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Ionic Raman Effect. II. The First-Order Ionic Raman Effect*

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A theory previously developed for the Raman scattering of infrared light by the modulation of the ionic contribution to the polarizability of a crystal by the displacements of the atoms from their equilibrium positions has been applied to the calculation of the scattering efficiency of a pure crystal having a first-order electric dipole moment and cubic anharmonicity in the potential energy. The requirements on crystal symmetry for a nonvanishing scattering efficiency are developed, and it is shown that only noncentrosymmetric crystals can exhibit the effect. The symmetries of the ionic Raman tensor are presented for the 21 crystal classes lacking a center of inversion. A numerical estimate of the scattering efficiency is given for the case of gallium arsenide.

I. INTRODUCTION

The Raman scattering of light by phonons in a crystal may be viewed as arising from the modulation of the crystal polarizability by the phonons. This modulation can take place in two ways. First, the *ionic* part of the polarizability may be modulated by the atomic displacements. Second, the *electronic* part of the polarizability may be modulated by the atomic displacements. If the incident and scattered frequencies are in the visible region, the first mechanism is usually negligible compared to the second.[1,2] However, with the development of infrared lasers such as the CO_2 laser, it is now possible to carry out Raman-scattering experiments in which the radiation frequencies are comparable to the energy separations of adjacent vibrational levels. Under the latter conditions, the contributions from the modulation of the ionic part of the polarizability may be significant.

For a harmonic crystal with a first-order electric dipole moment, there is no Raman scattering arising from the ionic polarizability modulation because a linear system cannot mix frequencies. In a previous paper[3] a general formulation of the ionic Raman effect was developed, and a specific calculation was presented for the case of U centers in CaF_2 vibrating under the influence of cubic and quartic terms in the potential energy. Only a first-order electric dipole moment associated with the localized mode was considered. It was found that an observable scattering should be observable under several conditions. These include a resonance scattering with frequency shift equal to the fundamental of the localized vibrational mode when the incident frequency is twice the localized-mode fundamental, and a resonance scattering with frequency shift equal to twice the localized-mode fundamental when the incident frequency is three times the localized-mode fundamental.

In the present paper, we discuss ionic Raman scattering by one-phonon processes from a pure crystal possessing a first-order electric dipole moment and cubic anharmonic terms in the crystal potential energy. Crystal symmetry requirements for a nonvanishing effect are developed. The results of some illustrative calculations are presented.

II. INTENSITY OF SCATTERED LIGHT IN FIRST-ORDER IONIC RAMAN EFFECT

The intensity of light scattered per unit solid angle into the frequency interval $(\omega_s, \omega_s + d\omega_s)$ by the modulation of the ionic part of the crystal polarizability tensor by the atomic displacements can be expressed as[1]

$$I(\omega_s)\, d\omega_s = \frac{\omega_s^4}{2\pi c^3} \sum_{\alpha\beta\gamma\lambda} n_\alpha n_\beta\, i_{\alpha\gamma\beta\lambda}(\Omega)\, E_\gamma^- E_\gamma^+\, d\omega_s\,. \tag{2.1}$$

Here c is the speed of light, $\vec{n}$ is a unit vector which defines the polarization of the scattered light, and $\vec{E}^+$ and $\vec{E}^- = (\vec{E}^+)^*$ are the amplitudes of the positive- and negative-frequency components of the incident light. It was shown in Ref. 3 that the tensor $i_{\alpha\gamma\beta\lambda}(\Omega)$ is given by

$$i_{\alpha\gamma\beta\lambda}(\Omega) = \frac{1}{2\pi\hbar^2}\int_{-\infty}^{\infty} ds\, e^{-is\Omega}\int_0^{\infty} dt\, e^{-i\omega t-\gamma t}\int_0^{\infty} dt'\, e^{i\omega t'-\gamma t'}$$

$$\times\langle [M_\lambda(s-t), M_\beta(s)][M_\alpha^+(0), M_\gamma^+(-t')]\rangle\,. \tag{2.2}$$

The frequency $\Omega = \omega_s - \omega$ is the shift in the frequency of the light on scattering, where ω is the frequency of the incident light. The operator $M_\alpha(t)$ is the α Cartesian component of the crystal–dipole-moment operator in the Heisenberg representation. The angular brackets $\langle \cdots \rangle$ denote an average over the canonical ensemble described by the vibrational Hamiltonian of the crystal. The damping constant γ is introduced phenomenologically to describe the broadening of the vibrational levels of the crystal. However, we will treat it here as a convergence factor to give meaning to the integrals over t and t', and will set it equal to zero at the end of the calculation. Our result will consequently be inaccurate in the immediate vicinity of the phonon frequencies at which $i_{\alpha\gamma\beta\lambda}(\Omega)$ considered as a function of ω has resonances.

For the purposes of this paper we find it convenient to rewrite Eq. (2.2) in an alternative, more compact, form. We first define an operator $P_{\lambda\beta}(s\,|\,t)$ by

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

In terms of this operator we define an operator $P_{\lambda\beta}(s\,|\,\omega)$ by

$$P_{\lambda\beta}(s\,|\,\omega)=\int_0^\infty dt\,e^{-i\omega t-\gamma t}\,P_{\lambda\beta}(s\,|\,t)\ . \tag{2.4}$$

The expression for $i_{\alpha\gamma\beta\lambda}(\Omega)$ which provides the starting point for the calculations to be described in this paper can now be written as

$$i_{\alpha\gamma\beta\lambda}(\Omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}ds\,e^{-is\Omega}\,\langle P_{\lambda\beta}(s\,|\,\omega)\,P^{+}_{\gamma\alpha}(0\,|\,\omega)\rangle\ . \tag{2.5}$$

Because the crystal–dipole-moment operator $M_\alpha(t)$ can be expanded in powers of the displacements of the atoms from their equilibrium positions, or equivalently in powers of phonon creation and destruction operators, it follows that the operator $P_{\lambda\beta}(s\,|\,\omega)$ can also be expanded in powers of phonon creation and destruction operators. From the form of the expression for $i_{\alpha\gamma\beta\lambda}(\Omega)$ given by Eq. (2.5), it is seen that if we are interested in the scattering of light by one-phonon processes, we require the contribution to the operator $P_{\lambda\beta}(s\,|\,\omega)$ which is linear in phonon creation and destruction operators. It is to the determination of this contribution that the major part of this paper is devoted.

In this paper we will be concerned with evaluating Eq. (2.5) for $i_{\alpha\gamma\beta\lambda}(\Omega)$ in the case where the crystal possesses a first-order dipole moment. This is because crystals lacking a first-order dipole moment can easily be shown to lack a first-order ionic Raman effect. Thus we assume that the α component of the crystal dipole moment can be expanded in powers of the displacements of the atoms from their equilibrium positions according to[4]

$$M_\alpha=\sum_{l\kappa\mu}M_{\alpha\mu}(l\kappa)\,u_\mu(l\kappa)+\tfrac{1}{2}\sum_{l\kappa\mu}\sum_{l\kappa\nu}M_{\alpha\mu\nu}(l\kappa;l'\kappa')\,u_\mu(l\kappa)\,u_\nu(l'\kappa')+\cdots\ . \tag{2.6}$$

In this expansion $u_\mu(l\kappa)$ is the μ Cartesian component of the displacement of the κth atom in the lth primitive unit cell. The coefficient $M_{\alpha\mu}(l\kappa)$ is the transverse effective charge tensor of the atom $(l\kappa)$, which governs the strength of the infrared lattice absorption by the crystal. It is the contribution to $i_{\alpha\gamma\beta\lambda}(\Omega)$ from the first term on the right-hand side of Eq. (2.6) that we will be concerned with here.

In evaluating $P_{\lambda\beta}(s\,|\,t)$, defined by Eq. (2.3), it is convenient to carry out the normal coordinate transformation from the atomic displacements and their conjugate momenta to the corresponding phonon operators:

$$u_\alpha(l\kappa)=\left(\frac{\hbar}{2NM_\kappa}\right)^{1/2}\sum_{\vec{k}j}\frac{e_\alpha(\kappa\,|\,\vec{k}j)}{[\omega_j(\vec{k})]^{1/2}}\,e^{i\vec{k}\cdot\vec{x}(l)}\,A_{\vec{k}j}\ , \tag{2.7a}$$

$$p_\alpha(l\kappa)=\frac{1}{i}\left(\frac{\hbar M_\kappa}{2N}\right)^{1/2}\sum_{\vec{k}j}[\omega_j(\vec{k})]^{1/2}\,e_\alpha(\kappa\,|\,\vec{k}j)\,e^{i\vec{k}\cdot\vec{x}(l)}\,B_{\vec{k}j}\ . \tag{2.7b}$$

Here N is the total number of primitive unit cells in the crystal, M_κ is the mass of the κth kind of atom, and $\vec{x}(l)$ is the position vector defining the location of the lth primitive unit cell. $\omega_j(\vec{k})$ 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. The allowed values of the wave vector $\vec{k}$ are defined by periodic boundary conditions on the displacements, and are uniformly and densely distributed throughout the first Brillouin zone of the crystal. The phonon field and momentum operators $A_{\vec{k}j}$ and $B_{\vec{k}j}$, respectively, are defined by

$$A_{\vec{k}j}=b_{\vec{k}j}+b^{+}_{-\vec{k}j}=A^{+}_{-\vec{k}j}\ , \tag{2.8a}$$

$$B_{\vec{k}j}=b_{\vec{k}j}-b^{+}_{-\vec{k}j}=-B^{+}_{-\vec{k}j}\ , \tag{2.8b}$$

where $b^{+}_{\vec{k}j}$ and $b_{\vec{k}j}$ are creation and destruction operators, respectively, for phonons in the mode $(\vec{k}j)$.

Using Eq. (2.7a) in the first term on the right-hand side of Eq. (2.6), we obtain for the first-order dipole moment the result that

$$M_\alpha=\textstyle\sum_j M_\alpha(j)\,A_{\vec{0}j}\ , \tag{2.9}$$

where

$$M_\alpha(j)=\left(\frac{\hbar N}{2\omega_j(\vec{0})}\right)^{1/2}\sum_{\kappa\mu}M_{\alpha\mu}(\kappa)\,\frac{e_\mu(\kappa\,|\,\vec{0}j)}{M_\kappa^{1/2}}\ . \tag{2.10}$$

In obtaining Eqs. (2.10) we have used the fact that, owing to the periodicity of the crystal, the effective charge tensor $M_{\alpha\mu}(l\kappa)$ is independent of the cell index l.[5] In what follows we denote this tensor by $M_{\alpha\mu}(\kappa)$.

With the aid of Eq. (2.9) we can express the operator $P_{\lambda\beta}(s\,|\,t)$ in the form

$$P_{\lambda\beta}(s\,|\,t)=\frac{1}{\hbar}\sum_{jj'}M_\lambda(j)\,M_\beta(j')\,[A_{\vec{0}j}(s-t),\ A_{\vec{0}j'}(s)]\ . \tag{2.11}$$

We now proceed to expand this operator in powers of phonon field operators.

