4s_4)$ and $V(-\vec{k}_2j_2;\vec{p}_3s_3;\vec{p}_4s_4)$, we discover that the even- and odd-order derivatives have different structures, and the general expressions take the following form:

$$\frac{d^{2n}}{ds^{2n}}(A_{\vec{k}_1j_1}A_{\vec{k}_2j_2})=a_{2n}A_{\vec{k}_1j_1}A_{\vec{k}_2j_2}+b_{2n}B_{\vec{k}_1j_1}B_{\vec{k}_2j_2}+\frac{6\omega_{j_1}(\vec{k}_1)}{\hbar}\sum_{\substack{\vec{p}_3s_3\\ \vec{p}_4s_4}}V(-\vec{k}_1j_1;\vec{p}_3s_3;\vec{p}_4s_4)\,(e_{2n}A_{\vec{p}_3s_3}A_{\vec{p}_4s_4}A_{\vec{k}_2j_2}$$

$$+f_{2n}B_{\vec{p}_3s_3}A_{\vec{p}_4s_4}B_{\vec{k}_2j_2}+g_{2n}A_{\vec{p}_3s_3}B_{\vec{p}_4s_4}B_{\vec{k}_2j_2}+h_{2n}B_{\vec{p}_3s_3}B_{\vec{p}_4s_4}A_{\vec{k}_2j_2})+\frac{6\omega_{j_2}(\vec{k}_2)}{\hbar}\sum_{\substack{\vec{p}_3s_3\\ \vec{p}_4s_4}}V(-\vec{k}_2j_2;\vec{p}_3s_3;\vec{p}_4s_4)$$

$$\times(i_{2n}A_{\vec{k}_1j_1}A_{\vec{p}_3s_3}A_{\vec{p}_4s_4}+j_{2n}B_{\vec{k}_1j_1}A_{\vec{p}_3s_3}B_{\vec{p}_4s_4}+k_{2n}A_{\vec{k}_1j_1}B_{\vec{p}_3s_3}B_{\vec{p}_4s_4}+l_{2n}B_{\vec{k}_1j_1}B_{\vec{p}_3s_3}A_{\vec{p}_4s_4})\,, \tag{2.16}$$

$$\frac{d^{2n+1}}{ds^{2n+1}}(A_{\vec{k}_1j_1}A_{\vec{k}_2j_2})=c_{2n+1}A_{\vec{k}_1j_1}B_{\vec{k}_2j_2}+d_{2n+1}B_{\vec{k}_1j_1}A_{\vec{k}_2j_2}+\frac{6i\omega_{j_1}(\vec{k}_1)}{\hbar}\sum_{\substack{\vec{p}_3s_3\\ \vec{p}_4s_4}}V(-\vec{k}_1j_1;\vec{p}_3s_3;\vec{p}_4s_4)(\alpha_{2n+1}A_{\vec{p}_3s_3}A_{\vec{p}_4s_4}B_{\vec{k}_2j_2}$$

$$+\beta_{2n+1}B_{\vec{p}_3s_3}A_{\vec{p}_4s_4}A_{\vec{k}_2j_2}+\gamma_{2n+1}A_{\vec{p}_3s_3}B_{\vec{p}_4s_4}A_{\vec{k}_2j_2}+\delta_{2n+1}B_{\vec{p}_3s_3}B_{\vec{p}_4s_4}B_{\vec{k}_2j_2})+\frac{6i\omega_{j_2}(\vec{k}_2)}{\hbar}\sum_{\substack{\vec{p}_3s_3\\ \vec{p}_4s_4}}V(-\vec{k}_2j_2;\vec{p}_3s_3;\vec{p}_4s_4)$$

$$\times(\eta_{2n+1}A_{\vec{k}_1j_1}A_{\vec{p}_3s_3}B_{\vec{p}_4s_4}+\mu_{2n+1}B_{\vec{k}_1j_1}A_{\vec{p}_3s_3}A_{\vec{p}_4s_4}+\rho_{2n+1}A_{\vec{k}_1j_1}B_{\vec{p}_3s_3}A_{\vec{p}_4s_4}+\sigma_{2n+1}B_{\vec{k}_1j_1}B_{\vec{p}_3s_3}B_{\vec{p}_4s_4})\,. \tag{2.17}$$

In these expressions, a_{2n}, b_{2n}, c_{2n+1}, and d_{2n+1} have the argument $(\vec{k}_1j_1;\vec{k}_2j_2)$. Similarly, each of the remaining coefficients has the argument $(\vec{k}_1j_1;\vec{k}_2j_2;\vec{p}_3s_3;\vec{p}_4s_4)$. This dependence is not indicated in order to simplify notation.

The recurrence formulas relating the coefficients in Eqs. (2.16) and (2.17) are obtained by equating the time derivative of Eq. (2.16) to the expression for

$$\frac{d^{2n+1}}{ds^{2n+1}}(A_{\vec{k}_1j_1}A_{\vec{k}_2j_2})$$

given by Eq. (2.17), and by equating the time derivative of Eq. (2.17) to the expression for

$$\frac{d^{2n+2}}{ds^{2n+2}}(A_{\vec{k}_1j_1}A_{\vec{k}_2j_2})$$

obtained from Eq. (2.16). The results of the first operation are

$$c_{2n+1}=-i\omega_1b_{2n}-i\omega_2a_{2n}\,, \tag{2.18a}$$

$$d_{2n+1}=-i\omega_1a_{2n}-i\omega_2b_{2n}\,, \tag{2.18b}$$

$$\alpha_{2n+1}=-b_{2n}/\omega_1-\omega_2e_{2n}-\omega_3f_{2n}-\omega_4g_{2n}\,, \tag{2.19a}$$

$$\beta_{2n+1}=-\omega_3e_{2n}-\omega_2f_{2n}-\omega_4h_{2n}\,, \tag{2.19b}$$

$$\gamma_{2n+1}=-\omega_4e_{2n}-\omega_2g_{2n}-\omega_3h_{2n}\,, \tag{2.19c}$$

$$\delta_{2n+1}=-\omega_4f_{2n}-\omega_3g_{2n}-\omega_2h_{2n}\,, \tag{2.19d}$$

$$\eta_{2n+1}=-\omega_4i_{2n}-\omega_1j_{2n}-\omega_3k_{2n}\,, \tag{2.19e}$$

$$\mu_{2n+1}=-b_{2n}/\omega_2-\omega_1i_{2n}-\omega_4j_{2n}-\omega_3l_{2n}\,, \tag{2.19f}$$

$$\rho_{2n+1}=-\omega_3i_{2n}-\omega_4k_{2n}-\omega_1l_{2n}\,, \tag{2.19g}$$

$$\sigma_{2n+1}=-\omega_3j_{2n}-\omega_1k_{2n}-\omega_4l_{2n}\,. \tag{2.19h}$$

The second operation yields the following relations:

$$a_{2n+2}=-i\omega_2c_{2n+1}-i\omega_1d_{2n+1}\,, \tag{2.20a}$$

$$b_{2n+2}=-i\omega_1c_{2n+1}-i\omega_2d_{2n+1}\,, \tag{2.20b}$$

$$e_{2n+2}=-id_{2n+1}/\omega_1+\omega_2\alpha_{2n+1}+\omega_3\beta_{2n+1}+\omega_4\gamma_{2n+1}\,, \tag{2.21a}$$

$$f_{2n+2}=\omega_3\alpha_{2n+1}+\omega_2\beta_{2n+1}+\omega_4\delta_{2n+1}\,, \tag{2.21b}$$

$$g_{2n+2}=\omega_4\alpha_{2n+1}+\omega_2\gamma_{2n+1}+\omega_3\delta_{2n+1}\,, \tag{2.21c}$$

$$h_{2n+2}=\omega_4\beta_{2n+1}+\omega_3\gamma_{2n+1}+\omega_2\delta_{2n+1}\,, \tag{2.21d}$$

$$i_{2n+2}=-ic_{2n+1}/\omega_2+\omega_4\eta_{2n+1}+\omega_1\mu_{2n+1}+\omega_3\rho_{2n+1}\,, \tag{2.21e}$$

$$j_{2n+2}=\omega_1\eta_{2n+1}+\omega_4\mu_{2n+1}+\omega_3\sigma_{2n+1}\,, \tag{2.21f}$$

$$k_{2n+2}=\omega_3\eta_{2n+1}+\omega_4\rho_{2n+1}+\omega_1\sigma_{2n+1}\,, \tag{2.21g}$$

$$l_{2n+2}=\omega_3\mu_{2n+1}+\omega_1\rho_{2n+1}+\omega_4\sigma_{2n+1}\,. \tag{2.21h}$$

