International Journal of Theoretical Physics, Vol. 31, No. 1, 1992

Raman Scattering in Impurity-Induced Anharmonic Crystals

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Received April 20, 1991

The theory of first-, second-, and third-order Raman scattering is investigated for isotopically disordered anharmonic crystals. The theory of time-dependent thermodynamic Zubarev Green's functions is adopted to obtain the Raman tensor, intensity of Raman lines, and differential cross sections of various orders of scatterings. It is observed that each class of scattering can be separated into diagonal and nondiagonal parts. The first-order and nondiagonal parts are absent in the case of chemically pure crystals. The diagonal parts are separated into anharmonic and interference terms. The interference terms arise due to the interactions of anharmonic phonons with the local phonons. The temperature and defect dependencies are discussed in detail along with the nature of continuous and line spectra. It is proposed that very high-power laser sources will reveal the third-order spectra, and that the resulting structure can be explained with the help of temperature-dependent one-, two-, and three-phonon density of states.

1. INTRODUCTION

A scattering medium can simultaneously absorb one photon and emit another of greater or smaller frequency compared to that of the absorbed one. This effect is known as the Raman effect (Raman, 1928). The energies of absorbed and emitted photons differ by an amount corresponding to the energy difference between two quantum levels of the scattering medium. The energies of photons employed in such experiments are of the order of 1–10 eV and are intermediate between the energies of neutrons used in scattering experiments from lattice vibrations ($\sim 10^{-2}$ eV) and the energies of X-rays used in diffraction studies ($\sim 10^{4}$ eV). In fact, Raman scattering by lattice

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vibrations in crystals is the inelastic scattering of photons caused by the fluctuations in the electronic polarizability of the crystals induced by the displacement of atoms from their equilibrium positions (Born and Huang, 1954; Loudon, 1964; Maradudin, 1966).

The measurements of Raman spectra have been a valuable tool in the investigation of vibrational and rotational energy levels of molecules and in the determination of lattice vibrational frequencies of crystalline solids. In crystals the incident light quantum is inelastically scattered and a change in energy is involved in creation or destruction of one or more phonons. First-order Raman (FOR) scattering due to the creation and annihilation of single optical phonon at the center of the Brillouin zone unambiguously identifies these phonons. In the FOR scattering the incident light photon is absorbed and the crystal makes a transition from the initial electronic and vibrational state $|\psi_e^i \psi_v^i\rangle$ to an intermediate state $|\psi_e' \psi_v'\rangle$. Subsequently the crystal makes the transition to the final state $|\psi_e^f \psi_v^f\rangle$, which differs from the initial state by one phonon, by emitting a secondary photon. Conservation of energy and momentum requires that only those optical modes can scatter light in the first-order processes which have nonzero frequencies for zero wave vector ($\mathbf{k}=0$). In other words, only those modes which transform as a second-rank tensor under point-group operations will be Raman-active (Loudon, 1964; Maradudin, 1966; Russell, 1966).

Second-order Raman (SOR) scattering occurs due to processes involving pairs of phonons of equal or equal and opposite wave vectors. The SOR effect provides information directly related to the two-phonon density of states (Loudon, 1964; Karo and Hardy, 1967; Benedek and Mulazzi, 1969). In the SOR effect two phonons participate in the scattering process. As a result of the interaction of light, both the phonons may be created (Stokes component) or one may be created and the other destroyed (Stokes and anti-Stokes components) or both may be destroyed (anti-Stokes component). The SOR effect gives rise to a line spectrum as well as to a continuous spectrum.

The symmetry of the crystals plays a vital role in the understanding of Raman scattering. In crystals of NaCl or CsCl structure the FOR scattering is completely ruled out and one has to rely upon infrared measurements to study the phonon spectrum. The information which can be obtained from the FOR and SOR scattering studies of crystals is similar to that from infrared measurements. However, in a crystal having inversion symmetry the two (Raman and infrared absorption) measurements are complementary, i.e., only even-parity phonons and phonon combinations are Raman-active, while the odd-parity phonons and their combinations are infrared-active. In the presence of impurities in crystals (particularly of NaCl or CsCl structure, in which FOR scattering is absent) the translational symmetry is removed and the forbidden FOR spectrum appears (Hoff *et al.*, 1975; Galeener and Sen, 1978; Chandrashekhar *et al.*, 1978; Haque *et al.*, 1977; Mokross *et al.*, 1977). These impurities can therefore be used as probes to study the phonon frequency spectrum in general. The appearance of resonance Raman scattering as a result of the presence of a finite concentration of *F*-centers and other color centers is an additional advantage of impurity effects (Dick, 1977; Hoff and Irwin, 1974; Renucci *et al.*, 1975; Yacoby and Yust, 1972; Negi and Ram, 1984; Hase, 1980; Esser, 1978; Trallero Giner and Costa, 1985).