III. EVALUATION OF $P_{\lambda\beta}(s|\omega)$

In the harmonic approximation, the commutator $[A_{\vec{0}j}(s-t),\ A_{\vec{0}j'}(s)]$ is a c number, independent of s. Consequently, we see from Eqs. (2.4) and (2.5) that in the harmonic approximation crystals possessing a first-order dipole moment do not display a first-order ionic Raman effect. A first-order ionic Raman effect in such crystals owes its existence to the anharmonicity of the interatomic forces.

In this section we obtain the operator $P_{\lambda\beta}(s|\omega)$ to first order in the cubic anharmonic force constants of the crystal, that is, to the lowest nonvanishing order in the anharmonic force constants. This approximation suffices to give the intensity of light scattered by one-phonon processes.

We begin by expanding the operator $A_{\vec{0}j}(s-t)$ in a Taylor series in powers of t to obtain for $P_{\lambda\beta}(s|t)$ the formal result

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

The superscript (n) denotes the nth derivative with respect to the argument. The motivation for making the expansion (3.1) is that through its use we have to deal with equal-time commutators only.

To obtain $A_{\vec{k}j}^{(n)}(s)$ to the lowest nonvanishing order in the anharmonic force constants we proceed as follows. From the Hamiltonian of the crystal through cubic anharmonic terms,

$$H=\sum_{\vec{p}s}\hbar\omega_s(\vec{p})\,b_{\vec{p}s}^{+}b_{\vec{p}s}+\sum_{\vec{p}_1s_1}\sum_{\vec{p}_2s_2}\sum_{\vec{p}_3s_3}V(\vec{p}_1s_1;\vec{p}_2s_2;\vec{p}_3s_3) \times A_{\vec{p}_1s_1}A_{\vec{p}_2s_2}A_{\vec{p}_3s_3}\ , \tag{3.2}$$

and repeated use of the Heisenberg equations of motion

$$i\hbar\frac{d}{dt}A_{\vec{k}j}=[A_{\vec{k}j},H]=\hbar\omega_j(\vec{k})B_{\vec{k}j}\ , \tag{3.3a}$$

$$i\hbar\frac{d}{dt}B_{\vec{k}j}=[B_{\vec{k}j},H]=\hbar\omega_j(\vec{k})A_{\vec{k}j} +6\sum_{\vec{p}_2s_2}\sum_{\vec{p}_3s_3}V(-\vec{k}j;\ \vec{p}_2s_2;\ \vec{p}_3s_3)A_{\vec{p}_2s_2}A_{\vec{p}_3s_3}\ , \tag{3.3b}$$

we obtain the following results:

$$A_{\vec{k}j}^{(0)}=A_{\vec{k}j}\ , \tag{3.4a}$$

$$A_{\vec{k}j}^{(1)}=-i\omega_j(\vec{k})B_{\vec{k}j}\ , \tag{3.4b}$$

$$A_{\vec{k}j}^{(2)}=[-i\omega_j(\vec{k})]^2A_{\vec{k}j} -\frac{6\omega_j(\vec{k})}{\hbar}\sum_{\vec{p}_2s_2}\sum_{\vec{p}_3s_3}V(-\vec{k}j;\vec{p}_2s_2;\vec{p}_3s_3)A_{\vec{p}_2s_2}A_{\vec{p}_3s_3}\ , \tag{3.4c}$$

$$A_{\vec{k}j}^{(3)}=[-i\omega_j(\vec{k})]^3B_{\vec{k}j} +\frac{6i\omega_j(\vec{k})}{\hbar}\sum_{\vec{p}_2s_2}\sum_{\vec{p}_3s_3}V(-\vec{k}j;\vec{p}_2s_2;\vec{p}_3s_3) \times[\omega_{s_2}(\vec{p}_2)B_{\vec{p}_2s_2}A_{\vec{p}_3s_3}+\omega_{s_3}(\vec{p}_3)A_{\vec{p}_2s_2}B_{\vec{p}_3s_3}]\ , \tag{3.4d}$$

$$A_{\vec{k}j}^{(4)}=[-i\omega_j(\vec{k})]^4A_{\vec{k}j} +\frac{6\omega_j(\vec{k})}{\hbar}\sum_{\vec{p}_2s_2}\sum_{\vec{p}_3s_3}V(-\vec{k}j;\vec{p}_2s_2;\vec{p}_3s_3) \times\{[\omega_j^2(\vec{k})+\omega_{s_2}^2(\vec{p}_2)+\omega_{s_3}^2(\vec{p}_3)]A_{\vec{p}_2s_2}A_{\vec{p}_3s_3} +2\omega_{s_2}(\vec{p}_2)\,\omega_{s_3}(\vec{p}_3)\,B_{\vec{p}_2s_2}B_{\vec{p}_3s_3}\}, \tag{3.4e}$$

$$\vdots$$

In obtaining 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 $(\vec{k}''j'')$. In each case we have retained all terms linear in $V(-\vec{k}j;\vec{p}_2s_2;\vec{p}_3s_3)$ and have neglected all higher-order terms.

We see from these results that the even- and odd-order derivatives have different structures and can be written generally as

$$A_{\vec{k}j}^{(2n)}=[-i\omega_j(\vec{k})]^{2n}A_{\vec{k}j} +\frac{6\omega_j(\vec{k})}{\hbar}\sum_{\vec{p}_2s_2}\sum_{\vec{p}_3s_3}V(-\vec{k}j;\vec{p}_2s_2;\vec{p}_3s_3) \times[f_{2n}(p_2s_2;p_3s_3)A_{\vec{p}_2s_2}A_{\vec{p}_3s_3} +g_{2n}(\vec{p}_2s_2;\vec{p}_3s_3)B_{\vec{p}_2s_2}B_{\vec{p}_3s_3}]\ , \tag{3.5a}$$

$$A_{\vec{k}j}^{(2n+1)}=[-i\omega_j(\vec{k})]^{2n+1}B_{\vec{k}j} +\frac{6i\omega_j(\vec{k})}{\hbar}\sum_{\vec{p}_2s_2}\sum_{\vec{p}_3s_3}V(-\vec{k}j;\vec{p}_2s_2;\vec{p}_3s_3) \times[\alpha_{2n+1}(\vec{p}_2s_2;\vec{p}_3s_3)B_{\vec{p}_2s_2}A_{\vec{p}_3s_3} +\beta_{2n+1}(\vec{p}_2s_2;\vec{p}_3s_3)A_{\vec{p}_2s_2}B_{\vec{p}_3s_3}]\ . \tag{3.5b}$$

The coefficients f_{2n}, g_{2n}, α_{2n+1}, β_{2n+1} in these expressions also depend parametrically on the mode index $(\vec{k}j)$. However, to simplify the notation this dependence will not be indicated explicitly.

The coefficients f_{2n}, g_{2n}, α_{2n+1}, and β_{2n+1} in Eqs. (3.5) are related by recurrence formulas. The latter are easily obtained by equating the time derivative of Eq. (3.5a) to the expression for $A_{\vec{k}j}^{(2n+1)}$ given by Eq. (3.5b), and by equating the time derivative of Eq. (3.5b) to the expression for $A_{\vec{k}j}^{(2n+2)}$ obtained from Eq. (3.5a). In this way we find that

$$\alpha_{2n+1}=-\omega_2f_{2n}-\omega_3g_{2n}\ , \tag{3.6a}$$

$$\beta_{2n+1} = -\omega_3 f_{2n} - \omega_2 g_{2n} , \tag{3.6b}$$

$$f_{2n+2} = -(-i\omega)^{2n} + \omega_2 \alpha_{2n+1} + \omega_3 \beta_{2n+1} , \tag{3.6c}$$

$$g_{2n+2} = \omega_3 \alpha_{2n+1} + \omega_2 \beta_{2n+1} . \tag{3.6d}$$

In writing these equations we have omitted arguments $(\vec{p}_2 s_2; \vec{p}_3 s_3)$ in the interest of simplifying the notation. We have also employed the abbreviations ω, ω_2, and ω_3 for $\omega_j(\vec{k})$, $\omega_{s_2}(\vec{p}_2)$, and $\omega_{s_3}(\vec{p}_3)$, respectively. These equations are to be solved subject to the initial conditions, which follow from Eqs. (3.4):

$$\begin{aligned} &f_0 = 0 , && g_0 = 0 , && \alpha_1 = 0 , && \beta_1 = 0 , \\ &f_2 = -1 , && g_2 = 0 , && \alpha_3 = \omega_2 , && \beta_3 = \omega_3 , \\ &f_4 = \omega^2 + \omega_2^2 + \omega_3^2, && g_4 = 2\omega_2\omega_3 . \end{aligned} \tag{3.7}$$

The system of Eqs. (3.6) and (3.7) is readily solved by the method of generating functions. We first eliminate α_{2n+1} and β_{2n+1} from Eqs. (3.6c) and (3.6d) by the use of Eqs. (3.6a) and (3.6b) to obtain the pair of coupled difference equations

$$f_{2n+2} = -(-1)^n \omega^{2n} - 2\omega_2\omega_3 g_{2n} - (\omega_2^2 + \omega_3^2) f_{2n} , \tag{3.8a}$$

$$g_{2n+2} = -2\omega_2\omega_3 f_{2n} - (\omega_2^2 + \omega_3^2) g_{2n} . \tag{3.8b}$$

We next introduce two generating functions $F(\vec{p}_2 s_2; \vec{p}_3 s_3; x)$ and $G(\vec{p}_2 s_2; \vec{p}_3 s_3; x)$ by

$$F(\vec{p}_2 s_2; \vec{p}_3 s_3; x) = \sum_{n=0}^{\infty} f_{2n}(\vec{p}_2 s_2; \vec{p}_3 s_3) x^{2n} , \tag{3.9a}$$

$$G(\vec{p}_2 s_2; \vec{p}_3 s_3; x) = \sum_{n=0}^{\infty} g_{2n}(\vec{p}_2 s_2; \vec{p}_3 s_3) x^{2n} . \tag{3.9b}$$

If we now multiply both sides of Eqs. (3.8a) and (3.8b) by x^{2n} and sum on n from 0 to ∞, then with the aid of the initial conditions (3.7) we find the equations satisfied by $F(x)$ and $G(x)$:

$$\left(\frac{1}{x^2} + \omega_2^2 + \omega_3^2\right) G(x) + 2\omega_2\omega_3 F(x) = 0 , \tag{3.10a}$$

$$2\omega_2\omega_3 G(x) + \left(\frac{1}{x^2} + \omega_2^2 + \omega_3^2\right) F(x) = -\frac{1}{1 + \omega^2 x^2} . \tag{3.10b}$$