Here $\omega_{j_1}(\vec{k}_1)$, $\omega_{j_2}(\vec{k}_2)$, $\omega_{s_3}(\vec{p}_3)$, and $\omega_{s_4}(\vec{p}_4)$ have been abbreviated by ω_1, ω_2, ω_3, ω_4, respectively. The initial conditions to be satisfied in solving this set of equations are

$$\begin{aligned} &a_0=1\,, && a_2=-(\omega_1^2+\omega_2^2)\,, && c_1=-i\omega_2\,,\\ &b_0=0\,, && b_2=-2\omega_1\omega_2\,, && d_1=-i\omega_1\,, \end{aligned} \tag{2.22}$$

$$\begin{aligned} &e_0=0\,, && e_2=-1\,, && \alpha_1=0\,,\\ &f_0=0\,, && f_2=0\,, && \beta_1=0\,,\\ &g_0=0\,, && g_2=0\,, && \gamma_1=0\,,\\ &h_0=0\,, && h_2=0\,, && \delta_1=0\,,\\ &i_0=0\,, && i_2=-1\,, && \eta_1=0\,,\\ &j_0=0\,, && j_2=0\,, && \mu_1=0\,,\\ &k_0=0\,, && k_2=0\,, && \rho_1=0\,,\\ &l_0=0\,, && l_2=0\,, && \sigma_1=0\,. \end{aligned} \tag{2.23}$$

The method of generating functions is employed to solve the system of equations (2.18)–(2.23). We will first solve Eqs. (2.18), (2.20), and (2.22), which constitutes considering the second-order dipole-moment contribution to $P_{\lambda\beta}(s\,|\,t)$ in the harmonic approximation and which are the necessary contributions to one-phonon, or first-order, Raman scattering. We eliminate c_{2n+1} and d_{2n+1} from Eqs. (2.20a) and (2.20b) by the use of Eqs. (2.18a) and (2.18b), and the result is the pair of coupled difference equations

$$a_{2n+2}=-2\omega_1\omega_2 b_{2n}-(\omega_1^2+\omega_2^2)a_{2n}\ , \tag{2.24a}$$

$$b_{2n+2}=-(\omega_1^2+\omega_2^2)b_{2n}-2\omega_1\omega_2 c_{2n}\ . \tag{2.24b}$$

We proceed to introduce the two generating functions $\mathcal{A}(\vec{k}_1 j_1;\ \vec{k}_2 j_2;\ x)$ and $\mathcal{B}(\vec{k}_1 j_1;\vec{k}_2 j_2;\ x)$ given by

$$\mathcal{A}(\vec{k}_1 j_1;\ \vec{k}_2 j_2;\ x)=\sum_{n=0}^{\infty} a_{2n}(\vec{k}_1 j_1;\ \vec{k}_2 j_2)x^{2n}\ , \tag{2.25a}$$

$$\mathcal{B}(\vec{k}_1 j_1;\vec{k}_2 j_2;x)=\sum_{n=0}^{\infty} b_{2n}(\vec{k}_1 j_1;\vec{k}_2 j_2)x^{2n}\ . \tag{2.25b}$$

Multiplying both sides of Eqs. (2.24a) and (2.24b) by x^{2n}, summing on n from 0 to ∞, and making use of the initial conditions, we arrive at the following equations for $\mathcal{A}(x)$ and $\mathcal{B}(x)$:

$$(1/x^2+\omega_1^2+\omega_2^2)\,\mathcal{A}(x)+2\omega_1\omega_2\,\mathcal{B}(x)=1/x^2\ , \tag{2.26a}$$

$$2\omega_1\omega_2\,\mathcal{A}(x)+(1/x^2+\omega_1^2+\omega_2^2)\,\mathcal{B}(x)=0\ . \tag{2.26b}$$

The solutions of these equations are given by

$$\mathcal{A}(\vec{k}_1 j_1;\vec{k}_2 j_2;x)=\frac{1+(\omega_1^2+\omega_2^2)x^2}{[1+(\omega_1+\omega_2)^2x^2]\,[1+(\omega_1-\omega_2)^2x^2]}\ , \tag{2.27a}$$

$$\mathcal{B}(\vec{k}_1 j_1;\vec{k}_2 j_2;x)=\frac{-2\omega_1\omega_2 x^2}{[1+(\omega_1+\omega_2)^2x^2]\,[1+(\omega_1-\omega_2)^2x^2]}\ . \tag{2.27b}$$

Also, because

$$\mathcal{A}(\vec{k}_1 j_1;\vec{k}_2 j_2;x)=\mathcal{A}(\vec{k}_2 j_2;\vec{k}_1 j_1;x)\ , \tag{2.28a}$$

$$\mathcal{B}(\vec{k}_1 j_1;\vec{k}_2 j_2;x)=\mathcal{B}(\vec{k}_2 j_2;\vec{k}_1 j_1;x)\ , \tag{2.28b}$$

it follows that

$$a_{2n}(\vec{k}_1 j_1;\vec{k}_2 j_2)=a_{2n}(\vec{k}_2 j_2;\vec{k}_1 j_1)\ , \tag{2.29a}$$

$$b_{2n}(\vec{k}_1 j_1;\vec{k}_2 j_2)=b_{2n}(\vec{k}_2 j_2;\vec{k}_1 j_1)\ . \tag{2.29b}$$

We next introduce two more generating functions

$$\mathcal{C}(\vec{k}_1 j_1;\vec{k}_2 j_2;x)=\sum_{n=0}^{\infty} c_{2n+1}(\vec{k}_1 j_1;\vec{k}_2 j_2)x^{2n+1}\ , \tag{2.30a}$$

$$\mathcal{D}(\vec{k}_1 j_1;\vec{k}_2 j_2;x)=\sum_{n=0}^{\infty} d_{2n+1}(\vec{k}_1 j_1;\vec{k}_2 j_2)x^{2n+1}\ . \tag{3.30b}$$

Multiplying both sides of Eqs. (2.18a) and (2.18b) by x^{2n+1} and summing on n from 0 to ∞ as before, we obtain the results

$$\mathcal{C}(x)=-i\omega_2 x\,\mathcal{A}(x)-i\omega_1 x\,\mathcal{B}(x)\ , \tag{2.31a}$$

$$\mathcal{D}(x)=-i\omega_1 x\,\mathcal{A}(x)-i\omega_2 x\,\mathcal{B}(x)\ . \tag{2.31b}$$

Substitution of the solutions for $\mathcal{A}(x)$ and $\mathcal{B}(x)$ yields

$$\mathcal{C}(\vec{k}_1 j_1;\vec{k}_2 j_2;x)=\frac{i\omega_2 x(\omega_1^2x^2-\omega_2^2x^2-1)}{[1+(\omega_1+\omega_2)^2x^2]\,[1+(\omega_1-\omega_2)^2x^2]}\ , \tag{2.32a}$$

$$\mathcal{D}(\vec{k}_1 j_1;\vec{k}_2 j_2;x)=\frac{i\omega_1 x(\omega_2^2x^2-\omega_1^2x^2-1)}{[1+(\omega_1+\omega_2)^2x^2]\,[1+(\omega_1-\omega_2)^2x^2]}\ . \tag{2.32b}$$

We see that

$$\mathcal{C}(\vec{k}_1 j_1;\vec{k}_2 j_2;x)=\mathcal{D}(\vec{k}_2 j_2;\vec{k}_1 j_1;x)\ . \tag{2.33}$$

Consequently, it follows that

$$c_{2n+1}(\vec{k}_1 j_1;\vec{k}_2 j_2)=d_{2n+1}(\vec{k}_2 j_2;\vec{k}_1 j_1)\ . \tag{2.34}$$

In the following sections, we will use these results to obtain expressions for $P_{\lambda\beta}(s\,|\,\omega_0)$ needed in the evaluation of the scattering efficiency.