The Raman scattering probabilities are low; a typical value for FOR scattering is $1:10^6$, while that for SOR scattering is $1:10^9$. This means that to observe the Raman spectrum, a highly intense monochromatic source of radiation is necessary. The advent of highly monochromatic laser sources has led to a renewed interest in the study of Raman scattering and in particular has increased the possibility of definitive measurements of SOR and higher-order Raman spectra (Hardy and Karo, 1969; Jaswal *et al.*, 1974; Agrawal *et al.*, 1975).

In recent years, a wealth of experimental information has been obtained on the Raman effect for a variety of crystals. These experiments have provided profound information on the optical mode frequencies and linewidths of pure and impure crystals (Wallis *et al.*, 1966; Cowley, 1965; Balkanski *et al.*, 1983; Hart *et al.*, 1970; Menendez and Cardona, 1984; Wanser and Wallis, 1981; Haro *et al.*, 1986). For these modes the line center and the linewidth of the scattered radiation are found to vary with temperature. Such a temperature dependence (just like the infrared absorption) cannot be explained on the basis of a harmonic approximation. The temperature-dependent phonon frequencies and linewidths can only be explained in terms of the anharmonic character of lattice vibrations. It is the crystal anharmonicity which can successfully explain the origin and nature of SOR and higher-order [third-order Raman (TOR)] scattering processes. We have found very little literature on SOR and TOR scattering in impurity-induced isotopically disordered crystals. In the present paper we investigate the theory of FOR, SOR, and TOR effects for impure anharmonic crystals on the basis of a many-body technique, which is briefly reviewed.

The organization of this paper consists of the formulation of the problem (Section 2), the multiphonon processes (Section 3), the first-order Raman effect (Section 4), the second-order Raman effect (Section 5), the third-order Raman effect (Section 6), and our conclusions (Section 7). The scattering intensity, differential cross sections, impurity concentration, and temperature dependence of Raman lines and linewidths are also obtained.

The effects of anharmonic interactions, the effects of interactions between anharmonic phonon fields and localized fields, are also investigated as a new feature of this work.

2. GENERAL THEORY

2.1. Raman Tensor

When the frequency of incident radiation (photons) is far from the frequencies of electronic transitions in the crystal, the intensity of Raman scattering per unit solid angle is given by (Born and Huang, 1954)

$$I(\omega_{\mathrm{R}}) = (\omega_0^4/2\pi c^3) \sum_{\alpha\beta,\gamma\lambda} n_\alpha n_\beta i_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}}) E_\gamma^- E_\lambda^+ \tag{1}$$

where ω_0 is the frequency of incident radiation, $\omega = \omega_0 + \omega_{\mathrm{R}}$ is the frequency of scattered light with the condition that ω_{R} stands for the Raman shift and $\omega_{\mathrm{R}} < 0$ corresponds to the Stokes spectrum (or line) while $\omega_{\mathrm{R}} > 0$ gives the anti-Stokes (Raman) spectrum (or line). n is the unit vector of the one linearly polarized component of the scattered light and is perpendicular to the direction of scattering, while E^+ and $E^- = (E^+)^*$ are the amplitudes of the positive- and negative-frequency components of the incident radiation, respectively. $i_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})$ is known as the Raman tensor and is given by

$$i_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}}) = (1/2\pi) \int_{-\infty}^{\infty} dt \exp(-i\omega_{\mathrm{R}} t) \, \langle P_{\beta\lambda}(t) P_{\alpha\gamma}(0) \rangle_T \tag{2}$$

where the subscript T stands for the time ordering and $P_{\beta\lambda}(t)$ is the electronic polarizability of the crystal. The electronic polarizability for N cells can be expanded in a Taylor series which is dependent on the normal coordinates $U(\begin{smallmatrix}\mathbf{k}\\ j\end{smallmatrix} | t)$ of the crystal, in the form (Born and Huang, 1954)