The solutions of these equations are

$$F(\vec{p}_2 s_2; \vec{p}_3 s_3; x) = \frac{-x^2\{1 + [\omega_{s_2}^2(\vec{p}_2) + \omega_{s_3}^2(\vec{p}_3)]x^2\}}{M[\omega_j(\vec{k}), \omega_{s_2}(\vec{p}_2), \omega_{s_3}(\vec{p}_3); x]} , \tag{3.11a}$$

$$G(\vec{p}_2 s_2; \vec{p}_3 s_3; x) = \frac{2\omega_{s_2}(\vec{p}_2)\omega_{s_3}(\vec{p}_3) x^4}{M[\omega_j(\vec{k}), \omega_{s_2}(\vec{p}_2), \omega_{s_3}(\vec{p}_3); x]} , \tag{3.11b}$$

where

$$\begin{aligned} M[\omega_j(\vec{k}), \omega_{s_2}(\vec{p}_2), \omega_{s_3}(\vec{p}_3); x] &= \{1 + [\omega_{s_2}(\vec{p}_2) + \omega_{s_3}(\vec{p}_3)]^2 x^2\} \\ &\quad \times \{1 + [\omega_{s_2}(\vec{p}_2) - \omega_{s_3}(\vec{p}_3)]^2 x^2\} [1 + \omega_j^2(\vec{k}) x^2] \\ &= M[\omega_j(\vec{k}), \omega_{s_3}(\vec{p}_3), \omega_{s_2}(\vec{p}_2); x] . \end{aligned} \tag{3.11c}$$

We note that because

$$F(\vec{p}_2 s_2; \vec{p}_3 s_3; x) = F(\vec{p}_3 s_3; \vec{p}_2 s_2; x) , \tag{3.12a}$$

$$G(\vec{p}_2 s_2; \vec{p}_3 s_3; x) = G(\vec{p}_3 s_3; \vec{p}_2 s_2; x) , \tag{3.12b}$$

we must have that

$$f_{2n}(\vec{p}_2 s_2; \vec{p}_3 s_3) = f_{2n}(\vec{p}_3 s_3; \vec{p}_2 s_2) , \tag{3.13a}$$

$$g_{2n}(\vec{p}_2 s_2; \vec{p}_3 s_3) = g_{2n}(\vec{p}_3 s_3; \vec{p}_2 s_2) . \tag{3.13b}$$

We now introduce two more generating functions

$$A(\vec{p}_2 s_2; \vec{p}_3 s_3; x) = \sum_{n=0}^{\infty} \alpha_{2n+1}(\vec{p}_2 s_2; \vec{p}_3 s_3) x^{2n+1} , \tag{3.14a}$$

$$B(\vec{p}_2 s_2; \vec{p}_3 s_3; x) = \sum_{n=0}^{\infty} \beta_{2n+1}(\vec{p}_2 s_2; \vec{p}_3 s_3) x^{2n+1} . \tag{3.14b}$$

Multiplying both sides of Eqs. (3.6a) and (3.6b) by x^{2n+1} and summing on n from 0 to ∞, we obtain the relations

$$A(x) = -\omega_2 x F(x) - \omega_3 x G(x) , \tag{3.15a}$$

$$B(x) = -\omega_3 x F(x) - \omega_2 x G(x) . \tag{3.15b}$$

It follows from these results and Eqs. (3.11) that

$$A(\vec{p}_2 s_2; \vec{p}_3 s_3; x) = \frac{\omega_{s_2}(\vec{p}_2) x^3\{1 + [\omega_{s_2}^2(\vec{p}_2) - \omega_{s_3}^2(\vec{p}_3)]x^2\}}{M[\omega_j(\vec{k}), \omega_{s_2}(\vec{p}_2), \omega_{s_3}(\vec{p}_3); x]} , \tag{3.16a}$$

$$B(p_2 s_2; p_3 s_3; x) = \frac{\omega_{s_3}(\vec{p}_3) x^3\{1 - [\omega_{s_2}^2(\vec{p}_2) - \omega_{s_3}^2(\vec{p}_3)]x^2\}}{M[\omega_j(\vec{k}), \omega_{s_2}(\vec{p}_2), \omega_{s_3}(\vec{p}_3); x]} . \tag{3.16b}$$

We see from Eqs. (3.16) that

$$A(\vec{p}_2 s_2; \vec{p}_3 s_3; x) = B(\vec{p}_3 s_3; \vec{p}_2 s_2; x) . \tag{3.17}$$

It follows, therefore, that

$$\alpha_{2n+1}(\vec{p}_2 s_2; \vec{p}_3 s_3) = \beta_{2n+1}(\vec{p}_3 s_3; \vec{p}_2 s_2) . \tag{3.18}$$

What makes the method of generating functions so useful in the context of the present problem is that, as we shall now see, it is the generating functions $A(x)$, $B(x)$, $F(x)$, and $G(x)$ which appear in the final expression for $i_{\alpha\gamma\beta\lambda}(\Omega)$, and not the coefficients α_{2n+1}, β_{2n+1}, f_{2n}, and g_{2n} obtained from them.

From Eqs. (3.5) we obtain the following needed commutators, exact to first order in the cubic anharmonic force constants:

$$\begin{aligned} [A_{\vec{k}j}^{(2n)}, A_{-\vec{k}j'}] = \frac{24\omega_j(\vec{k})}{\hbar} \sum_{\vec{p}s} V(-\vec{k}j; \vec{k}j'; \vec{p}s) \\ \times g_{2n}(\vec{k}j'; \vec{p}s) B_{\vec{p}s} , \end{aligned} \tag{3.19a}$$

$$[A^{(2n+1)}_{\vec{k}j}, A_{-\vec{k}j'}] = 2[-i\omega_j(\vec{k})]^{2n+1}\delta_{jj'} + \frac{24i\omega_j(\vec{k})}{\hbar} \times \sum_{\vec{p}s} V(-\vec{k}j;\vec{k}j';\vec{p}s)\,\alpha_{2n+1}(\vec{k}j';\vec{p}s)A_{\vec{p}s} \;. \tag{3.19b}$$

The symmetry of the V coefficients in their arguments, and the relations (3.13b) and (3.18) have been used in obtaining Eqs. (3.19).

Combining these results with Eq. (3.1), we obtain for the operator $P_{\lambda\beta}(s\,|\,t)$ the expression

$$P_{\lambda\beta}(s\,|\,t) = \frac{2i}{\hbar}\sum_j M_\lambda(j)M_\beta(j)\sin\omega_j(\vec{0})t + \frac{24}{\hbar^2}\sum_{jj'j''} M_\lambda(j)M_\beta(j')\omega_j(\vec{0})V(\vec{0}j;\vec{0}j';\vec{0}''_j) \times \sum_{n=0}^{\infty}\left(\frac{t^{2n}}{(2n)!}\,g_{2n}(\vec{0}j';\vec{0}j'')B_{\vec{0}j''}(s) - i\,\frac{t^{2n+1}}{(2n+1)!}\,\alpha_{2n+1}(\vec{0}j';\vec{0}j'')A_{\vec{0}j''}(s)\right). \tag{3.20}$$

The first term on the right-hand side of this expression is the operator $P_{\lambda\beta}(s\,|\,t)$ in the harmonic approximation. It is seen to be a c number, independent of s, and therefore cannot describe the inelastic scattering of light. We will drop this term in all that follows.

The particular form of the anharmonic contribution to $P_{\lambda\beta}(s\,|\,t)$ stems from the fact that the coefficient $V(\vec{k}j;\vec{k}'j';\vec{k}''j'')$ vanishes unless $\vec{k}+\vec{k}'+\vec{k}''$ is a translation vector of the reciprocal lattice. If both $\vec{k}$ and $\vec{k}'$ are zero, then $\vec{k}''$ must also be zero, because this is the only reciprocal-lattice vector that a wave vector confined to the first Brillouin zone can equal.

The integration over t in Eq. (2.4) can be carried out immediately by the use of Eq. (3.20), and we obtain for the operator $P_{\lambda\beta}(s\,|\,\omega)$ the simple result

$$\begin{aligned} P_{\lambda\beta}(s\,|\,\omega) &= \frac{24}{\hbar}\sum_{jj'j''} M_\lambda(j)M_\beta(j')\omega_j(\vec{0})V(\vec{0}j;\vec{0}j';\vec{0}''_j)\,\frac{1}{i\omega+\gamma}\sum_{n=0}^{\infty}\left(\frac{g_{2n}(\vec{0}j';\vec{0}j'')}{(\gamma+i\omega)^{2n}}\,B_{\vec{0}j''}(s) - i\,\frac{\alpha_{2n+1}(\vec{0}j';\vec{0}''_j)}{(\gamma+i\omega)^{2n+1}}\,A_{\vec{0}j''}(s)\right) \\ &= i\sum_j\left(P^{(1)}_{\lambda\beta}(j\,|\,\omega)B_{\vec{0}j}(s) - P^{(2)}_{\lambda\beta}(j\,|\,\omega)A_{\vec{0}j}(s)\right) \;, \end{aligned} \tag{3.21}$$

where

$$P^{(1)}_{\lambda\beta}(j\,|\,\omega) = \frac{48\omega}{\hbar^2}\sum_{j'j''}\frac{M_\lambda(j')M_\beta(j'')\omega_{j'}(\vec{0})\omega_{j''}(\vec{0})\omega_j(\vec{0})V(\vec{0}j';\vec{0}j'';\vec{0}j)}{[\omega^2_{j'}(\vec{0})-\omega^2]\{[\omega_{j''}(\vec{0})+\omega_j(\vec{0})]^2-\omega^2\}\{[\omega_{j''}(\vec{0})-\omega_j(\vec{0})]^2-\omega^2\}} \;, \tag{3.22a}$$

$$P^{(2)}_{\lambda\beta}(j\,|\,\omega) = \frac{24}{\hbar^2}\sum_{j'j''}\frac{M_\lambda(j')M_\beta(j'')\omega_{j'}(\vec{0})\omega_{j''}(\vec{0})[\omega^2_{j''}(\vec{0})-\omega^2_j(\vec{0})-\omega^2]}{[\omega^2_{j'}(\vec{0})-\omega^2]\{[\omega_{j''}(\vec{0})+\omega_j(\vec{0})]^2-\omega^2\}}\;\frac{V(\vec{0}j';\vec{0}j'';\vec{0}j)}{\{[\omega_{j''}(\vec{0})-\omega_j(\vec{0})]^2-\omega^2\}} \;. \tag{3.22b}$$

In obtaining this result we have used Eqs. (3.9b), (3.11), (3.14a), and (3.16a), and, as promised, have set the damping constant γ equal to zero in Eqs. (3.22).

In the next paper in this series, which is devoted to the second-order ionic Raman effect, the method of this section will be applied to obtain the contribution to the operator $P_{\lambda\beta}(s\,|\,\omega)$ which is of second order in the phonon operators $A_{\vec{k}j}$ and $B_{\vec{k}j}$.

The results of the Appendix show that the coefficients $P^{(1)}_{\lambda\beta}(j\,|\,\omega)$ and $P^{(2)}_{\lambda\beta}(j\,|\,\omega)$ are real, because the coefficients $M_\alpha(j)$ and $V(\vec{0}j;\vec{0}j';\vec{0}j'')$ are real. However, it should be noted that they are not symmetric in the indices λ and β. They become symmetric in λ and β when the frequency of the incident light ω is much greater than any of the phonon frequencies.