III. SECOND-ORDER DIPOLE-MOMENT CONTRIBUTION TO ONE-PHONON SCATTERING

We begin by using the preceding results to obtain the expression for $P_{\lambda\beta}(s\,|\,\omega_0)$ describing the contribution of the second-order dipole moment to one-phonon scattering processes. The three processes which occur in the first-order ionic Raman scattering are shown in diagrammatic form in Fig. 1. In case (a), the incident photon interacts with the lattice through the first-order dipole moment $M^{(1)}$ to create a phonon. The phonon created decays into two phonons via the cubic anharmonic terms in the potential energy of the crystal, denoted by V_3 in the figure. One of these phonons leads to the emission of a photon with scattered frequency ω_s through the crystal's first-order dipole moment. Anharmonicity is required in this process because, in the harmonic approximation, even crystals possessing a first-order dipole moment cannot scatter light inelastically by a one-phonon process.

In case (b), the incident light directly excites two phonons through the second-order dipole moment of the crystal, $M^{(2)}$. One of the phonons created in this way leads to the emission of a photon with scattered frequency ω_s through the crystal's first-order dipole moment. Case (c) illustrates this process with the roles of the first- and second-order dipole moments reversed. The latter two processes occur in the harmonic approximation for the lattice vibrations, although they require electrical anharmonicity in the form of a second-order dipole moment. It should be noted

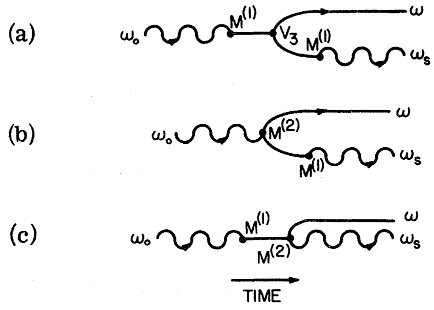

FIG. 1. Processes contributing to the first-order ionic Raman effect described in Sec. III. Photons are described by wavy lines and phonons by solid lines.

that infrared-active phonons are necessary for a first-order ionic Raman effect to be exhibited, and a crystal such as diamond would not display this effect.

In a previous paper, Wallis and Maradudin[3] obtained the expression for the contribution of the first-order dipole moment to $P_{\lambda\beta}(s\,|\,\omega_0)$ to terms linear in the phonon field and momentum operators. This is the contribution associated with Fig. 1(a). Here we determine the additional contributions due to the second-order dipole moment, and associated with Figs. 1(b) and 1(c).

The result obtained in Ref. 3 for the first-order dipole-moment contribution to $P_{\lambda\beta}(s\,|\,t)$ is given by

$$P_{\lambda\beta}(s\,|\,t)=\frac{1}{\hbar}\sum_{n=0}^{\infty}\frac{(-1)^n t^n}{n!}\sum_{jj'}M_\lambda(j)M_\beta(j')\times[A_{\vec{0}j}^{(n)}(s),A_{\vec{0}j'}(s)]\,,\tag{3.1}$$

where (n) denotes the nth derivative with respect to argument.

Evaluation of the operator $P_{\lambda\beta}(s\,|\,t)$, and consequently $P_{\lambda\beta}(s\,|\,\omega_0)$, yields

$$P_{\lambda\beta}(s\,|\,\omega_0)=i\sum_j[P_{\lambda\beta}^{(1)}(j\,|\,\omega_0)B_{\vec{0}j}(s)-P_{\lambda\beta}^{(2)}(j\,|\,\omega_0)A_{\vec{0}j}(s)]\,,\tag{3.2}$$

where

$$P_{\lambda\beta}^{(1)}(j\,|\,\omega_0)=\frac{48\omega_0}{\hbar^2}\sum_{j'j''}\frac{M_\lambda(j')M_\beta(j'')\omega_{j'}(\vec{0})\omega_{j''}(\vec{0})\omega_j(\vec{0})V(\vec{0}j';\vec{0}j'';\vec{0}j)}{[\omega_{j'}^2(\vec{0})-\omega_0^2]\{[\omega_{j''}(\vec{0})+\omega_j(\vec{0})]^2-\omega_0^2\}\{[\omega_{j''}(\vec{0})-\omega_j(\vec{0})]^2-\omega_0^2\}}\,,\tag{3.3a}$$

$$P_{\lambda\beta}^{(2)}(j\,|\,\omega_0)=\frac{24}{\hbar^2}\sum_{j'j''}\frac{M_\lambda(j')M_\beta(j'')\omega_{j'}(\vec{0})\omega_{j''}(\vec{0})[\omega_{j''}^2(\vec{0})-\omega_j^2(\vec{0})-\omega_0^2]\,V(\vec{0}j';\vec{0}j'';\vec{0}j)}{[\omega_{j'}^2(\vec{0})-\omega_0^2]\{[\omega_{j''}(\vec{0})+\omega_j(\vec{0})]^2-\omega_0^2\}\{[\omega_{j''}(\vec{0})-\omega_j(\vec{0})]^2-\omega_0^2\}}\,.\tag{3.3b}$$

We now consider the contribution $P_{\lambda\beta}(s\,|\,t)$ from both the first- and second-order dipole moments which is linear in $A_{\vec{k}j}$ and $B_{\vec{k}j}$. We have two types of terms to evaluate:

$$P_{\lambda\beta}^{(M_1M_2)}(s\,|\,t)=\frac{1}{2\hbar}\sum_{n=0}^{\infty}\frac{(-1)^n t^n}{n!}\sum_{j_1}M_\lambda(j_1)\sum_{\substack{\vec{k}_2j_2\\ \vec{k}_3j_3}}M_\beta(\vec{k}_2j_2;\vec{k}_3j_3)\,[A_{\vec{0}j_1}^{(n)}(s),A_{\vec{k}_2j_2}(s)A_{\vec{k}_3j_3}(s)]\,,\tag{3.4a}$$

$$P_{\lambda\beta}^{(M_2M_1)}(s\,|\,t)=\frac{1}{2\hbar}\sum_{n=0}^{\infty}\frac{(-1)^n t^n}{n!}\sum_{\substack{\vec{k}_2j_2\\ \vec{k}_3j_3}}M_\lambda(\vec{k}_2j_2;\vec{k}_3j_3)\sum_{j_1}M_\beta(j_1)\left[\frac{d^n}{ds^n}[A_{\vec{k}_2j_2}(s)A_{\vec{k}_3j_3}(s)],A_{\vec{0}j_1}(s)\right].\tag{3.4b}$$

First we consider the operator $P_{\lambda\beta}^{(M_1M_2)}(s\,|\,t)$. From Eq. (3.5a) of Ref. 3 we see that in the harmonic approximation the commutator $[A_{\vec{k}_1j_1}^{(2n)}(s),A_{\vec{k}_2j_2}(s)A_{\vec{k}_3j_3}(s)]$ vanishes, and to first order in the cubic anharmonic force constants it is quadratic $A_{\vec{k}j}$ and $B_{\vec{k}j}$. Using Eq. (3.5b) of Ref. 3 for $A_{\vec{k}j}^{(2n+1)}(s)$, we find that in the harmonic approximation,

$$[A_{\vec{k}_1j_1}^{(2n+1)}(s),A_{\vec{k}_2j_2}(s)A_{\vec{k}_3j_3}(s)]=[-i\omega_{j_1}(\vec{k}_1)]^{2n+1}[2\Delta(\vec{k}_1+\vec{k}_2)\,\delta_{j_1j_2}A_{\vec{k}_3j_3}+2\Delta(\vec{k}_1+\vec{k}_3)\delta_{j_1j_3}A_{\vec{k}_2j_2}]\,,\tag{3.5}$$

as

$$A_{\vec{k}_1j_1}^{(2n+1)}=[-i\omega_{j_1}(\vec{k}_1)]^{2n+1}B_{\vec{k}_1j_1}\,.\tag{3.6}$$