$$\begin{aligned} P_{\beta\lambda}(t) = {} & P_{\beta\lambda}^{(0)} + N^{1/2} \sum_{k_1 j_1} P_{\beta\lambda}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix} U\left(\begin{matrix}\mathbf{k}_1\\ j_1\end{matrix}\middle| t\right) \\ & + (1/2!) \sum_{k_1 j_1, k_2 j_2} P_{\beta\lambda}\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2\\ j_1 & j_2\end{pmatrix} U\left(\begin{matrix}\mathbf{k}_1\\ j_1\end{matrix}\middle| t\right) U\left(\begin{matrix}\mathbf{k}_2\\ j_2\end{matrix}\middle| t\right) \\ & + (1/3!) \sum_{k_1 j_1, k_2 j_2, k_3 j_3} P_{\beta\lambda}\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2 & \mathbf{k}_3\\ j_1 & j_2 & j_3\end{pmatrix} U\left(\begin{matrix}\mathbf{k}_1\\ j_1\end{matrix}\middle| t\right) U\left(\begin{matrix}\mathbf{k}_2\\ j_2\end{matrix}\middle| t\right) U\left(\begin{matrix}\mathbf{k}_3\\ j_3\end{matrix}\middle| t\right) \\ & + \cdots \end{aligned} \tag{3}$$

The first term in equation (3) contributes to Rayleigh scattering (elastic scattering), the second term to one-phonon Raman scattering (FORS), the next to SOR scattering, and so on. Since we are not interested in Rayleigh scattering, we shall neglect the first term in equation (3) and the remaining terms are

$$P_{\beta\lambda}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}=\sum_{k_1j_1,\gamma}P_{\beta\lambda,\gamma}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}, l_1\Big)(m_{k_1})^{-1/2}e_\gamma\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\exp(2\pi i\mathbf{k}_1\cdot\mathbf{R}_{l_1}) \tag{4a}$$

$$\begin{aligned}P_{\beta\lambda}\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2\\ j_1 & j_2\end{pmatrix}=\sum_{\substack{k_1j_1,k_2j_2\\ \gamma,\delta,l_1}}P_{\beta\lambda,\gamma\delta}\left(\begin{matrix}\mathbf{k}_1 & \mathbf{k}_2\\ j_1 & j_2\end{matrix}, l_1l_2\right)(m_{k_1}m_{k_2})^{-1/2}\\ \times e_\gamma\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}e_\delta\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}\exp[2\pi i(\mathbf{k}_1\cdot\mathbf{R}_{l_1}+\mathbf{k}_2\cdot\mathbf{R}_{l_2})]\end{aligned} \tag{4b}$$

and

$$\begin{aligned}P_{\beta\lambda}\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2 & \mathbf{k}_3\\ j_1 & j_2 & j_3\end{pmatrix}=\sum_{\substack{k_1j_1,k_2j_2,k_3j_3\\ \gamma,\delta,\sigma\\ l_1,l_2}}P_{\beta\lambda,\gamma\delta\sigma}\left(\begin{matrix}\mathbf{k}_1 & \mathbf{k}_2 & \mathbf{k}_3\\ j_1 & j_2 & j_3\end{matrix}, l_1l_2l_3\right)\\ \times(m_{k_1}m_{k_2}m_{k_3})^{-1/2}e_\gamma\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}e_\delta\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}e_\sigma\begin{pmatrix}\mathbf{k}_3\\ j_3\end{pmatrix}\\ \times\exp[2\pi i(\mathbf{k}_1\cdot\mathbf{R}_{l_1}+\mathbf{k}_2\cdot\mathbf{R}_{l_2}+\mathbf{k}_3\cdot\mathbf{R}_{l_3})]\end{aligned} \tag{4c}$$

with

$$P_{\beta\lambda,\gamma}\left(\begin{matrix}\mathbf{k}_1\\ j_1\end{matrix}, l_1\right)=\left[\partial P_{\beta\lambda}/\partial U_\gamma\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\right]_0 \tag{5a}$$

$$P_{\beta\lambda,\gamma\delta}\left(\begin{matrix}\mathbf{k}_1 & \mathbf{k}_2\\ j_1 & j_2\end{matrix}, l_1l_2\right)=\left[\partial^2P_{\beta\lambda}/\partial U_\gamma\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\partial U_\delta\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}\right]_0 \tag{5b}$$

$$P_{\beta\lambda,\gamma\delta\sigma}\left(\begin{matrix}\mathbf{k}_1 & \mathbf{k}_2 & \mathbf{k}_3\\ j_1 & j_2 & j_3\end{matrix}, l_1l_2l_3\right)=\left[\partial^3P_{\beta\lambda}/\partial U_\gamma\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\partial U_\delta\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}\partial U_\sigma\begin{pmatrix}\mathbf{k}_3\\ j_3\end{pmatrix}\right]_0 \tag{5c}$$

and so on, defined as coefficients of expansion.