IV. COEFFICIENT $i_{\alpha\gamma\beta\lambda}(\Omega)$

When we substitute Eq. (3.21) into Eq. (2.5), the tensor $i_{\alpha\gamma\beta\lambda}(\Omega)$ takes the form

$$\begin{aligned} i_{\alpha\gamma\beta\lambda}(\Omega) = \frac{1}{2\pi}\sum_{jj'}\int_{-\infty}^{\infty} ds\, e^{-is\Omega}\big[&P^{(1)}_{\lambda\beta}(j\,|\,\omega)P^{(1)}_{\gamma\alpha}(j'\,|\,\omega)\langle B_{\vec{0}j}(s)B^{+}_{\vec{0}j'}(0)\rangle - P^{(1)}_{\lambda\beta}(j\,|\,\omega)P^{(2)}_{\gamma\alpha}(j'\,|\,\omega)\langle B_{\vec{0}j}(s)A^{+}_{\vec{0}j'}(0)\rangle \\ &- P^{(2)}_{\lambda\beta}(j\,|\,\omega)P^{(1)}_{\gamma\alpha}(j'\,|\,\omega)\langle A_{\vec{0}j}(s)B^{+}_{\vec{0}j'}(0)\rangle + P^{(2)}_{\lambda\beta}(j\,|\,\omega)P^{(2)}_{\gamma\alpha}(j'\,|\,\omega)\langle A_{\vec{0}j}(s)A^{+}_{\vec{0}j'}(0)\rangle\big] \;. \end{aligned} \tag{4.1}$$

The four correlation functions appearing in this expression are not all independent, and their Fourier transforms can all be expressed in terms of the Fourier transform of the last correlation function. This last function can be obtained from the general result that[6]

$$\begin{aligned} \int_{-\infty}^{\infty} ds\, e^{-is\Omega}\langle A_{\vec{k}j}(s)A_{-\vec{k}j'}(0)\rangle &= 2\pi\beta\hbar n(\Omega)\,\frac{D_{jj'}(\vec{k};\Omega+i0)-D_{jj'}(\vec{k};\Omega-i0)}{2\pi i} \\ &\equiv 2\pi\beta\hbar n(\Omega)\bar{D}_{jj'}(\vec{k};\Omega) \;, \end{aligned} \tag{4.2}$$

where $D_{jj'}(\vec{k};z)$ is the analytic continuation to the complex z plane of the Fourier-series coefficient (phonon propagator)

$$D_{jj'}(\vec{k};i\omega_l)=\frac{1}{\beta}\int_0^\beta du\, e^{-i\hbar\omega_l u}\langle T_u e^{uH}A_{\vec{k}j}e^{-uH}A_{-\vec{k}j'}\rangle \ . \tag{4.3}$$

In this expression $\omega_l=2\pi l/\beta\hbar$; l is an integer and $\beta=(k_BT)^{-1}$, where k_B is Boltzmann's constant and T is the absolute temperature. T_u is the usual ordering operator for pure imaginary times.[6] With the aid of the equation of motion (3.3a) we can readily establish the results that

$$\int_{-\infty}^{\infty} ds\, e^{-is\Omega}\langle A_{\vec{k}j}(s)B_{-\vec{k}j'}(0)\rangle = \frac{\Omega}{\omega_{j'}(\vec{k})}\,2\pi\beta\hbar n(\Omega)\bar{D}_{jj'}(\vec{k};\Omega)\ , \tag{4.4a}$$

$$\int_{-\infty}^{\infty} ds\, e^{-is\Omega}\langle B_{\vec{k}j}(s)A_{-\vec{k}j'}(0)\rangle = -\frac{\Omega}{\omega_{j}(\vec{k})}\,2\pi\beta\hbar n(\Omega)\bar{D}_{jj'}(\vec{k};\Omega)\ , \tag{4.4b}$$

$$\int_{-\infty}^{\infty} ds\, e^{-is\Omega}\langle B_{\vec{k}j}(s)B_{-\vec{k}j'}(0)\rangle = -\frac{\Omega^2}{\omega_{j}(\vec{k})\omega_{j'}(\vec{k})}\,2\pi\beta\hbar n(\Omega)\bar{D}_{jj'}(\vec{k};\Omega)\ . \tag{4.4c}$$

Substituting the results given by Eqs. (4.2) and (4.4) into Eq. (4.1) and recalling Eq. (2.8), we obtain for $i_{\alpha\gamma\beta\lambda}(\Omega)$ the result that

$$i_{\alpha\gamma\beta\lambda}(\Omega)=\beta\hbar n(\Omega)\sum_{jj'}P_{\lambda\beta}(j\,|\,\omega,\Omega)P_{\gamma\alpha}(j\,|\,\omega,\Omega)\bar{D}_{jj'}(\vec{0};\Omega)\ , \tag{4.5}$$

where

$$P_{\lambda\beta}(j\,|\,\omega,\Omega)=\frac{\Omega}{\omega_j(\vec{0})}P^{(1)}_{\lambda\beta}(j\,|\,\omega)+P^{(2)}_{\lambda\beta}(j\,|\,\omega)$$
$$=\frac{24}{\hbar^2}\sum_{j'j''}\frac{\omega_{j'}(\vec{0})\omega_{j''}(\vec{0})M_\lambda(j')M_\beta(j'')V(\vec{0}j';\vec{0}j'';\vec{0}j)\,[\omega^2_{j''}(\vec{0})-\omega^2_j(\vec{0})+2\Omega\omega-\omega^2]}{[\omega^2_{j'}(\vec{0})-\omega^2]\{[\omega_{j''}(\vec{0})+\omega_j(\vec{0})]^2-\omega^2\}\{[\omega_{j''}(\vec{0})-\omega_j(\vec{0})]^2-\omega^2\}}\ . \tag{4.6}$$

The harmonic approximation to $\bar{D}_{jj'}(\vec{0};\Omega)$ suffices for a qualitative description of several features of the spectrum of scattered light. In this approximation we have that

$$\bar{D}_{jj'}(\vec{0};\Omega)=(\delta_{jj'}/\beta\hbar)\,[\delta(\Omega-\omega_j(\vec{0}))-\delta(\Omega+\omega_j(\vec{0}))]\ . \tag{4.7}$$

Consequently, we find in this approximation that

$$i_{\alpha\gamma\beta\lambda}(\Omega)=n(\Omega)\sum_j P_{\lambda\beta}(j\,|\,\omega,\Omega)P_{\gamma\alpha}(j\,|\,\omega,\Omega)\times[\delta(\Omega-\omega_j(\vec{0}))-\delta(\Omega+\omega_j(\vec{0}))]\ . \tag{4.8}$$

The first term on the right-hand side of this equation describes the anti-Stokes scattering processes, while the second term describes the Stokes processes.

Because the coefficient $P_{\alpha\beta}(j\,|\,\omega,-\omega_j(\vec{0}))$ is unequal to the coefficient $P_{\alpha\beta}(j\,|\,\omega,-\omega_j(\vec{0}))$, as can be seen from Eq. (4.6), it follows from Eq. (4.8) that because of this the intensities of the Stokes lines are different from those of the corresponding anti-Stokes lines, quite apart from any differences due to the different temperature factors $[n(\omega_j(\vec{0}))+1$ and $n(\omega_j(\vec{0}))$, respectively] associated with these two kinds of scattering processes.

If anharmonic contributions to $\bar{D}_{jj'}(\vec{0};\Omega)$ are taken into account, the theory presented in this paper is capable of describing interferences between one-phonon scattering processes if among the $\vec{k}=0$ optical modes of the crystal two or more modes with different frequencies are found which belong to the same irreducible representation of the point group of the crystal.[7] By taking into account anharmonic contributions to $\bar{D}_{jj'}(\vec{0};\Omega)$ it is also possible to describe interferences between one- and two-phonon scattering processes within the framework of the present theory. Some of these effects will be discussed in the next paper in this series.

We conclude this section with an estimate of the scattering efficiency of the first-order ionic Raman effect. The calculation is carried out for the Stokes line in which a long-wavelength TO mode is excited with a resonance of the incident light at twice the TO-mode frequency. Specific numerical results are obtained for a simplified model of GaAs at 0 °K with parallel polarization.

Among the ingredients required for the calculation is the anharmonic coefficient $V(\vec{0}j;\vec{0}j';\vec{0}j'')$ for which we use the Peierls's approximation[8]

$$V(\vec{0}j;\vec{0}j';\vec{0}j'')=\tfrac{1}{12}N^{1/2}(\tfrac{1}{2}\hbar)^{3/2}\times[\omega_j(\vec{0})\omega_{j'}(\vec{0})\omega_{j''}(\vec{0})]^{1/2}C_3\ , \tag{4.9}$$

where C_3 is taken to be a constant. For an order-of-magnitude estimate of $|C_3|^2$ we take the value 1×10^{12} erg^{-1} appropriate to NaCl.[9] While this value is probably not correct for GaAs, we feel that it is close enough to give an order-of-magnitude estimate.

For the case under consideration, the integrated scattering efficiency per unit length per unit solid angle can now be written as

$$\int \mathcal{S}(\Omega)\, d\Omega = (\omega_s^4/c^4V) \left| P_{zz}(T \,|\, \omega, -\omega_T) \right|^2 , \qquad (4.10)$$

where

$$P_{zz}(T \,|\, \omega, -\omega_T) = \frac{N^{1/2} e^{*2} C_3}{M\omega_T^2} \left(\frac{\hbar\omega_T}{2} \right)^{1/2} \times \frac{\omega_T^4}{(\omega_T^2 - \omega^2)(2\omega_T - \omega)\omega} ; \qquad (4.11)$$

e^* is the so-called Born effective charge, M is the mean mass of the gallium and arsenic atoms, N is the number of unit cells in the crystal, and ω_T is the long-wavelength TO-mode frequency. For $|e^*|$ we have taken the value[10] $2.23e$, while for ω_T we have taken the value[11] 272 cm^{-1}.

The calculated result for the integrated scattering efficiency as a function of incident frequency ω is shown in Fig. 1. One sees that the efficiency is very low except in the vicinity of the resonance at $\omega = 2\omega_T$. At this resonance, the scattered radiation has the frequency ω_T and hence will be absorbed by the crystal, thus complicating its experimental observation. In order for the ionic Raman scattering to be observable, it must be greater than the ordinary scattering due to the modulation of the electronic polarizability by the ionic motion. We have estimated the integrated scattering efficiency for the latter process using Bennett's[12] calculated values for the Raman tensor and have found the value 1.5×10^{-12} cm^{-1} sr^{-1} at $\omega = 2\omega_T$. From this result we see that the ionic Raman scattering can only be observed in the immediate vicinity of the resonance.

V. SELECTION RULES

The question naturally arises, what kinds of crystals can display the first-order ionic Raman effect? From Eq. (4.5) we can say that the effect occurs for crystals for which the coefficient $P_{\lambda\beta}(j \,|\, \omega, \Omega)$ defined by Eq. (4.6) is nonzero.