Substitution of Eq. (3.5) into Eq. (3.4a) yields the expression

$$\begin{aligned}P_{\lambda\beta}^{(M_1M_2)}(s\,|\,t)&=\frac{-1}{2\hbar}\sum_{n=0}^{\infty}\frac{t^{2n+1}}{(2n+1)!}\sum_{j_1}\sum_{\substack{\vec{k}_2j_2\\ \vec{k}_3j_3}}M_\lambda(j_1)M_\beta(\vec{k}_2j_2;\vec{k}_3j_3)\,[-i\omega_{j_1}(\vec{0})]^{2n+1}[2\Delta(\vec{k}_2)\delta_{j_1j_2}A_{\vec{k}_3j_3}+2\Delta(\vec{k}_3)\delta_{j_1j_3}A_{\vec{k}_2j_2}]\\&=\frac{2i}{\hbar}\sum_{j_1j_2}M_\lambda(j_1)M_\beta(j_1j_2)\,(\sin\omega_j(\vec{0})\,t)A_{\vec{0}j_2}\,,\end{aligned}\tag{3.7}$$

where $M_\beta(j_1j_2)\equiv M_\beta(\vec{0}j_1;\vec{0}j_2)$, and the operator $P_{\lambda\beta}^{(M_1M_2)}(s\,|\,\omega_0)$ is given by

$$P_{\lambda\beta}^{(M_1M_2)}(s\,|\,\omega_0)=\frac{2i}{\hbar}\sum_{jj'}M_\lambda(j')\,M_\beta(j'j)\times\frac{\omega_{j'}(\vec{0})}{\omega_{j'}^2(\vec{0})-\omega_0^2}\,A_{\vec{0}j}\,.\tag{3.8}$$

We next consider the contribution from $P_{\lambda\beta}^{(M_2M_1)}(s\,|\,t)$. From Eqs. (2.16) and (2.17) we find that

$$\left[\frac{d^{2n}}{ds^{2n}}(A_{\vec{k}_2j_2}A_{\vec{k}_3j_3}),\ A_{\vec{k}_1j_1}\right]=b_{2n}[2\Delta(\vec{k}_2+\vec{k}_1)\,\delta_{j_2j_1}B_{\vec{k}_3j_3}+2\Delta(\vec{k}_3+\vec{k}_1)\,\delta_{j_3j_1}B_{\vec{k}_2j_2}]\,, \tag{3.9a}$$

$$\left[\frac{d^{2n+1}}{ds^{2n+1}}(A_{\vec{k}_2j_2}A_{\vec{k}_3j_3}),\ A_{\vec{k}_1j_1}\right]=[2\Delta(\vec{k}_3+\vec{k}_1)\,\delta_{j_3j_1}A_{\vec{k}_2j_2}+2\Delta(\vec{k}_2+\vec{k}_1)\,\delta_{j_2j_1}A_{\vec{k}_3j_3}]\,. \tag{3.9b}$$

The operator $P_{\lambda\beta}^{(M_2M_1)}(s\,|\,t)$ then takes the form

$$P_{\lambda\beta}^{(M_2M_1)}(s\,|\,t)=\frac{1}{2\hbar}\sum_{\substack{\vec{k}_2j_2\\ \vec{k}_3j_3\\ j_1}}M_\lambda(\vec{k}_2j_2;\vec{k}_3j_3)\,M_\beta(j_1)\left(\sum_{n=0}^{\infty}\frac{t^{2n}}{(2n)!}\,b_{2n}[2\Delta(\vec{k}_2)\,\delta_{j_2j_1}B_{\vec{k}_3j_3}+2\Delta(\vec{k}_3)\,\delta_{j_3j_1}B_{\vec{k}_2j_2}]\right.$$
$$\left.-\sum_{n=0}^{\infty}\frac{t^{2n+1}}{(2n+1)!}\{c_{2n+1}[2\Delta(\vec{k}_3)\,\delta_{j_3j_1}A_{\vec{k}_2j_2}]+d_{2n+1}[2\Delta(\vec{k}_2)\,\delta_{j_2j_1}A_{\vec{k}_3j_3}]\}\right)\,. \tag{3.10}$$

From this it follows that $P_{\lambda\beta}^{(M_2M_1)}(s\,|\,\omega_0)$ is given by

$$P_{\lambda\beta}^{(M_2M_1)}(s\,|\,\omega_0)=\frac{1}{\hbar}\sum_{j_1j_2}M_\lambda(j_2j_1)\,M_\beta(j_1)$$
$$\times\left(\frac{-4i\omega_0\,\omega_{j_1}(\vec{0})\,\omega_{j_2}(\vec{0})\,B_{\vec{0}j_2}}{\{[\omega_{j_1}(\vec{0})-\omega_{j_2}(\vec{0})]^2-\omega_0^2\}\{[\omega_{j_1}(\vec{0})+\omega_{j_2}(\vec{0})]^2-\omega_0^2\}}-\frac{-2i\omega_{j_1}(\vec{0})\,[\omega_0^2+\omega_{j_2}^2(\vec{0})-\omega_{j_1}^2(\vec{0})]\,A_{\vec{0}j_2}}{\{[\omega_{j_1}(\vec{0})-\omega_{j_2}(\vec{0})]^2-\omega_0^2\}\{[\omega_{j_1}(\vec{0})+\omega_{j_2}(\vec{0})]^2-\omega_0^2\}}\right)\,, \tag{3.11}$$

where we have made use of the generating functions

$$\mathcal{B}(\vec{k}_1j_1;\vec{k}_2j_2;x),\quad \mathcal{C}(\vec{k}_1j_1;\vec{k}_2j_2;x)\,,\quad\text{and}\quad \mathcal{D}(\vec{k}_1j_1;\vec{k}_2j_2;x)\,,$$

and necessarily have set $1/x=i\omega_0$.

Combining the contributions $P_{\lambda\beta}^{(M_1M_2)}(s\,|\,\omega_0)$ and $P_{\lambda\beta}^{(M_2M_1)}(s\,|\,\omega_0)$ with the result for $P_{\lambda\beta}^{(M_1M_1)}(s\,|\,\omega_0)$ obtained by Wallis and Maradudin,[3] we arrive at the following expression for $P_{\lambda\beta}(s\,|\,\omega_0)$:

$$P_{\lambda\beta}(s\,|\,\omega_0)=i\sum_j[P_{\lambda\beta}^{(1)}(j\,|\,\omega_0)\,B_{\vec{0}j}(s)-P_{\lambda\beta}^{(2)}(j\,|\,\omega_0)\,A_{\vec{0}j}(s)]\,, \tag{3.12}$$

where

$$P_{\lambda\beta}^{(1)}(j\,|\,\omega_0)=\frac{48\omega_0}{\hbar^2}\sum_{j'j''}M_\lambda(j')\,M_\beta(j'')\,\omega_{j'}(\vec{0})\,\omega_{j''}(\vec{0})\,\omega_j(\vec{0})\,\frac{V(\vec{0}j';\vec{0}j'';\vec{0}j)}{[\omega_{j'}^2(\vec{0})-\omega_0^2]\{[\omega_{j''}(\vec{0})+\omega_j(\vec{0})]^2-\omega_0^2\}\,\{[\omega_{j''}(\vec{0})-\omega_j(\vec{0})]^2-\omega_0^2\}}$$
$$-\frac{4\omega_0}{\hbar}\sum_{j''}M_\lambda(j;j'')\,M_\beta(j'')\,\frac{\omega_{j''}(\vec{0})\,\omega_j(\vec{0})}{\{[\omega_{j''}(\vec{0})+\omega_j(\vec{0})]^2-\omega_0^2\}\,\{[\omega_{j''}(\vec{0})-\omega_j(\vec{0})]^2-\omega_0^2\}}\,, \tag{3.13a}$$

$$P_{\lambda\beta}^{(2)}(j\,|\,\omega_0)=\frac{24}{\hbar^2}\sum_{j'j''}M_\lambda(j')\,M_\beta(j'')\,\omega_{j'}(\vec{0})\,\omega_{j''}(\vec{0})\,\frac{[\omega_{j''}^2(\vec{0})-\omega_j^2(\vec{0})-\omega_0^2]\,V(\vec{0}j';\vec{0}j'';\vec{0}j)}{[\omega_{j'}^2(\vec{0})-\omega_0^2]\,\{[\omega_{j''}(\vec{0})+\omega_j(\vec{0})]^2-\omega_0^2\}\,\{[\omega_{j''}(\vec{0})-\omega_j(\vec{0})]^2-\omega_0^2\}}$$
$$-\frac{2}{\hbar}\sum_{j'}M_\lambda(j')\,M_\beta(j;j')\,\frac{\omega_{j'}(\vec{0})}{\omega_{j'}^2(\vec{0})-\omega_0^2}+\frac{2}{\hbar}\sum_{j''}M_\lambda(j;j'')\,M_\beta(j'')\,\frac{\omega_{j''}(\vec{0})\,[\omega_0^2+\omega_j^2(\vec{0})-\omega_{j''}^2(\vec{0})]}{\{[\omega_{j''}(\vec{0})+\omega_j(\vec{0})]^2-\omega_0^2\}\{[\omega_{j''}(\vec{0})-\omega_j(\vec{0})]^2-\omega_0^2\}}\,. \tag{3.13b}$$

The expressions given by Eqs. (3.13) satisfy relation (2.4).