Substitution of equation (3) in equation (2) followed by second quantized normal coordinate transformation yields

$$i_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})=i^{(1)}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})+i^{(2)}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})+i^{(3)}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}}) \tag{6}$$

where

$$i^{(1)}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}}) = (1/2\pi)\sum_{k_1 j_1}\sum_{k'_1 j'_1}\int_{-\infty}^{\infty} dt\,\exp(-i\omega_{\mathrm{R}}t)\,P^{(1)}_{\alpha\gamma,\beta\lambda}\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}'_1\\ j_1 & j'_1\end{pmatrix} \times \langle A_{k_1 j_1}(t)A_{k'_1 j'_1}(0)\rangle \tag{7a}$$

$$i^{(2)}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}}) = (1/2\pi)\sum_{k_1 j_1, k_2 j_2}\;\sum_{k'_1 j'_1, k'_2 j'_2}\int_{-\infty}^{\infty} dt\,\exp(-i\omega_{\mathrm{R}}t) \times P^{(2)}_{\alpha\gamma,\beta\lambda}\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2 & \mathbf{k}'_1 & \mathbf{k}'_2\\ j_1 & j_2 & j'_1 & j'_2\end{pmatrix}\langle A_{k_1 j_1}(t)A_{k_2 j_2}(t)A_{k'_1 j'_1}(0)A_{k'_2 j'_2}(0)\rangle \tag{7b}$$

and

$$i^{(3)}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}}) = (1/2\pi)\sum_{k_1 j_1, k_2 j_2, k_3 j_3}\;\sum_{k'_1 j'_1, k'_2 j'_2, k'_3 j'_3}\int_{-\infty}^{\infty} dt\,\exp(-i\omega_{\mathrm{R}}t) \times P^{(3)}_{\alpha\gamma,\beta\lambda}\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2 & \mathbf{k}_3 & \mathbf{k}'_1 & \mathbf{k}'_2 & \mathbf{k}'_3\\ j_1 & j_2 & j_3 & j'_1 & j'_2 & j'_3\end{pmatrix} \times \langle A_{k_1 j_1}(t)A_{k_2 j_2}(t)A_{k_3 j_3}(t)A_{k'_1 j'_1}(0)A_{k'_2 j'_2}(0)A_{k'_3 j'_3}(0)\rangle \tag{7c}$$

In obtaining equations (6) and (7) we have ignored the contributions from equal time correlation functions. The various coefficients appearing in equation (7) are given by

$$P^{(1)}_{\alpha\gamma,\beta\lambda}\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}'_1\\ j_1 & j'_1\end{pmatrix} = (\hbar/2M)\Delta(\mathbf{k}_1+\mathbf{k}'_1)e\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}e\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}P_{\beta\lambda,\gamma\delta}\left(\begin{matrix}\mathbf{k}_1\\ j_1\end{matrix}, l_1\,\middle|\,\begin{matrix}\mathbf{k}'_1\\ j'_1\end{matrix}, l'_1\right) \times\left[\omega\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\omega\begin{pmatrix}\mathbf{k}'_1\\ j'_1\end{pmatrix}\right]^{-1/2}\exp[2\pi i(\mathbf{k}_1+\mathbf{k}'_1)\cdot\mathbf{R}_{l_1}] \tag{8a}$$