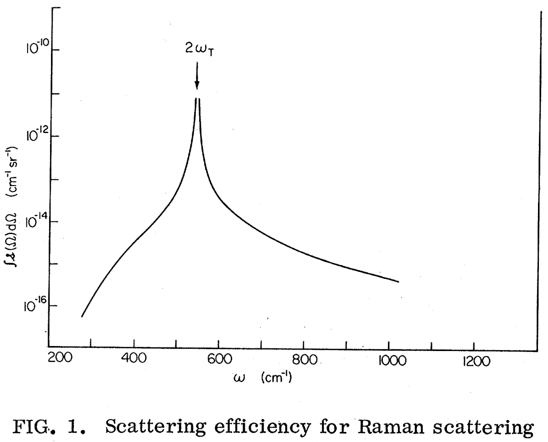

FIG. 1. Scattering efficiency for Raman scattering from the fundamental TO mode of GaAs plotted as a function of the incident light ($\omega_T = 272$ cm^{-1}).

The results obtained in the Appendix show that the coefficient $V(\vec{0}j; \vec{0}j'; \vec{0}j'')$ vanishes in general if any of the branch indices j, j', or j'' refers to any of the three acoustic branches of the phonon spectrum. Thus $P_{\lambda\beta}(j \,|\, \omega, \Omega)$ vanishes unless the index j labels an optical mode. The coefficient $V(\vec{0}j; \vec{0}j'; \vec{0}j'')$ is also shown to vanish if the crystal possesses a center of inversion. Consequently $P_{\lambda\beta}(j \,|\, \omega, \Omega)$ is nonzero only for optical modes in noncentrosymmetric crystals.

We now replace the single-branch index j by the triple index $(sa\lambda)$ as explained in the Appendix, where s labels the irreducible representation of the point group of the crystal to which the mode j belongs, λ distinguishes the partner functions in the case where the representation s is multidimensional, and a is a repetition index which differentiates among modes of different frequencies which belong to the same irreducible representation. Then, substituting the results expressed by Eqs. (A21) and (A23) into Eq. (4.6), we obtain as the transformation law for the coefficient $P_{\gamma\alpha}(sa\lambda \,|\, \omega, \Omega)$ when the crystal is subjected to an operation from its space group

$$P_{\gamma\alpha}(sa\lambda \,|\, \omega, \Omega) = \sum_{\delta\beta} \sum_{\lambda'} S_{\gamma\delta}\, S_{\alpha\beta}\, \tau_{\lambda\lambda'}^{(s)}(\vec{S})\, P_{\delta\beta}(sa\lambda' \,|\, \omega, \Omega) . \qquad (5.1)$$

In this expression $\vec{S}$ is a real orthogonal 3×3 matrix representation of one of the proper or improper rotations comprising the point group of the crystal, and $\tau^{(s)}(\vec{S})$ is a unitary matrix representation of the sth irreducible representation of this group corresponding to the rotation $\vec{S}$.

The use of Eq. (5.1) together with a table[13] of the matrices $\tau^{(s)}(\vec{S})$ for each of the noncentrosymmetric crystallographic point groups allows us to determine the form of the tensor $P_{\gamma\alpha}(sa\lambda \,|\, \omega, \Omega)$ for each irreducible representation of each of these point groups. The results obtained in this way are displayed in Table I, where the notation of Koster *et al.*[14] for the irreducible representations has been used. The representations enclosed in parentheses are pairs of complex-conjugate one-dimensional irreducible representations which are degenerate by time-reversal symmetry. They have been treated as a single real two-dimensional representation. The results presented in Table I, together with Eqs. (2.1) and (4.5), indicate directly the symmetries of the optical vibration modes observed for a given scattering geometry.

It should be emphasized that the reason we can use the point group of the wave vector $\vec{k} = 0$, the point group of the crystal, in obtaining the forms of the tensors $P_{\gamma\alpha}(sa\lambda \,|\, \omega, \Omega)$ is that the finite wave vector of the incident light has been neglected in the derivation of Eq. (2.2), upon which the analysis

TABLE I. Form of the tensor $P_{\gamma\alpha}(s\alpha\lambda \mid \omega, \Omega)$ for the possible Raman-active modes belonging to each noncentrosymmetric crystallographic point group.

C_1	$\Gamma_1 : \begin{pmatrix} a_1 & a_2 & a_3 \\ a_4 & a_5 & a_6 \\ a_7 & a_8 & a_9 \end{pmatrix}$				
C_2	$\Gamma_1 : \overset{(z)}{\begin{pmatrix} a_1 & a_2 & 0 \\ a_3 & a_4 & 0 \\ 0 & 0 & a_5 \end{pmatrix}}$	$\Gamma_2 : \overset{(x,y)}{\begin{pmatrix} 0 & 0 & a_6 \\ 0 & 0 & a_7 \\ a_8 & a_9 & 0 \end{pmatrix}}$			
C_s	$\Gamma_1 : \overset{(x,y)}{\begin{pmatrix} a_1 & a_2 & 0 \\ a_3 & a_4 & 0 \\ 0 & 0 & a_5 \end{pmatrix}}$	$\Gamma_2 : \overset{(z)}{\begin{pmatrix} 0 & 0 & a_6 \\ 0 & 0 & a_7 \\ a_8 & a_9 & 0 \end{pmatrix}}$			
D_2	$\Gamma_1 : \begin{pmatrix} a_1 & 0 & 0 \\ 0 & a_2 & 0 \\ 0 & 0 & a_3 \end{pmatrix}$	$\Gamma_2 : \overset{(y)}{\begin{pmatrix} 0 & 0 & a_4 \\ 0 & 0 & 0 \\ a_5 & 0 & 0 \end{pmatrix}}$	$\Gamma_3 : \overset{(z)}{\begin{pmatrix} 0 & a_6 & 0 \\ a_7 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}}$	$\Gamma_4 : \overset{(x)}{\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & a_8 \\ 0 & a_9 & 0 \end{pmatrix}}$	
C_{2v}	$\Gamma_1 : \overset{(z)}{\begin{pmatrix} a_1 & 0 & 0 \\ 0 & a_2 & 0 \\ 0 & 0 & a_3 \end{pmatrix}}$	$\Gamma_2 : \overset{(x)}{\begin{pmatrix} 0 & 0 & a_4 \\ 0 & 0 & 0 \\ a_5 & 0 & 0 \end{pmatrix}}$	$\Gamma_3 : \begin{pmatrix} 0 & a_6 & 0 \\ a_7 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\Gamma_4 : \overset{(y)}{\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & a_8 \\ 0 & a_9 & 0 \end{pmatrix}}$	
C_4	$\Gamma_1 : \overset{(z)}{\begin{pmatrix} a_1 & a_2 & 0 \\ -a_2 & a_1 & 0 \\ 0 & 0 & a_3 \end{pmatrix}}$	$\Gamma_2 : \begin{pmatrix} a_4 & a_5 & 0 \\ a_5 & -a_4 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$(\Gamma_3+\Gamma_4) : \overset{(y)}{\begin{pmatrix} 0 & 0 & a_6 \\ 0 & 0 & a_7 \\ a_8 & a_9 & 0 \end{pmatrix}} ; \overset{(x)}{\begin{pmatrix} 0 & 0 & a_7 \\ 0 & 0 & -a_6 \\ a_9 & -a_8 & 0 \end{pmatrix}}$		
S_4	$\Gamma_1 : \begin{pmatrix} a_1 & a_2 & 0 \\ -a_2 & a_1 & 0 \\ 0 & 0 & a_3 \end{pmatrix}$	$\Gamma_2 : \overset{(z)}{\begin{pmatrix} a_4 & a_5 & 0 \\ a_5 & -a_4 & 0 \\ 0 & 0 & 0 \end{pmatrix}}$	$(\Gamma_3+\Gamma_4) : \overset{(x)}{\begin{pmatrix} 0 & 0 & a_6 \\ 0 & 0 & a_7 \\ a_8 & a_9 & 0 \end{pmatrix}} ; \overset{(y)}{\begin{pmatrix} 0 & 0 & a_7 \\ 0 & 0 & -a_6 \\ a_9 & -a_8 & 0 \end{pmatrix}}$		
D_4	$\Gamma_1 : \begin{pmatrix} a_1 & 0 & 0 \\ 0 & a_1 & 0 \\ 0 & 0 & a_2 \end{pmatrix}$	$\Gamma_2 : \overset{(z)}{\begin{pmatrix} 0 & a_3 & 0 \\ -a_3 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}}$	$\Gamma_3 : \begin{pmatrix} a_4 & 0 & 0 \\ 0 & -a_4 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\Gamma_4 : \begin{pmatrix} 0 & a_5 & 0 \\ a_5 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\Gamma_5 : \overset{(x)}{\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & a_6 \\ 0 & a_7 & 0 \end{pmatrix}} ; \overset{(y)}{\begin{pmatrix} 0 & 0 & -a_6 \\ 0 & 0 & 0 \\ -a_7 & 0 & 0 \end{pmatrix}}$
C_{4v}	$\Gamma_1 : \overset{(z)}{\begin{pmatrix} a_1 & 0 & 0 \\ 0 & a_1 & 0 \\ 0 & 0 & a_2 \end{pmatrix}}$	$\Gamma_2 : \begin{pmatrix} 0 & a_3 & 0 \\ -a_3 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\Gamma_3 : \begin{pmatrix} a_4 & 0 & 0 \\ 0 & -a_4 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\Gamma_4 : \begin{pmatrix} 0 & a_5 & 0 \\ a_5 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\Gamma_5 : \overset{(x)}{\begin{pmatrix} 0 & 0 & a_6 \\ 0 & 0 & 0 \\ a_7 & 0 & 0 \end{pmatrix}} ; \overset{(y)}{\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & a_6 \\ 0 & a_7 & 0 \end{pmatrix}}$
D_{2d}	$\Gamma_1 : \begin{pmatrix} a_1 & 0 & 0 \\ 0 & a_1 & 0 \\ 0 & 0 & a_2 \end{pmatrix}$	$\Gamma_2 : \begin{pmatrix} 0 & a_3 & 0 \\ -a_3 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\Gamma_3 : \begin{pmatrix} a_4 & 0 & 0 \\ 0 & -a_4 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\Gamma_4 : \overset{(z)}{\begin{pmatrix} 0 & a_5 & 0 \\ a_5 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}}$	$\Gamma_5 : \overset{(x)}{\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & a_6 \\ 0 & a_7 & 0 \end{pmatrix}} ; \overset{(y)}{\begin{pmatrix} 0 & 0 & a_6 \\ 0 & 0 & 0 \\ a_7 & 0 & 0 \end{pmatrix}}$
C_3	$\Gamma_1 : \overset{(z)}{\begin{pmatrix} a_1 & a_2 & 0 \\ -a_2 & a_1 & 0 \\ 0 & 0 & a_3 \end{pmatrix}}$	$(\Gamma_2+\Gamma_3) : \overset{(x)}{\begin{pmatrix} a_4 & a_5 & a_6 \\ a_5 & -a_4 & a_7 \\ a_8 & a_9 & 0 \end{pmatrix}} ; \overset{(y)}{\begin{pmatrix} a_5 & -a_4 & -a_7 \\ -a_4 & -a_5 & a_6 \\ -a_9 & a_8 & 0 \end{pmatrix}}$			
D_3	$\Gamma_1 : \begin{pmatrix} a_1 & 0 & 0 \\ 0 & a_1 & 0 \\ 0 & 0 & a_2 \end{pmatrix}$	$\Gamma_2 : \overset{(z)}{\begin{pmatrix} 0 & a_3 & 0 \\ -a_3 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}}$	$\Gamma_3 : \overset{(x)}{\begin{pmatrix} 0 & a_4 & 0 \\ a_4 & 0 & a_5 \\ 0 & a_6 & 0 \end{pmatrix}} ; \overset{(y)}{\begin{pmatrix} a_4 & 0 & -a_5 \\ 0 & -a_4 & 0 \\ -a_6 & 0 & 0 \end{pmatrix}}$		
C_{3v}	$\Gamma_1 \overset{(z)}{\begin{pmatrix} a_1 & 0 & 0 \\ 0 & a_1 & 0 \\ 0 & 0 & a_2 \end{pmatrix}}$	$\Gamma_2 : \begin{pmatrix} 0 & a_3 & 0 \\ -a_3 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\Gamma_3 : \begin{pmatrix} a_4 & 0 & a_5 \\ 0 & -a_4 & 0 \\ a_6 & 0 & 0 \end{pmatrix} ; \begin{pmatrix} 0 & -a_4 & 0 \\ -a_4 & 0 & a_5 \\ 0 & a_6 & 0 \end{pmatrix}$		
C_6	$\Gamma_1 : \overset{(z)}{\begin{pmatrix} a_1 & a_2 & 0 \\ -a_2 & a_1 & 0 \\ 0 & 0 & a_3 \end{pmatrix}}$	$(\Gamma_2+\Gamma_3) : \begin{pmatrix} a_4 & a_5 & 0 \\ a_5 & -a_4 & 0 \\ 0 & 0 & 0 \end{pmatrix} ; \begin{pmatrix} a_5 & -a_4 & 0 \\ -a_4 & -a_5 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$(\Gamma_5+\Gamma_6) : \overset{(x)}{\begin{pmatrix} 0 & 0 & a_6 \\ 0 & 0 & a_7 \\ a_8 & a_9 & 0 \end{pmatrix}} ; \overset{(y)}{\begin{pmatrix} 0 & 0 & -a_7 \\ 0 & 0 & a_6 \\ -a_9 & a_8 & 0 \end{pmatrix}}$		