The group-theoretic selection rules governing the first-order ionic Raman effect obtained by Wallis and Maradudin[3] are not altered by the additional contributions to the coefficients $P_{\lambda\beta}^{(1)}$ and $P_{\lambda\beta}^{(2)}$ given here. If we use the expression for $i_{\alpha\gamma\beta\lambda}(\Omega)$ given by Eq. (2.2), we find that in the harmonic approximation this tensor is given by

$$i_{\alpha\gamma\beta\lambda}(\Omega)=n(\Omega)\sum_j P_{\lambda\beta}(j\,|\,\omega_0,\Omega)\,P_{\gamma\alpha}(j\,|\,\omega_0,\Omega)$$
$$\times[\delta(\Omega-\omega_j(\vec{0}))-\delta(\Omega+\omega_j(\vec{0}))]\,, \tag{3.14}$$

where

$$P_{\lambda\beta}(j\,|\,\omega_0,\Omega)=[\Omega/\omega_j(\vec{0})]\,P_{\lambda\beta}^{(1)}(j\,|\,\omega_0)+P_{\lambda\beta}^{(2)}(j\,|\,\omega_0)\,. \tag{3.15}$$

In this expression, $P_{\lambda\beta}^{(1)}(j\,|\,\omega_0)$ and $P_{\lambda\beta}^{(2)}(j\,|\,\omega_0)$ are given by Eqs. (3.13a) and (3.13b). The first term on the right-hand side of Eq. (3.14) describes the anti-Stokes scattering processes, while the second term describes the Stokes processes.

We conclude this section with an order-of-magnitude estimate of the scattering efficiency [Eq. (2.1)] for ω_0 in the vicinity of $2\omega_T$ for GaAs. To simplify this calculation we neglect the small difference between the frequencies of the $\vec{k}=0$ transverse- and longitudinal-optical modes ($\omega_T = 273$ cm^{-1}, $\omega_L = 297$ cm^{-1}),[5] and equate all optical-mode frequencies to ω_T. Then, labeling the three optical branches by $j = 1, 2, 3$, we obtain for $\omega_0 \approx 2\omega_T$,

$$P^{(1)}_{\lambda\beta}(j\,|\,\omega_0) \approx \frac{1}{4\omega_T^2 - \omega_0^2}\left(\frac{8}{\hbar^2}\sum_{j'j''} M_\lambda(j')\,M_\beta(j'') \times V(\vec{0}j'; \vec{0}j''; \vec{0}j) + \frac{2\omega_T}{\hbar}\sum_{j'} M_\lambda(jj')\,M_\beta(j')\right) . \tag{3.16a}$$

With the same approximations we find that

$$P^{(2)}_{\lambda\beta}(j\,|\,\omega_0) = -P^{(1)}_{\lambda\beta}(j\,|\,\omega_0) . \tag{3.16b}$$

Combining Eqs. (3.15) and (3.16) yields the result that the coefficient $P_{\lambda\beta}(j\,|\,\omega_0, \Omega)$ is given by

$$P_{\lambda\beta}(j\,|\,\omega_0, \Omega) \approx (\Omega/\omega_T - 1)\,P^{(1)}_{\lambda\beta}(j\,|\,\omega_0) . \tag{3.17}$$

This result in Eq. (3.14) enables the scattering tensor $i_{\alpha\gamma\beta\lambda}(\Omega)$ describing Stokes scattering to be written as

$$i_{\alpha\gamma\beta\lambda}(\Omega)_{\text{Stokes}} = 4[n(\omega_T) + 1] \times \textstyle\sum_j P^{(1)}_{\lambda\beta}(j\,|\,\omega_0)\,P^{(1)}_{\gamma\alpha}(j\,|\,\omega_0)\,\delta(\Omega + \omega_T) . \tag{3.18}$$

To evaluate the coefficient $P^{(1)}_{\lambda\beta}(j\,|\,\omega_0)$ we must obtain expressions for the first- and second-order dipole-moment coefficients $M_\lambda(j)$ and $M_\lambda(jj')$, and the cubic anharmonic coefficient $V(\vec{0}j; \vec{0}j'; \vec{0}j'')$. The latter is given by[3]

$$V(\vec{0}j; \vec{0}j'; \vec{0}j'') = \frac{1}{6}\left(\frac{\hbar}{2N}\right)^{3/2} \frac{1}{[\omega_j(\vec{0})\,\omega_{j'}(\vec{0})\,\omega_{j''}(\vec{0})]^{1/2}} \sum_{l\kappa\alpha}\sum_{l'\kappa'\beta}\sum_{l''\kappa''\gamma} \Phi_{\alpha\beta\gamma}(l\kappa; l'\kappa'; l''\kappa'')\frac{e_\alpha(\kappa\,|\,j)}{(M_\kappa)^{1/2}}\,\frac{e_\beta(\kappa'\,|\,j')}{(M_{\kappa'})^{1/2}}\,\frac{e_\gamma(\kappa''\,|\,j'')}{(M_{\kappa''})^{1/2}} , \tag{3.19}$$

where $\Phi_{\alpha\beta\gamma}(l\kappa;\ l'\kappa';\ l''\kappa'')$ is a cubic anharmonic force constant. At this point it is convenient to introduce the coefficient $f_{\alpha\beta\gamma}(\kappa\kappa'\kappa'')$ defined by

$$\sum_{ll'l''} \Phi_{\alpha\beta\gamma}(l\kappa;\ l'\kappa';\ l''\kappa'') = N f_{\alpha\beta\gamma}(\kappa\kappa'\kappa'') . \tag{3.20}$$

Infinitesimal translational invariance and the T_d symmetry at each ion site in the zinc-blende structure have the consequence that $f_{\alpha\beta\gamma}(\kappa\kappa'\kappa'')$ can be written as

$$f_{\alpha\beta\gamma}(\kappa\kappa'\kappa'') = (\operatorname{sgn}\kappa)\,(\operatorname{sgn}\kappa')\,(\operatorname{sgn}\kappa'')\,|\,\epsilon_{\alpha\beta\gamma}|f , \tag{3.21}$$

where $\operatorname{sgn}\kappa = \pm 1$ when $\kappa = \pm$, and $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita tensor. With the assumptions we have made, the eigenvector $e_\alpha(\kappa\,|\,j)$ can be shown to be given by[6]

$$e_\alpha(\kappa\,|\,j) = (\operatorname{sgn}\kappa)\,(\mu/M_\kappa)^{1/2}\,\xi_\alpha(j) , \quad j = 1, 2, 3 \tag{3.22}$$

where μ is the reduced mass of the two ions in a primitive unit cell, and the $\{\vec{\xi}(j)\}$ are any three mutually perpendicular unit vectors. Combining Eqs. (3.19)–(3.22), we obtain for $V(\vec{0}j; \vec{0}j'; \vec{0}j'')$,

$$V(\vec{0}j; \vec{0}j'; \vec{0}j'') = \frac{f}{6N^{1/2}}\left(\frac{\hbar}{2\mu\omega_T}\right)^{3/2} \times \sum_{\alpha\beta\gamma} |\epsilon_{\alpha\beta\gamma}|\,\epsilon_\alpha(j)\,\xi_\beta(j')\,\xi_\gamma(j'') . \tag{3.23}$$

In the same way the first-order dipole-moment coefficient $M_\lambda(j)$ is found to be given by

$$M_\lambda(j) = (\hbar N/2\mu\omega_T)^{1/2}\,e_T^*\,\xi_\lambda(j) , \tag{3.24}$$

where e_T^* is the transverse effective charge of the ions in the crystal.