$$P^{(2)}_{\alpha\gamma,\beta\lambda}\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2 & \mathbf{k}'_1 & \mathbf{k}'_2\\ j_1 & j_2 & j'_1 & j'_2\end{pmatrix} = (\hbar/4MN)^2\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}'_1+\mathbf{k}'_2)e\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}e\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}e\begin{pmatrix}\mathbf{k}'_1\\ j'_1\end{pmatrix}e\begin{pmatrix}\mathbf{k}'_2\\ j'_2\end{pmatrix} \times P_{\beta\lambda,\gamma\delta}\left(\begin{matrix}\mathbf{k}_1 & \mathbf{k}_2\\ j_1 & j_2\end{matrix}, l_1 l_2\,\middle|\,\begin{matrix}\mathbf{k}'_1 & \mathbf{k}'_2\\ j'_1 & j'_2\end{matrix}, l'_1 l'_2\right) \times\left[\omega\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\omega\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}\omega\begin{pmatrix}\mathbf{k}'_1\\ j'_1\end{pmatrix}\omega\begin{pmatrix}\mathbf{k}'_2\\ j'_2\end{pmatrix}\right]^{-1/2} \times\exp\{2\pi i[(\mathbf{k}_1+\mathbf{k}'_1)\cdot\mathbf{R}_{l_1}+(\mathbf{k}_2+\mathbf{k}'_2)\cdot\mathbf{R}_{l_2}]\} \tag{8b}$$

and

$$P^{(3)}_{\alpha\gamma,\beta\lambda}\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2 & \mathbf{k}_3 & \mathbf{k}'_1 & \mathbf{k}'_2 & \mathbf{k}'_3\\ j_1 & j_2 & j_3 & j'_1 & j'_2 & j'_3\end{pmatrix}$$

$$=(\hbar/2MN)^3(1/6)^2\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}'_1+\mathbf{k}'_2+\mathbf{k}'_3)e\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}e\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}e\begin{pmatrix}\mathbf{k}_3\\ j_3\end{pmatrix}$$

$$\times e\begin{pmatrix}\mathbf{k}'_1\\ j'_1\end{pmatrix}e\begin{pmatrix}\mathbf{k}'_2\\ j'_2\end{pmatrix}e\begin{pmatrix}\mathbf{k}'_3\\ j'_3\end{pmatrix}P_{\beta\lambda,\gamma\delta\sigma}\left(\begin{matrix}\mathbf{k}_1 & \mathbf{k}_2 & \mathbf{k}_3\\ j_1 & j_2 & j_3\end{matrix}, l_1l_2l_3\,\middle|\,\begin{matrix}\mathbf{k}'_1 & \mathbf{k}'_2 & \mathbf{k}'_3\\ j'_1 & j'_2 & j'_3\end{matrix}, l'_1l'_2l'_3\right)$$

$$\times\left[\omega\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\omega\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}\omega\begin{pmatrix}\mathbf{k}_3\\ j_3\end{pmatrix}\omega\begin{pmatrix}\mathbf{k}'_1\\ j'_1\end{pmatrix}\omega\begin{pmatrix}\mathbf{k}'_2\\ j'_2\end{pmatrix}\omega\begin{pmatrix}\mathbf{k}'_3\\ j'_3\end{pmatrix}\right]^{-1/2}$$

$$\times\exp\{2\pi i[(\mathbf{k}_1+\mathbf{k}'_1)\cdot\mathbf{R}_{l_1}+(\mathbf{k}_2+\mathbf{k}'_2)\cdot\mathbf{R}_{l_2}+(\mathbf{k}_3+\mathbf{k}'_3)\cdot\mathbf{R}_{l_3}]\}\tag{8c}$$

where

$$P_{\beta\lambda,\gamma\ldots}\left(\begin{matrix}\mathbf{k}_1 & \mathbf{k}_2\\ j_1 & j_2\end{matrix}\ldots, l_1l_2\ldots\,\middle|\,\begin{matrix}\mathbf{k}'_1 & \mathbf{k}'_2\\ j'_1 & j'_2\end{matrix}\ldots, l'_1l'_2\ldots\right)$$

$$=P_{\beta\lambda,\gamma\ldots}\left(\begin{matrix}\mathbf{k}_1 & \mathbf{k}_2\\ j_1 & j_2\end{matrix}\ldots, l_1l_2\ldots\right)P_{\beta\lambda,\gamma\ldots}\left(\begin{matrix}\mathbf{k}'_1 & \mathbf{k}'_2\\ j'_1 & j'_2\end{matrix}\ldots, l'_1l'_2\ldots\right)$$

and

$$\Delta(\mathbf{k})=\begin{cases}1 & \text{if}\quad \mathbf{k}=0,\quad\text{or reciprocal lattice vector}\\ 0 & \text{otherwise}\end{cases}$$

The correlation functions

$$\langle A_{k_1j_1}(t)\ldots A_{k'_1j'_1}(0)\ldots\rangle$$

appearing in equations (7) contain the entire physics of Raman scattering and the evaluation of these correlation functions will be carried out in the following sections. The problem of one-, two-, and three-phonon bound states will also be investigated from these correlation functions.