TABLE I. (*continued*)

C_{3h}	$\Gamma_1 : \begin{pmatrix} a_1 & a_2 & 0 \\ -a_2 & a_1 & 0 \\ 0 & 0 & a_3 \end{pmatrix}$	$(\Gamma_2+\Gamma_3) : \overset{(x)}{\begin{pmatrix} a_4 & a_5 & 0 \\ a_5 & -a_4 & 0 \\ 0 & 0 & 0 \end{pmatrix}} ; \overset{(y)}{\begin{pmatrix} a_5 & -a_4 & 0 \\ -a_4 & -a_5 & 0 \\ 0 & 0 & 0 \end{pmatrix}}$		$(\Gamma_5+\Gamma_6) : \begin{pmatrix} 0 & 0 & a_6 \\ 0 & 0 & a_7 \\ a_8 & a_9 & 0 \end{pmatrix} ; \begin{pmatrix} 0 & 0 & -a_7 \\ 0 & 0 & a_6 \\ -a_9 & a_8 & 0 \end{pmatrix}$
D_6	$\Gamma_1 : \begin{pmatrix} a_1 & 0 & 0 \\ 0 & a_1 & 0 \\ 0 & 0 & a_2 \end{pmatrix}$	$\Gamma_2 : \overset{(z)}{\begin{pmatrix} 0 & a_3 & 0 \\ -a_3 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}}$	$\Gamma_5 : \overset{(x)}{\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & a_4 \\ 0 & a_5 & 0 \end{pmatrix}} ; \overset{(y)}{\begin{pmatrix} 0 & 0 & -a_4 \\ 0 & 0 & 0 \\ -a_5 & 0 & 0 \end{pmatrix}}$	$\Gamma_6 : \begin{pmatrix} 0 & a_6 & 0 \\ a_6 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} ; \begin{pmatrix} a_6 & 0 & 0 \\ 0 & -a_6 & 0 \\ 0 & 0 & 0 \end{pmatrix}$
C_{6v}	$\Gamma_1 : \overset{(z)}{\begin{pmatrix} a_1 & 0 & 0 \\ 0 & a_1 & 0 \\ 0 & 0 & a_2 \end{pmatrix}}$	$\Gamma_2 : \begin{pmatrix} 0 & a_3 & 0 \\ -a_3 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\Gamma_5 : \overset{(x)}{\begin{pmatrix} 0 & 0 & a_4 \\ 0 & 0 & 0 \\ a_5 & 0 & 0 \end{pmatrix}} ; \overset{(y)}{\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & a_4 \\ 0 & a_5 & 0 \end{pmatrix}}$	$\Gamma_6 : \begin{pmatrix} a_6 & 0 & 0 \\ 0 & -a_6 & 0 \\ 0 & 0 & 0 \end{pmatrix} ; \begin{pmatrix} 0 & -a_6 & 0 \\ -a_6 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$
D_{3h}	$\Gamma_1 : \begin{pmatrix} a_1 & 0 & 0 \\ 0 & a_1 & 0 \\ 0 & 0 & a_2 \end{pmatrix}$	$\Gamma_2 : \begin{pmatrix} 0 & a_3 & 0 \\ -a_3 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\Gamma_5 : \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & a_4 \\ 0 & a_5 & 0 \end{pmatrix} ; \begin{pmatrix} 0 & 0 & -a_4 \\ 0 & 0 & 0 \\ -a_5 & 0 & 0 \end{pmatrix}$	$\Gamma_6 : \overset{(x)}{\begin{pmatrix} 0 & a_6 & 0 \\ a_6 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}} ; \overset{(y)}{\begin{pmatrix} a_6 & 0 & 0 \\ 0 & -a_6 & 0 \\ 0 & 0 & 0 \end{pmatrix}}$
T	$\Gamma_1 : \begin{pmatrix} a_1 & 0 & 0 \\ 0 & a_1 & 0 \\ 0 & 0 & a_1 \end{pmatrix}$	$(\Gamma_2+\Gamma_3) : \begin{pmatrix} a_2 & 0 & 0 \\ 0 & a_3 & 0 \\ 0 & 0 & -(a_2+a_3) \end{pmatrix} ; \frac{2}{\sqrt{3}} \begin{pmatrix} a_3+\frac{1}{2}a_2 & 0 & 0 \\ 0 & -(a_2+\frac{1}{2}a_3) & 0 \\ 0 & 0 & \frac{1}{2}(a_2-a_2) \end{pmatrix}$		$\Gamma_4 : \overset{(x)}{\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & a_4 \\ 0 & a_5 & 0 \end{pmatrix}} ; \overset{(y)}{\begin{pmatrix} 0 & 0 & a_5 \\ 0 & 0 & 0 \\ a_4 & 0 & 0 \end{pmatrix}} ; \overset{(z)}{\begin{pmatrix} 0 & a_4 & 0 \\ a_5 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}}$
O	$\Gamma_1 : \begin{pmatrix} a_1 & 0 & 0 \\ 0 & a_1 & 0 \\ 0 & 0 & a_1 \end{pmatrix}$	$\Gamma_3 : \begin{pmatrix} a_2 & 0 & 0 \\ 0 & a_2 & 0 \\ 0 & 0 & -2a_2 \end{pmatrix} ; \sqrt{3} \begin{pmatrix} -a_2 & 0 & 0 \\ 0 & a_2 & 0 \\ 0 & 0 & 0 \end{pmatrix}$		$\Gamma_4 : \overset{(x)}{\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & a_3 \\ 0 & -a_3 & 0 \end{pmatrix}} ; \overset{(y)}{\begin{pmatrix} 0 & 0 & -a_3 \\ 0 & 0 & 0 \\ a_3 & 0 & 0 \end{pmatrix}} ; \overset{(z)}{\begin{pmatrix} 0 & a_3 & 0 \\ -a_3 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}}$
			$\Gamma_5 : \begin{pmatrix} 0 & a_4 & 0 \\ a_4 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} ; \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & a_4 \\ 0 & a_4 & 0 \end{pmatrix} ; \begin{pmatrix} 0 & 0 & a_4 \\ 0 & 0 & 0 \\ a_4 & 0 & 0 \end{pmatrix}$	
T_d	$\Gamma_1 : \begin{pmatrix} a_1 & 0 & 0 \\ 0 & a_1 & 0 \\ 0 & 0 & a_1 \end{pmatrix}$	$\Gamma_3 : \begin{pmatrix} a_2 & 0 & 0 \\ 0 & a_2 & 0 \\ 0 & 0 & -2a_2 \end{pmatrix} ; \sqrt{3} \begin{pmatrix} -a_2 & 0 & 0 \\ 0 & a_2 & 0 \\ 0 & 0 & 0 \end{pmatrix}$		$\Gamma_4 \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & a_3 \\ 0 & -a_3 & 0 \end{pmatrix} ; \begin{pmatrix} 0 & 0 & -a_3 \\ 0 & 0 & 0 \\ a_3 & 0 & 0 \end{pmatrix} ; \begin{pmatrix} 0 & a_3 & 0 \\ -a_3 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$
			$\Gamma_5 : \overset{(x)}{\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & a_4 \\ 0 & a_4 & 0 \end{pmatrix}} ; \overset{(y)}{\begin{pmatrix} 0 & 0 & a_4 \\ 0 & 0 & 0 \\ a_4 & 0 & 0 \end{pmatrix}} ; \overset{(z)}{\begin{pmatrix} 0 & a_4 & 0 \\ a_4 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}}$	

of this paper is based. It is well known[15] that, strictly speaking, this approximation is invalid for Raman-active modes which are also infrared active. This is because the macroscopic fields which are associated with the $\vec{k} \cong 0$ infrared-active longitudinal optical modes split the group-theoretical degeneracies predicted for $\vec{k} \cong 0$ modes in the absence of long-range electrostatic forces. In addition, these forces alter the angular dependence of the scattering efficiency from that obtained in their absence. Consequently, in Table I we indicate the infrared-active modes by adding x, y, or z in parentheses above the corresponding Raman tensor, where x, y, or z label the polarization direction of the mode. The theory of the ionic Raman effect from these infrared-active modes differs in detail from the theory for nonpolar modes developed here, and will be presented in a subsequent paper.