In determining the second-order dipole-moment coefficient $M_\lambda(jj')$, we require its sign relative to that of $V(\vec{0}j;\vec{0}j';\vec{0}j'')$, as well as its magnitude. We find that $M_\lambda(jj')$ can be expressed as

$$M_\lambda(jj') = m\left(\frac{\hbar}{2\mu\omega_T}\right)\sum_{\alpha\beta} |\,\epsilon_{\lambda\alpha\beta}|\,\xi_\alpha(j)\,\xi_\beta(j') , \tag{3.25}$$

where the coefficient m is defined by

$$\sum_{ll'} M_{\lambda\alpha\beta}(l\kappa; l'\kappa') = N(\operatorname{sgn}\kappa)\,(\operatorname{sgn}\kappa')\,|\,\epsilon_{\lambda\alpha\beta}|\,m . \tag{3.26}$$

With the preceding results, $P^{(1)}_{\lambda\beta}(j\,|\,\omega_0)$ becomes

$$P^{(1)}_{\lambda\beta}(j\,|\,\omega_0) = \frac{N^{1/2}}{4\omega_T^2 - \omega_0^2}\left(\frac{\hbar}{2\mu\omega_T}\right)^{3/2}\left[\frac{4f(e_T^*)^2}{3\hbar^2}\left(\frac{\hbar}{2\mu\omega_T}\right) + \frac{2\omega_T}{\hbar}\,m\,e_T^*\right]\sum_\alpha |\,\epsilon_{\lambda\beta\alpha}|\,\xi_\alpha(j) . \tag{3.27}$$

A lattice-dynamical calculation of the coefficients f and m appearing in Eq. (3.27) has been carried out for GaAs by Humphreys and Maradudin recently in another context.[7] For the details of the model used, and the calculation, the reader is referred to their paper. The values obtained are

$$f = 78.5189 \times 10^{12}\ \text{erg/cm}^3 , \tag{3.28a}$$

$$m = (4.0431 \times 10^{8})\,e_T^*\ \text{cm}^{-1} . \tag{3.28b}$$

The second-order dipole-moment contribution to the coefficient $P^{(1)}_{\lambda\beta}(j\,|\,\omega_0)$ is of the same order of magnitude as the cubic anharmonic contribution, and has the same sign. For ω_0 in the vicinity of $2\omega_T$ for GaAs, an order-of-magnitude estimate of the integrated scattering efficiency for the Stokes portion of the spectrum at 0 °K, per unit length per unit solid angle is obtained by combining Eq. (3.27) with Eq. (3.18) and substituting the result into Eq. (2.1). The estimate is

$$\int_{-\infty}^{0} \mathcal{S}(\Omega)_{\text{Stokes}}\, d\Omega = \frac{1.33\times 10^{-13}}{(2-\omega_0/\omega_T)^2}\ \text{cm}^{-1}\,\text{sr}^{-1} \qquad (3.29)$$

for incident light polarized along the y direction and scattered light along the x direction. The result for the integrated scattering efficiency presented here is an order of magnitude greater than those obtained previously by Wallis and Maradudin[3] and by Humphreys.[8] This is attributed to the use of a more realistic model of GaAs in obtaining the estimates given by Eqs. (3.28). An integrated scattering efficiency of 10^{-11} cm^{-1} sr^{-1} for one-phonon scattering is at the limits of detectability at the present time for incident light in the infrared.[9] The result given by Eq. (3.29) indicates, therefore, that the first-order ionic Raman effect can only be observed for frequencies of the incident light in the immediate vicinity of the resonance frequency, i.e., within about 10% or 27 cm^{-1} of $2\omega_T$. For such frequencies the integrated scattering efficiency exceeds 10^{-11} cm^{-1} sr^{-1}.

IV. SECOND-ORDER IONIC RAMAN EFFECT

The processes describing two-phonon, or second-order, ionic Raman scattering are shown in Fig. 2. In what follows it will be shown that the general expression for the operator $P^{(2)}_{\lambda\beta}(0\,|\,\omega_0)$ describing the second-order ionic Raman effect is

$$P^{(2)}_{\lambda\beta}(0\,|\,\omega_0)=\sum_{\vec{k}j}\sum_{\vec{k}'j'}\big[Q^{(1)}_{\lambda\beta}(\vec{k}j;\vec{k}'j')A_{\vec{k}j}A_{\vec{k}'j'} + Q^{(2)}_{\lambda\beta}(\vec{k}j;\vec{k}'j')A_{\vec{k}j}B_{\vec{k}'j'} + Q^{(3)}_{\lambda\beta}(\vec{k}j;\vec{k}'j')B_{\vec{k}j}A_{\vec{k}'j'} + Q^{(4)}_{\lambda\beta}(\vec{k}j;\vec{k}'j')B_{\vec{k}j}B_{\vec{k}'j'}\big]\,. \qquad (4.1)$$

Thus, unlike the situation for the electronic contribution to the second-order Raman effect, where only the first term on the right-hand side of Eq. (4.1) appears, in the second-order ionic Raman effect the operator $P_{\lambda\beta}(0\,|\,\omega_0)$ is modulated by second-order terms in the atomic momenta as well as in the atomic displacements. We make use of Eq. (2.4) to determine the required relationships among the coefficients $\{Q^{(r)}_{\lambda\beta}(\vec{k}j;\vec{k}'j')\}$. We find

$$Q^{(1)}_{\lambda\beta}(-\vec{k}j;-\vec{k}'j'\,|\,\omega_0)^* = -Q^{(1)}_{\lambda\beta}(\vec{k}j;\vec{k}'j'\,|\,-\omega_0)\,, \qquad (4.2a)$$

$$Q^{(2)}_{\lambda\beta}(-\vec{k}'j';-\vec{k}j\,|\,\omega_0)^* = Q^{(3)}_{\lambda\beta}(\vec{k}j;\vec{k}'j'\,|\,-\omega_0)\,, \qquad (4.2b)$$

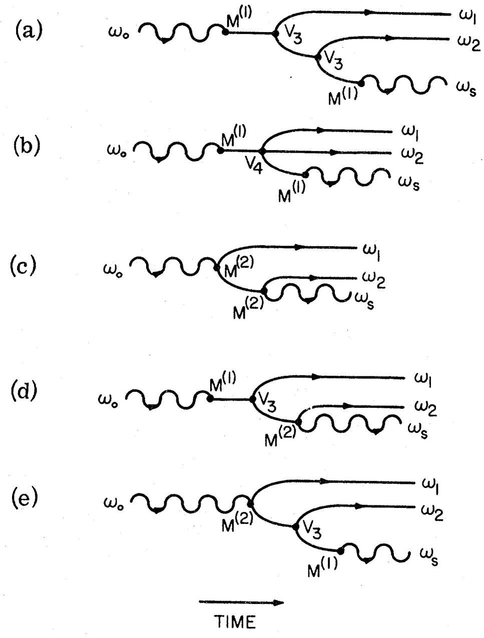

FIG. 2. Processes contributing to the second-order ionic Raman effect described in Sec. IV. Photons are described by wavy lines and phonons by solid lines.

$$Q^{(3)}_{\lambda\beta}(-\vec{k}'j';-\vec{k}j\,|\,\omega_0)^* = Q^{(2)}_{\lambda\beta}(\vec{k}j;\vec{k}'j'\,|\,-\omega_0)\,, \qquad (4.2c)$$

$$Q^{(4)}_{\lambda\beta}(-\vec{k}j;-\vec{k}'j'\,|\,\omega_0)^* = -Q^{(4)}_{\lambda\beta}(\vec{k}j;\vec{k}'j'\,|\,-\omega_0)\,. \qquad (4.2d)$$

We now turn to the determination of the coefficients $\{Q^{(r)}_{\lambda\beta}(\vec{k}j;\vec{k}'j')\}$ for two types of crystals.