2.2. Differential Cross Section for Raman Scattering

The differential scattering cross section per unit solid angle per unit frequency interval for Raman scattering is given by (Cowley, 1964; Dick, 1985)

$$(d^2\sigma/d\Omega\,d\omega_{\mathrm{R}})=(\omega/c)^4\sum_{\alpha\beta\gamma\lambda}n_\alpha n_\beta i_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})m_\gamma m_\lambda\tag{9}$$

where m are the unit polarization vectors of the radiation. Evidently, the differential cross section depends on the Raman intensity tensor $i_{\alpha\gamma,\beta\lambda}(\omega_R)$, which will describe the one-, two-, and three-phonon differential cross sections for Raman scattering in the following sections.

3. THE MULTIPHONON PROCESSES

To investigate the multiphonon processes in order to explain the various orders of Raman scattering, we start with the Hamiltonian of an impurity-induced anharmonic crystal. The Hamiltonian in such a case can be expressed as the sum of an unperturbed (harmonic) Hamiltonian H_0, an anharmonic Hamiltonian (Pathak, 1965; Semwal and Sharma, 1974; Indu, 1990) H_A, and a defect Hamiltonian (Indu, 1990; Sharma and Bahadur, 1975; Sahu and Sharma, 1983) H_D and is given by

$$H = H_0 + H_A + H_D \tag{10}$$

where

$$H_0 = (\hbar/4) \sum_{kj} \omega\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}(A^*_{kj}A_{kj} + B^*_{kj}B_{kj}) \tag{11}$$

$$H_A = \hbar \sum_{s\geq 3} \sum_{k_1j_1,k_2j_2,\ldots,k_sj_s} V_s\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2 & \ldots & \mathbf{k}_s\\ j_1 & j_2 & & j_s\end{pmatrix} A_{k_1j_1}A_{k_2j_2}\ldots A_{k_sj_s} \tag{12}$$

and

$$H_D = -\hbar \sum_{k_1j_1,k_2j_2}\left[C\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2\\ j_1 & j_2\end{pmatrix}B_{k_1j_1}B_{k_2j_2} - D\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2\\ j_1 & j_2\end{pmatrix}A_{k_1j_1}A_{k_2j_2}\right] \tag{13}$$

Here

$$V_s\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2 & \ldots & \mathbf{k}_s\\ j_1 & j_2 & & j_s\end{pmatrix}$$

denotes the anharmonic coupling coefficients and

$$C\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2\\ j_1 & j_2\end{pmatrix} \quad \text{and} \quad D\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2\\ j_1 & j_2\end{pmatrix}$$

describe the mass and force constant change parameters, respectively (Pathak, 1965; Semwal and Sharma, 1974; Indu, 1990; Sharma and Bahadur, 1975; Sahu and Sharma, 1983).

The correlation functions appearing in equation (7) are the direct consequence of the double-time thermodynamic Green's functions (GF)

(Zubarev, 1960). Hence, it is essential to evaluate the Green's functions for our purpose. To investigate the first-, second-, and third-order Raman scattering, let us consider the evaluation of one-, two-, and three-phonon GFs,

$$
\begin{aligned}
G_1(t, t') &= G_{kjk'j'}(t-t') \\
&= \langle\langle A_{kj}(t); A_{k'j'}(t') \rangle\rangle && (14) \\
G_2(t, t') &= G_{k_1 j_1 k_2 j_2 k_1' j_1' k_2' j_2'}(t-t') \\
&= \langle\langle A_{k_1 j_1}(t) A_{k_2 j_2}(t); A_{k_1' j_1'}(t') A_{k_2' j_2'}(t') \rangle\rangle && (15) \\
G_3(t, t') &= G_{k_1 j_1 k_2 j_2 k_3 j_3 k_1' j_1' k_2' j_2' k_3' j_3'}(t-t') \\
&= \langle\langle A_{k_1 j_1}(t) A_{k_2 j_2}(t) A_{k_3 j_3}(t); A_{k_1' j_1'}(t') A_{k_2' j_2'}(t') A_{k_3' j_3'}(t') \rangle\rangle && (16)
\end{aligned}
$$