APPENDIX

The coefficient $V(\vec{0}j;\vec{0}j';\vec{0}j'')$ which plays a central role in the theory developed in this paper is a special case of the general Fourier-transformed cubic anharmonic force constant $V(\vec{k}j;\vec{k}'j';\vec{k}''j'')$ which is defined by[16]

$$V(\vec{k}j;\vec{k}'j';\vec{k}''j'')=\frac{1}{6}\left(\frac{\hbar}{2N}\right)^{3/2}\frac{1}{[\omega_j(\vec{k})\omega_{j'}(\vec{k}')\omega_{j''}(\vec{k}'')]^{1/2}}$$

$$\times\sum_{l\kappa\alpha}\sum_{l'\kappa'\beta}\sum_{l''\kappa''\gamma}\Phi_{\alpha\beta\gamma}(l\kappa;l'\kappa';l''\kappa'')$$

$$\times\frac{e_\alpha(\kappa|\vec{k}j)}{M_\kappa^{1/2}}\frac{e_\beta(\kappa'|\vec{k}'j')}{M_{\kappa'}^{1/2}}\frac{e_\gamma(\kappa''|\vec{k}''j'')}{M_{\kappa''}^{1/2}}$$

$$\times e^{i\vec{k}\cdot\vec{x}(l)+i\vec{k}'\cdot\vec{x}(l')+i\vec{k}''\cdot\vec{x}(l'')}. \tag{A1}$$

In this expression $\Phi_{\alpha\beta\gamma}(l\kappa;l'\kappa';l''\kappa'')$ is a cubic anharmonic force constant. It is completely symmetric in the interchange of any pair of the indices $(l\kappa\alpha)$, $(l'\kappa'\beta)$, and $l''\kappa''\gamma)$, and is invariant under the addition of the same cell index to each of the indices l, l', l''[17]:

$$\Phi_{\alpha\beta\gamma}(l+\bar{l}\kappa;l'+\bar{l}\kappa';l''+\bar{l}\kappa'')=\Phi_{\alpha\beta\gamma}(l\kappa;l'\kappa;l''\kappa''). \tag{A2}$$

The coefficient $V(\vec{k}j;\vec{k}'j';\vec{k}''j'')$ has several useful properties which are independent of the structure and symmetry of a particular crystal.

We see, first of all, that $V(\vec{k}j;\vec{k}'j';\vec{k}''j'')$ is completely symmetric in the indices $(\vec{k}j)$, $(\vec{k}'j')$, and $(\vec{k}''j'')$.

The property of the cubic anharmonic force constants expressed by Eq. (A2) has the immediate consequence that $V(\vec{k}j;\vec{k}'j';\vec{k}''j'')$ vanishes unless the sum of the wave vectors appearing in its argument, $\vec{k}+\vec{k}'+\vec{k}''$, equals a translation vector of the reciprocal lattice.

From Eq. (A1) and the choice of the convention[18]

$$e_\alpha(\kappa|-\vec{k}j)=e_\alpha^*(\kappa|\vec{k}j), \tag{A3}$$

together with the following consequence of time-reversal symmetry[19]:

$$\omega_j(-\vec{k})=\omega_j(\vec{k}), \tag{A4}$$

we find that

$$V(-\vec{k}j;-\vec{k}'j';-\vec{k}''j'')=V\ (\vec{k}j;\vec{k}'j';\vec{k}''j''). \tag{A5}$$

Consequently $V(\vec{0}j;\vec{0}j';\vec{0}j'')$ is real.

To determine the restrictions placed on $V(0j;0j';0j'')$ by the symmetry and structure of the crystal, we begin by introducing the representation of an operation of the space group of the crystal. In the Seitz[20] notation such a symmetry operation is denoted by $\{\vec{S}|\vec{v}(S)+\vec{x}(m)\}$. Applied to the position vector $\vec{x}(l\kappa)$, this operation transforms it according to the rule

$$\begin{aligned}\{\vec{S}|\vec{v}(S)+\vec{x}(m)\}\vec{x}(l\kappa)&=\vec{S}\vec{x}(l\kappa)+\vec{v}(S)+\vec{x}(m)\\&\equiv\vec{x}(LK),\end{aligned} \tag{A6}$$

which is to be interpreted in the active sense.[21] $\vec{S}$ is a 3×3 real orthogonal matrix representation of one of the proper or improper rotations of the point group of the space group, $\vec{v}(S)$ is a vector which is smaller than any primitive translation vector of the crystal, and $\vec{x}(m)$ is a translation vector of the crystal. The vector $\vec{v}(S)$ is nonzero only if the space group is nonsymmorphic. The second equality in Eq. (A6) expresses the fact that because the operation $\{\vec{S}|\vec{v}(S)+\vec{x}(m)\}$ sends the crystal into itself, the site $(l\kappa)$ must be sent into an equivalent site, which we label by (LK). Where no confusion can result from doing so, we will use capital letters to denote the site into which the site denoted by the corresponding lower-case letters is sent by a space-group operation.

Under a space-group operation the force constants $\{\Phi_{\alpha\beta\gamma}(l\kappa;l'\kappa';l''\kappa'')\}$ transform according to[22]

$$\Phi_{\alpha\beta\gamma}(LK;L'K';L''K'')=\sum_{\lambda\mu\nu}S_{\alpha\lambda}S_{\beta\mu}S_{\gamma\nu}\Phi_{\lambda\mu\nu}(l\kappa;l'\kappa';l''\kappa''). \tag{A7}$$

If the point group of the space group contains the inversion $\vec{I}$, i.e., if the crystal has a center of inversion, and if we denote by $(\overline{l\kappa})$ the site into which $(l\kappa)$ is taken by the space-group operation $\{\vec{I}|\vec{v}(I)+\vec{x}(m)\}$, then with the conventional choice of phases[23]

$$e_\alpha^*(\bar{\kappa}|\vec{k}j)=e^{-i\vec{k}\cdot[\vec{x}(\bar{\kappa})+\vec{x}(\kappa)]}e_\alpha(\kappa|\vec{k}j) \tag{A8}$$

together with the relation

$$\vec{I}\vec{x}(l)=\vec{x}(\bar{l})+\vec{x}(\kappa)-\{\vec{I}|\vec{v}(I)+\vec{x}(m)\}\vec{x}(\kappa), \tag{A9}$$

which follows from Eq. (A6), we can rewrite Eq. (A1) as

$$V(\vec{k}j;\vec{k}'j';\vec{k}''j'')$$

$$= -\frac{1}{6}\left(\frac{\hbar}{2N}\right)^{3/2}\frac{1}{[\omega_j(\vec{k})\,\omega_{j'}(\vec{k}')\,\omega_{j''}(\vec{k}'')]^{1/2}}\sum_{l\kappa\alpha}\sum_{l'\kappa'\beta'}\sum_{l''\kappa''\gamma''}\Phi_{\alpha\beta\gamma}(\bar{l}\bar{\kappa};\bar{l}'\bar{\kappa}';\bar{l}''\bar{\kappa}'')\,\frac{e^*_\alpha(\bar{\kappa}|\vec{k}j)}{M^{1/2}_{\bar{\kappa}}}\,\frac{e^*_\beta(\kappa'|\vec{k}'j')}{M^{1/2}_{\bar{\kappa}'}}\,\frac{e^*_\gamma(\kappa''|\vec{k}''j'')}{M^{1/2}_{\bar{\kappa}''}}$$

$$\times e^{i\vec{k}\cdot[\vec{x}(\bar{\kappa})+\vec{x}(\kappa)]}\,e^{i\vec{k}'\cdot[\vec{x}(\bar{\kappa}')+\vec{x}(\kappa')]}\,e^{i\vec{k}''\cdot[\vec{x}(\bar{\kappa}'')+\vec{x}(\kappa'')]}\,e^{-i\vec{k}\cdot[\vec{x}(\bar{l})+\vec{x}(\bar{\kappa})+\vec{x}(\bar{\kappa})-\vec{v}(I)]}\,e^{-i\vec{k}'\cdot[\vec{x}(\bar{l}')+\vec{x}(\bar{\kappa}')+\vec{x}(\kappa')-\vec{v}(I)]}\,e^{-i\vec{k}''\cdot[\vec{x}(\bar{l}'')+\vec{x}(\bar{\kappa}'')+\vec{x}(\kappa'')-\vec{v}(I)]}. \tag{A10}$$

In writing this expression we have noted that because the symmetry operation $\{\vec{S}|\vec{v}(S)+\vec{x}(m)\}$ takes an atom of type κ into an atom of type K, which must be the same kind of atom as κ, we must have that, in general,

$$M_\kappa = M_K. \tag{A11}$$

With a change of dummy summation variables, we find that Eq. (A10) is equivalent to

$$V(\vec{k}j;\vec{k}'j';\vec{k}''j'') = -e^{i(\vec{k}+\vec{k}'+\vec{k}'')\cdot\vec{v}(I)}\,V^*(\vec{k}j;\vec{k}'j';\vec{k}''j''). \tag{A12}$$

It follows immediately that

$$V(\vec{0}j;\vec{0}j';\vec{0}j'') = -V^*(\vec{0}j;\vec{0}j';\vec{0}j''). \tag{A13}$$

This result, in conjunction with the consequence of Eq. (A5) that $V(\vec{0}j;\vec{0}j';\vec{0}j'')$ is real, implies that $V(\vec{0}j;\vec{0}j';\vec{0}j'')$ vanishes for centrosymmetric crystals. In view of Eqs. (4.5) and (4.6) this result means that the first-order ionic Raman effect considered in this paper is absent from crystals possessing a center of inversion. In what follows, therefore, we consider only noncentrosymmetric crystals.

We turn now to a discussion of the symmetry properties of the coefficient $V(\vec{0}j;\vec{0}j';\vec{0}j'')$ itself.

The dynamical matrix of the crystal, whose eigenvectors are the vectors $\{e_\alpha(\kappa|\vec{k}j)\}$, is a real symmetric matrix when $\vec{k}=0$. Consequently, the eigenvectors $\{e_\alpha(\kappa|\vec{0}j)\}$ can be chosen to be real with no loss of generality, and we make this choice in what follows.

If we use the result that $e_\alpha(\kappa|\vec{0}j)/M_\kappa^{1/2}$ is independent of the basis index κ when j refers to any one of the three acoustic branches of the phonon spectrum[24] it follows that $V(\vec{0}j;\vec{0}j';\vec{0}j'')$ vanishes when any of the branch indices j, j', or j'' refers to an acoustic branch owing to the property of the force constant $\Phi_{\alpha\beta\gamma}(l\kappa;l'\kappa';l''\kappa'')$ that[25]

$$\sum_{l\kappa}\Phi_{\alpha\beta\gamma}(l\kappa;l'\kappa';l''\kappa'') = \sum_{l'\kappa'}\Phi_{\alpha\beta\gamma}(l\kappa;l'\kappa';l''\kappa'') = \sum_{l''\kappa''}\Phi_{\alpha\beta\gamma}(l\kappa;l'\kappa';l''\kappa'') = 0. \tag{A14}$$

Consequently, in what follows we assume that j, j', and j'' all label optical branches only.

To proceed farther it is convenient to replace the single-branch index j by the triple index $(sa\lambda)$. Here s labels the irreducible representation of the point group of the wave vector $\vec{k}$ to which the mode belongs, λ distinguishes the partner functions in the case that the representation s is multidimensional, and a is a repetition index which differentiates among modes of different frequencies which belong to the same irreducible representation. In the present case the wave vector $\vec{k}=0$, so that the point group of the wave vector is the point group of the space group of the crystal, the crystal class.