The first case we consider is case 2(c) which exhibits the contribution from the second-order dipole-moment alone. In the absence of a first-order dipole moment in a crystal, e.g., for diamond, this would be the only second-order process. The incident light excites two phonons through the second-order dipole moment $M^{(2)}$. One phonon of frequency ω_1 is created and the second phonon interacts with the lattice again through the second-order dipole moment $M^{(2)}$ to create a phonon of frequency ω_2 and emit a photon of frequency ω_s. This process occurs in the harmonic approximation for lattice vibrations.

In this process, the operator $P_{\lambda\beta}(s\,|\,t)$ is given by

$$P_{\lambda\beta}(s\,|\,t)=\frac{1}{4\hbar}\sum_{n=0}^{\infty}\frac{(-1)^n t^n}{n!}\sum_{\substack{\vec{k}_1\vec{k}_2\\ j_1j_2}}\sum_{\substack{\vec{k}_3\vec{k}_4\\ j_3j_4}} M_\lambda(\vec{k}_1j_1;\vec{k}_2j_2)\,M_\beta(\vec{k}_3j_3;\vec{k}_4j_4)\left[\frac{d^n}{ds^n}[A_{\vec{k}_1j_1}(s)A_{\vec{k}_2j_2}(s)]\,,\ A_{\vec{k}_3j_3}(s)A_{\vec{k}_4j_4}(s)\right]\,. \qquad (4.3)$$

To evaluate the commutator in Eq. (4.3) we use the expressions for the even and odd derivatives of $A_{\vec{k}_1j_1}A_{\vec{k}_2j_2}$ given by Eqs. (2.16) and (2.17). We combine these equations, perform the integration over t, and arrive at the following expression for the operator $P_{\lambda\beta}(s\,|\,\omega_0)$:

$$\begin{aligned}P_{\lambda\beta}(s\,|\,\omega_0)=\frac{1}{4\hbar}\sum_{\substack{\vec{k}_1\vec{k}_2\\ j_1j_2}}\sum_{\substack{\vec{k}_3\vec{k}_4\\ j_3j_4}} M_\lambda(\vec{k}_1j_1;\vec{k}_2j_2)\,M_\beta(\vec{k}_3j_3;\vec{k}_4j_4)\,\frac{1}{i\omega_0}\Bigg(\sum_{n=0}^{\infty}\frac{b_{2n}}{(i\omega_0)^{2n}}\big[&2\Delta(\vec{k}_2+\vec{k}_3)\,\delta_{j_2j_3}\,B_{\vec{k}_1j_1}A_{\vec{k}_4j_4}\\
&+2\Delta(\vec{k}_2+\vec{k}_4)\,\delta_{j_2j_4}\,B_{\vec{k}_1j_1}A_{\vec{k}_3j_3}+2\Delta(\vec{k}_1+\vec{k}_3)\,\delta_{j_1j_3}\,A_{\vec{k}_4j_4}B_{\vec{k}_2j_2}+2\Delta(\vec{k}_1+\vec{k}_4)\,\delta_{j_1j_4}\,A_{\vec{k}_3j_3}B_{\vec{k}_2j_2}\big]\\
&-\sum_{n=0}^{\infty}\frac{c_{2n+1}}{(i\omega_0)^{2n+1}}\big[2\Delta(\vec{k}_2+\vec{k}_3)\,\delta_{j_2j_3}\,A_{\vec{k}_1j_1}A_{\vec{k}_4j_4}+2\Delta(\vec{k}_2+\vec{k}_4)\,\delta_{j_2j_4}\,A_{\vec{k}_1j_1}A_{\vec{k}_3j_3}\big]\\
&-\sum_{n=0}^{\infty}\frac{d_{2n+1}}{(i\omega_0)^{2n+1}}\big[2\Delta(\vec{k}_1+\vec{k}_3)\,\delta_{j_1j_3}\,A_{\vec{k}_4j_4}A_{\vec{k}_2j_2}+2\Delta(\vec{k}_1+\vec{k}_4)\,\delta_{j_1j_4}\,A_{\vec{k}_3j_3}A_{\vec{k}_2j_2}\big]\Bigg)\,. \qquad (4.4)\end{aligned}$$

In writing this equation, we have assumed that ω_0 has a small negative imaginary part which has been omitted here to simplify the notation. We perform the summations in the above equation by utilizing the generating functions given by Eqs. (2.27a), (2.27b), (2.32a), and (2.32b) in which we have set $x=1/i\omega_0$. We make use of the fact that $M_\lambda(\vec{k}_1j_1;\vec{k}_2j_2)$ vanishes unless $\vec{k}_2=-\vec{k}_1$, and obtain the final result for $P_{\lambda\beta}(0|\omega_0)$ given in the form of Eq. (4.1), where

$$\begin{aligned}Q^{(1)}_{\lambda\beta}(\vec{k}j;-\vec{k}j')=-\frac{1}{\hbar}\Bigg[&\sum_{j_1}M_\lambda(\vec{k}j_1;-\vec{k}j')\,M_\beta(\vec{k}j;-\vec{k}j_1)\left(\frac{\omega_{j_1}(\vec{k})\,[\omega_0^2+\omega_{j'}^2(\vec{k})-\omega_{j_1}^2(\vec{k})]}{\{[\omega_{j_1}(\vec{k})+\omega_{j'}(\vec{k})]^2-\omega_0^2\}\{[\omega_{j_1}(\vec{k})-\omega_{j'}(\vec{k})]^2-\omega_0^2\}}\right)\\
&+\sum_{j_1}M_\lambda(-\vec{k}j_1;\vec{k}j)\,M_\beta(-\vec{k}j';\vec{k}j_1)\left(\frac{\omega_{j_1}(\vec{k})\,[\omega_0^2+\omega_{j}^2(\vec{k})-\omega_{j_1}^2(\vec{k})]}{\{[\omega_{j_1}(\vec{k})+\omega_{j}(\vec{k})]^2-\omega_0^2\}\{[\omega_{j_1}(\vec{k})-\omega_{j}(\vec{k})]^2-\omega_0^2\}}\right)\Bigg]\,, \qquad (4.5\text{a})\end{aligned}$$

$$Q^{(2)}_{\lambda\beta}(\vec{k}j;-\vec{k}j')=-\frac{2i}{\hbar}\sum_{j_1}M_\lambda(\vec{k}j_1;-\vec{k}j')\,M_\beta(\vec{k}j;-\vec{k}j_1)\left(\frac{\omega_0\,\omega_{j_1}(\vec{k})\,\omega_{j'}(\vec{k})}{\{[\omega_{j_1}(\vec{k})+\omega_{j'}(\vec{k})]^2-\omega_0^2\}\{[\omega_{j_1}(\vec{k})-\omega_{j'}(\vec{k})]^2-\omega_0^2\}}\right)\,, \qquad (4.5\text{b})$$

$$Q^{(3)}_{\lambda\beta}(\vec{k}j;-\vec{k}j')=-\frac{2i}{\hbar}\sum_{j_1}M_\lambda(-\vec{k}j_1;\vec{k}j)\,M_\beta(-\vec{k}j';\vec{k}j_1)\left(\frac{\omega_0\,\omega_{j_1}(\vec{k})\,\omega_{j}(\vec{k})}{\{[\omega_{j_1}(\vec{k})+\omega_{j}(\vec{k})]^2-\omega_0^2\}\{[\omega_{j_1}(\vec{k})-\omega_{j}(\vec{k})]^2-\omega_0^2\}}\right)\,, \qquad (4.5\text{c})$$

$$Q^{(4)}_{\lambda\beta}(\vec{k}j;-\vec{k}j')\equiv 0\,. \qquad (4.5\text{d})$$

Due to the restrictions on the dipole moment, the coefficients $\{Q^{(r)}_{\lambda\beta}(\vec{k}j;\vec{k}'j')\}$ vanish unless $\vec{k}'=-\vec{k}$. We have written $Q^{(1)}_{\lambda\beta}(\vec{k}j;-\vec{k}j')$ in symmetric form as this is the form in which it contributes to $P_{\lambda\beta}$.