respectively, with the help of the Hamiltonian (10), using the equation of motion method of quantum dynamics (Semwal and Sharma, 1974; Indu, 1990; Sharma and Bahadur, 1975; Sahu and Sharma, 1983; Zubarev, 1960). The one-phonon Green's function can be evaluated in the form (Indu, 1990)

$$
G_{kjk'j'}(\omega + i\varepsilon) = \pi^{-1} \omega\begin{pmatrix} \mathbf{k} \\ j \end{pmatrix} \eta_{kjk'j'} \left[\omega^2 - \tilde{\tilde{\omega}}^2 \begin{pmatrix} \mathbf{k} \\ j \end{pmatrix} + 2i\omega \begin{pmatrix} \mathbf{k} \\ j \end{pmatrix} \Gamma_{kj}(\omega) \right]^{-1} \tag{17}
$$

where ε is a small value and the perturbed mode frequency $\tilde{\tilde{\omega}}\binom{\mathbf{k}}{j}$ can be expressed in terms of renormalized mode frequency $\tilde{\omega}\binom{\mathbf{k}}{j}$ as

$$
\tilde{\tilde{\omega}}^2 \begin{pmatrix} \mathbf{k} \\ j \end{pmatrix} = \tilde{\omega}^2 \begin{pmatrix} \mathbf{k} \\ j \end{pmatrix} + 2\omega \begin{pmatrix} \mathbf{k} \\ j \end{pmatrix} \Delta_{kj}(\omega) \tag{18}
$$

and

$$
\eta_{kjk'j'} = \delta_{kk'} \delta_{jj'} + 4C \begin{pmatrix} -\mathbf{k} & \mathbf{k}' \\ j & j' \end{pmatrix} \Big/ \omega \begin{pmatrix} \mathbf{k} \\ j \end{pmatrix} \tag{19}
$$

$\Delta_{kj}(\omega)$ is the phonon frequency shift, which describes the real part of the phonon self-energy (Indu, 1990) $P\left(\begin{smallmatrix} \mathbf{k} & \mathbf{k}' \\ j & j' \end{smallmatrix}, \omega + i\varepsilon\right)$ and $\Gamma_{kj}(\omega)$ is the phonon linewidth at the half-maximum and is derivable from the imaginary part of the phonon self-energy.

The evaluation of two- and three-phonon Green's functions using the Hamiltonian (10) is quite complicated, but the evaluation of these GFs can be made easily with the help of the equivalent renormalized Hamiltonian

$$
H_{\text{ren}}^{(0)} = (\hbar/4) \sum_{kj} \left\{ \left[\tilde{\omega}^2 \begin{pmatrix} \mathbf{k} \\ j \end{pmatrix} \Big/ \omega \begin{pmatrix} \mathbf{k} \\ j \end{pmatrix} \right] A_{kj}^* A_{kj} + B_{kj}^* B_{kj} \right\} \tag{20}
$$

Writing the equations of motion for $G_2(t, t')$ and $G_3(t, t')$ given in equations (15) and (16) with the help of equation (20), performing the Fourier transforms, and solving these equations for $G_2(\omega)$ and $G_3(\omega)$, we obtain (Semwal and Sharma, 1974; Indu, 1990; Bahuguna *et al.*, 1991)

$$G_2(\omega) = (\delta^{(1)}/2\pi)\eta_1 \sum_{\mu=\pm 1} \left[n\binom{\mathbf{k}_2}{j_2} + \mu n\binom{\mathbf{k}_1}{j_1} \right] \left[\tilde{\omega}\binom{\mathbf{k}_1}{j_1} + \mu\tilde{\omega}\binom{\mathbf{k}_2}{j_2} \right] \times \left[\omega^2 - \left\{ \tilde{\omega}\binom{\mathbf{k}_1}{j_1} + \mu\tilde{\omega}\binom{\mathbf{k}_2}{j_2} \right\}^2 \right]^{-1} \tag{21}$$