The expression for $V(\vec{0}j;\vec{0}j';\vec{0}j'')$ obtained from Eq. (A1) in the new notation takes the form

$$V(sa\lambda;s'a'\lambda';s''a''\lambda'') = \frac{1}{6}\left(\frac{\hbar}{2N}\right)^{3/2}\frac{1}{(\omega_{sa}\omega_{s'a'}\omega_{s''a''})^{1/2}}$$

$$\times\sum_{l\kappa\alpha}\sum_{l'\kappa'\beta}\sum_{l''\kappa''\gamma}\Phi_{\alpha\beta\gamma}(l\kappa;l'\kappa';l''\kappa'')$$

$$\times\frac{e_\alpha(\kappa|sa\lambda)}{M^{1/2}_\kappa}\,\frac{e_\beta(\kappa'|s'a'\lambda')}{M^{1/2}_{\kappa'}}\,\frac{e_\gamma(\kappa''|s''a''\lambda'')}{M^{1/2}_{\kappa''}}, \tag{A15}$$

where we have suppressed all reference to the wave vectors $\vec{k}=\vec{k}'=\vec{k}''=0$. Using Eqs. (A7) and (A11) in Eq. (A15), we rewrite it in the form

$$V(sa\lambda;s'a'\lambda';s''a''\lambda'') = \frac{1}{6}\left(\frac{\hbar}{2N}\right)^{3/2}\frac{1}{\omega_{sa}\omega_{s'a'}\omega_{s''a''})^{1/2}}$$

$$\times\sum_{l\kappa\alpha}\sum_{l'\kappa'\beta}\sum_{l''\kappa''\gamma}\sum_{\alpha'\beta'\gamma'}\sum_{\kappa_1\kappa_2\kappa_3}\frac{\Phi_{\alpha'\beta'\gamma'}(l\kappa;l'\kappa';l''\kappa'')}{(M_\kappa M_{\kappa'}M_{\kappa''})^{1/2}}$$

$$\times e_\alpha(\kappa_1|sa\lambda)\,T_{\alpha\alpha'}(\kappa_1\kappa|\vec{S})\,e_\beta(\kappa_2|s'a'\lambda')$$

$$\times T_{\beta\beta'}(\kappa_2\kappa'|\vec{S})\,e_\gamma(\kappa_3|s''a''\lambda'')\,T_{\gamma\gamma'}(\kappa_3\kappa''|\vec{S}), \tag{A16}$$

where the matrix $T_{\alpha\beta}(\kappa\kappa'|\vec{S})$ is defined by

$$T_{\alpha\beta}(\kappa\kappa'|\vec{S}) = S_{\alpha\beta}\,\delta(\kappa, F_0(\kappa'\vec{S})). \tag{A17}$$

We have denoted by $F_0(\kappa;\vec{S}) = K$ the index of the atom into which the atom κ is sent by a space-group operation whose rotational element is described by the matrix $\vec{S}$. The matrix $T_{\alpha\beta}(\kappa\kappa'|\vec{S})$ is a real, orthogonal matrix

$$T^{-1}_{\alpha\beta}(\kappa\kappa'|S) = T_{\beta\alpha}(\kappa'\kappa|\vec{S}). \tag{A18}$$

The effect of multiplying the eigenvector $e_\alpha^{(0)}(\kappa|sa\lambda)$ into the matrix $T_{\alpha\beta}(\kappa\kappa'|\vec{\mathrm{S}})$ has been shown to be[26]

$$\sum_{\kappa\beta} e_\beta^{(0)}(\kappa'|\, sa\lambda)\, T_{\beta\alpha}(\kappa'\kappa|\vec{\mathrm{S}}) = \sum_{\lambda'} \tau_{\lambda\lambda'}^{(s)}(\vec{\mathrm{S}})\, e_\alpha^{(0)}(\kappa|\, sa\lambda'), \tag{A19}$$

where $\vec{\tau}^{(s)}(\vec{\mathrm{S}})$ is a $d_s \times d_s$ unitary matrix representation of the sth irreducible representation of the point group of the crystal.

In obtaining Eq. (A19) we have taken note of the fact that certain of the crystallographic point groups (viz., C_4, S_4, C_{4h}, C_3, S_6, C_6, C_{3h}, C_{6h}, T, and T_h) have pairs of complex-conjugate one-dimensional irreducible representations which are degenerate by time-reversal symmetry. Complex irreducible representations are incompatible with Eq. (A19) and our assumption that the eigenvector $e_\alpha^{(0)}(\kappa|sa\lambda)$ can be assumed to be real. This inconsistency is removed by replacing each pair of complex-conjugate one-dimensional irreducible representations by a single real two-dimensional representation, constructed from the pair according to[27]

$$\vec{\tau}^{(ss^*)}(\vec{\mathrm{S}}) = \begin{pmatrix} \frac{1}{2}[\tau^{(s)}(\vec{\mathrm{S}}) + \tau^{(s^*)}(\vec{\mathrm{S}})] & (1/2i)[\tau^{(s)}(\vec{\mathrm{S}}) - \tau^{(s^*)}(\vec{\mathrm{S}})] \\ -(1/2i)[\tau^{(s)}(\vec{\mathrm{S}}) - \tau^{(s^*)}(\vec{\mathrm{S}})] & \frac{1}{2}[\tau^{(s)}(\vec{\mathrm{S}}) + \tau^{(s^*)}(\vec{\mathrm{S}})] \end{pmatrix}, \tag{A20}$$

where $\tau^{(s^*)}(\vec{\mathrm{S}}) = \tau^{(s)}(\vec{\mathrm{S}})^*$. All of the matrices $\{\vec{\tau}^{(s)}(\vec{\mathrm{S}})\}$ entering Eq. (A19) become real orthogonal matrices.

It follows from Eqs. (A16) and (A19) that the transformation law for $V(sa\lambda;\, s'a'\lambda';\, s''a''\lambda'')$ is

$$V(sa\lambda;\, s'a'\lambda';\, s''a''\lambda'') = \sum_{\lambda_1\lambda_2\lambda_3} \tau_{\lambda\lambda_1}^{(s)}(\vec{\mathrm{S}})\, \tau_{\lambda'\lambda_2}^{(s')}(\vec{\mathrm{S}})\, \tau_{\lambda''\lambda_3}^{(s'')}(\vec{\mathrm{S}}) \times V(sa\lambda_1;\, s'a'\lambda_2;\, s''a''\lambda_3)\,. \tag{A21}$$

If we use the fact that the first-order dipole-moment coefficients $\{M_{\alpha\mu}(l\kappa)\}$ transform under a space-group operation according to[28]

$$M_{\alpha\mu}(L K) = \sum_{\beta\nu} S_{\alpha\beta} S_{\mu\nu} M_{\beta\nu}(l\kappa), \tag{A22}$$

the arguments which led to Eq. (A21) yield as the transformation law for the Fourier-transformed dipole-moment coefficients $\{M_\alpha(j)\}$ the result that

$$M_\alpha(sa\lambda) = \sum_\beta \sum_{\lambda'} S_{\alpha\beta}\, \tau_{\lambda\lambda'}^{(s)}(\vec{\mathrm{S}}) M_\beta(sa\lambda'). \tag{A23}$$

It should also be pointed out that because $e_\alpha(\kappa|\vec{0}j)/M_\kappa^{1/2}$ is independent of the basis index κ when the branch index j refers to any of the three acoustic modes, the coefficient $M_\alpha(j)$ vanishes for an acoustic mode. This is a consequence of the definition of this coefficient, Eq. (2.10), and the fact that the first-order dipole-moment coefficients $\{M_{\alpha\mu}(l\kappa)\}$ obey the condition[29]

$$\sum_{l\kappa} M_{\alpha\mu}(l\kappa) = 0, \tag{A24}$$

which follows from the invariance of the crystal dipole moment against an infinitesimal rigid-body displacement of the crystal.

The results expressed by Eqs. (A21) and (A23) are used in Sec. V of the text to establish the selection rules governing the first-order ionic Raman effect.

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Microwave Absorption of Semiconducting Cadmium Fluoride at 77°K

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The microwave absorption of semiconducting $CdF_2:Gd^{3+}$ crystals at 77 °K was measured from 0.1 to 11 GHz, and at 17.5 and 37 GHz. σ_{mi} increases with frequency at an increasing rate in the 0.1–10-GHz region. At higher frequencies, σ_{mi} decreases with increasing frequency, indicating the presence of a conductivity peak near 12 GHz which may arise from intertrap tunneling of semiconducting electrons. Absorption from 40 GHz to 3×10^{12} Hz may originate from the hopping process.

Kingsley and Prenner[1] discovered in 1962 that CdF_2 with a trivalent dopant can be made semiconducting by baking in cadmium vapor. Since then many electrical, magnetic, and optical studies have been made on this semiconductor.[2-9] Eisenberger *et al.*[2] observed near-[5] and far-infrared[3] photoconductivity and a large polaron mass[2] in the microwave region. In this paper, the microwave absorption spectrum of semiconducting CdF_2 from 0.1 to 37 GHz is reported. These experimental data intend to bridge the gap from the dc electrical to the far-infrared data and are interpreted to explain the semiconducting mechanism, especially in the far-infrared and cyclotron-resonance regions.

The main features of the data are (i) the presence of a microwave absorption peak near 12 GHz, (ii) higher low-frequency background absorption, e.g., the absorption at 3 GHz is greater than absorption at 37 GHz, and (iii) indication of a smooth extrapolation of ac conductivity from the far infrared down to about 40 GHz. These features may be interpreted, respectively, as (a) tunneling of semiconducting electrons from one trap to the other (e.g., intertrap tunneling), (b) band conduction of polarons, and (c) electron hopping on cations around the trivalent dopant.

Two measuring techniques were employed: the transmission technique below 10 GHz and the resonance-cavity method for frequencies at 10.8, 17.5, and 37 GHz. In the transmission-line method, semiconducting $CdF_2:Gd^{3+}$ single crystals 2 mm in diameter and 0.2–1.5 mm in thickness were electroded on opposite flat faces by rubbing with In-Hg amalgam or hot indium solder. Samples were mounted directly on an OSM connector at one end of a 50-Ω coaxial line. The line had Teflon insulation with solid copper shield and was submerged in liquid nitrogen at the sample end. Hewlett-Packard model No. HP 8410A network analyzer, model No. HP 8411A harmonic frequency converter, and model No. HP 8741A or HP 8742A reflection test units were used to display the series impedance between 0.1 and 10 GHz on the Smith chart. The series impedance of the sample at each frequency was deduced by comparing two measurements, one with the sample at the end of the transmission line and the other with the end short-circuited. From the measured series impedance of the sample, the equivalent parallel resistance of the sample and hence the corresponding microwave conductivity $\sigma_{mi}(f)$ was calculated. The data up to 6 GHz, where $\sigma_{mi}(f)$ rises appreciably, have been checked by comparing the semiconducting sample with an identical, except unconverted, CdF_2 at the end of another "identical" transmission line. This method, however, cannot be used above 6 GHz