We obtain an expression for the tensor $i_{\alpha\gamma\beta\lambda}(\Omega)$ as given by Eq. (2.2) in terms of the coefficients $\{Q^{(r)}_{\lambda\beta}(\vec{k}j;-\vec{k}j')\}$ by evaluating the necessary correlation functions. We find that

$$\begin{aligned}i_{\alpha\gamma\beta\lambda}(\Omega)=&\;2\sum_{\vec{k}jj'}(n_{\vec{k}j}+1)(n_{-\vec{k}j'}+1)\,\delta(\Omega+\omega_j(\vec{k})+\omega_{j'}(\vec{k}))\,[(q_1+q_2+q_3+q_4)(q_1^*+q_2^*+q_3^*+q_4^*)]\\
&+2\sum_{\vec{k}jj'}n_{-\vec{k}j}n_{\vec{k}j'}\,\delta(\Omega-\omega_j(\vec{k})-\omega_{j'}(\vec{k}))\,[(q_1-q_2-q_3+q_4)(q_1^*-q_2^*-q_3^*+q_4^*)]\\
&+2\sum_{\vec{k}jj'}(n_{\vec{k}j}+1)n_{\vec{k}j'}\,\delta(\Omega+\omega_j(\vec{k})-\omega_{j'}(\vec{k}))\,[(q_1-q_2+q_3-q_4)(q_1^*-q_2^*+q_3^*-q_4^*)]\\
&+2\sum_{\vec{k}jj'}n_{-\vec{k}j}(n_{-\vec{k}j'}+1)\,\delta(\Omega-\omega_j(\vec{k})+\omega_{j'}(\vec{k}))\,[(q_1+q_2-q_3-q_4)(q_1^*+q_2^*-q_3^*-q_4^*)]\,. \qquad (4.6)\end{aligned}$$

We have simplified notation in this expression by defining

$$q_r=Q^{(r)}_{\lambda\beta}(\vec{k}j;-\vec{k}j')\,, \qquad (4.7\text{a})$$

$$q_r^*=Q^{(r)*}_{\gamma\alpha}(\vec{k}j;-\vec{k}j')\,. \qquad (4.7\text{b})$$

In Eq. (4.6), we have used the following relations:

$$Q^{(1)*}_{\lambda\beta}(\vec{k}j;-\vec{k}j')=Q^{(1)*}_{\lambda\beta}(-\vec{k}j';\vec{k}j)\,, \qquad (4.8\text{a})$$

$$Q^{(2)*}_{\lambda\beta}(\vec{k}j;-\vec{k}j')=Q^{(3)*}_{\lambda\beta}(-\vec{k}j';\vec{k}j)\,, \qquad (4.8\text{b})$$

$$Q^{(3)*}_{\lambda\beta}(\vec{k}j;-\vec{k}j')=Q^{(2)*}_{\lambda\beta}(-\vec{k}j';\vec{k}j)\,, \qquad (4.8\text{c})$$

$$Q^{(4)*}_{\lambda\beta}(\vec{k}j;-\vec{k}j')=Q^{(4)*}_{\lambda\beta}(-\vec{k}j';\vec{k}j)\,. \qquad (4.8\text{d})$$

In view of the complexity of expressions (4.5a)–(4.5d), it is difficult to make more than a crude estimate of the scattering efficiency for the second-order ionic Raman effect. If we make the approximation of the absolute zero of temperature for diamond, we find

$$i_{\alpha\gamma\beta\lambda}(\Omega)=\sum_{\vec{k}jj'}\delta(\Omega+\omega_j(\vec{k})+\omega_{j'}(\vec{k}))\,|(q_1+q_2+q_3)|^2\,. \tag{4.9}$$

For the incident light polarized along the y direction and the scattered light along the x direction, the integrated scattering efficiency for the Stokes portion of the spectrum is given by

$$\int_{-\infty}^{0} S(\Omega)\,d\Omega=\frac{1}{A}\,\frac{1}{c^4}\int_{-\infty}^{0} d\Omega\, i_{xyxy}(\Omega)\,(\omega_0+\Omega)^4\,. \tag{4.10}$$

If we assume that ω_0 is somewhat greater than $2\omega_R$, where ω_R is the Raman frequency for crystals of the diamond structure, none of the denominators in Eqs. (4.5) can vanish. We make the approximation that the $q_{(r)}$ each contribute equally to the scattering efficiency and choose $q_{(2)}$ which has the most simple form. We substitute Eq. (4.9) into Eq. (4.10) to obtain

$$\int_{-\infty}^{0} S(\Omega)\,d\Omega\cong\frac{18}{A}\,\frac{1}{c^4}\sum_{\vec{k}jj'}|q_2|^2[\omega_0-\omega_j(\vec{k})-\omega_{j'}(\vec{k})]^2\,. \tag{4.11}$$

We integrate k over the first Brillouin zone and substitute the expressions for the second-order dipole-moment coefficients obtained in Sec. III for GaAs. We set $\omega_0=2\omega_R$ and all other frequencies equal to the Raman frequency. The resulting expression for the integrated scattering efficiency per unit length per unit solid angle is given by

$$\int_{-\infty}^{0} S(\Omega)\,d\Omega\cong\frac{72}{\hbar^2 v_a}\,\frac{1}{c^4}\left(\frac{\hbar m}{M}\right)^4\frac{1}{(2\omega_R)^2}\,, \tag{4.12}$$

where v_a is the volume of a unit cell, m is the second-order dipole-moment contribution, and M is the diamond mass. An order-of-magnitude estimate is

$$\int_{-\infty}^{0} S(\Omega)\,d\Omega\sim 7.234\times10^{-12}\,\mathrm{cm^{-1}\,sr^{-1}}\,. \tag{4.13}$$

If we divide this by $2\omega_R=2664\ \mathrm{cm^{-1}}$, we find that the average scattering efficiency per unit length per unit solid angle per unit frequency interval is $1.44\times10^{-26}\ \mathrm{cm^{-1}\,sr^{-1}\,sec}$. If the spectrometer accepts all the radiation scattered into a frequency range of $d\omega_s=5\ \mathrm{cm^{-1}}$ ($=9.4\times10^{11}$ rad/sec), the average scattering efficiency for scattering into this frequency interval is $1.35\times10^{-14}\ \mathrm{cm^{-1}\,sr^{-1}}$. The results given by Eq. (4.13) and the average scattering efficiency are about three orders of magnitude greater than those obtained in a previous paper.[8] This is due to the use of the value of m given by Eq. (3.28b) in Eq. (4.12), rather than the smaller value used in Ref. 8.

In the case of a crystal which also possesses a first-order dipole moment, there are additional scattering mechanisms that contribute to the two-phonon or second-order ionic Raman effect. These processes are shown in Fig. 2. Figures 2(a) and 2(b) display contributions from the first-order dipole moment alone. Figure 2(a) exhibits contributions proportional to the squares of the cubic anharmonic force constants, and Fig. 2(b) exhibits contributions proportional to the quartic anharmonic force constants. In addition, there are the contributions proportional to the product of the cubic anharmonic force constants and the second-order dipole-moment coefficients that are shown in Figs. 2(d) and 2(e). The general form for $P^{(2)}_{\lambda\beta}(0\,|\,\omega_0)$ given by Eq. (4.1) is still valid with the coefficients $\{Q^{(r)}_{\lambda\beta}(\vec{k}j;\vec{k}'j')\}$ modified to include these processes. However, the expressions for these coefficients and operators describing these processes are extremely lengthy and cumbersome. It is reasonable to assume, however, that the scattering efficiency for scattering by these mechanisms is comparable to that for the second-order ionic Raman effect in crystals without a first-order dipole moment. We have estimated this to be a small effect and consequently, we will present the complicated expressions elsewhere.

In this paper, we have presented a theory of the first-order ionic Raman effect from infrared-inactive optical modes of crystals, as well as a theory of the second-order ionic Raman effect in crystals possessing a first-order dipole moment and in crystals lacking a first-order dipole moment. Numerical estimates of the magnitudes of the scattering efficiencies obtained indicate that the first-order ionic Raman effect is on the limits of detectability, but that the second-order ionic Raman effect is too small to be observed at the present time.

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