and

$$\begin{aligned} G_3(\omega) = (\delta^{(2)}/2\pi)\eta_2 \sum_{\mu=\pm 1} & \left[1 + \mu n\binom{\mathbf{k}_1}{j_1} n\binom{\mathbf{k}_2}{j_2} \right. \\ & \left. + n\binom{\mathbf{k}_2}{j_2} n\binom{\mathbf{k}_3}{j_3} + \mu n\binom{\mathbf{k}_3}{j_3} n\binom{\mathbf{k}_1}{j_1} \right] \\ & \times \left[\tilde{\omega}\binom{\mathbf{k}_1}{j_1} + \mu\tilde{\omega}\binom{\mathbf{k}_2}{j_2} + \mu\tilde{\omega}\binom{\mathbf{k}_3}{j_3} \right] \\ & \times \left[\omega^2 - \left\{ \tilde{\omega}\binom{\mathbf{k}_1}{j_1} + \mu\tilde{\omega}\binom{\mathbf{k}_2}{j_2} + \mu\tilde{\omega}\binom{\mathbf{k}_3}{j_3} \right\}^2 \right]^{-1} \\ & + \left\{ \tilde{\omega}\binom{\mathbf{k}_1}{j_1} \leftrightarrow \tilde{\omega}\binom{\mathbf{k}_2}{j_2} \right\} \\ & + \left\{ \tilde{\omega}\binom{\mathbf{k}_1}{j_1} \leftrightarrow \tilde{\omega}\binom{\mathbf{k}_3}{j_3} \right\} \end{aligned} \tag{22}$$

with

$$\delta^{(1)} = \delta_{k_1 k_1'}\delta_{j_1 j_1'}\delta_{k_2 k_2'}\delta_{j_2 j_2'} + \delta_{k_1 k_1'}\delta_{j_1 j_2'}\delta_{k_2 k_1'}\delta_{j_2 j_1'} \tag{23a}$$

$$\delta^{(2)} = \delta_{123} + \delta_{231} + \delta_{321} \tag{23b}$$

$$\delta_{123} = \delta_{k_1 k_1'}\delta_{j_1 j_1'}(\delta_{k_2 k_2'}\delta_{j_2 j_2'}\delta_{k_3 k_3'}\delta_{j_3 j_3'} + \delta_{k_2 k_3'}\delta_{j_2 j_3'}\delta_{k_3 k_2'}\delta_{j_3 j_2'}) \tag{23c}$$

$$\eta_{i-1} = \omega\binom{\mathbf{k}_1}{j_1}\omega\binom{\mathbf{k}_2}{j_2}\ldots\omega\binom{\mathbf{k}_i}{j_i} \Big/ \tilde{\omega}\binom{\mathbf{k}_1}{j_1}\tilde{\omega}\binom{\mathbf{k}_2}{j_2}\ldots\tilde{\omega}\binom{\mathbf{k}_i}{j_i} \tag{23d}$$

In equation (22),

$$\left\{\tilde{\omega}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix} \leftrightarrow \tilde{\omega}\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}\right\} \quad \text{and} \quad \left\{\tilde{\omega}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix} \leftrightarrow \tilde{\omega}\begin{pmatrix}\mathbf{k}_3\\ j_3\end{pmatrix}\right\}$$

represent two further terms which are obtained by interchanging

$$\tilde{\omega}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix} \quad \text{and} \quad \tilde{\omega}\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}, \quad \text{and} \quad \tilde{\omega}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix} \quad \text{and} \quad \tilde{\omega}\begin{pmatrix}\mathbf{k}_3\\ j_3\end{pmatrix}$$

in the preceding term.

The response function in the lowest-order approximation can be evaluated in the form

$$\begin{aligned}
&P\begin{pmatrix}\mathbf{k} & \mathbf{k}'\\ j & j'\end{pmatrix}, \omega\Big) \\
&= 8\pi \sum_{kj,k'j'} R\begin{pmatrix}\mathbf{k}_1 & -\mathbf{k}\\ j_1 & j\end{pmatrix} R^*\begin{pmatrix}\mathbf{k}'_1 & -\mathbf{k}\\ j'_1 & j\end{pmatrix} G_1(\omega) \\
&\quad + 18\pi \sum_{k_1 j_1, k_2 j_2} \sum_{k'_1 j'_1, k'_2 j'_2} \\
&\quad \times V_3\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2 & -\mathbf{k}\\ j_1 & j_2 & j\end{pmatrix} V_3\begin{pmatrix}\mathbf{k}'_1 & \mathbf{k}'_2 & -\mathbf{k}'\\ j'_1 & j'_2 & j'\end{pmatrix} G_2(\omega) \\
&\quad + 32\pi \sum_{k_1 j_1, k_2 j_2, k_3 j_3} \sum_{k'_1 j'_1 k'_2 j'_2 k'_3 j'_3} \\
&\quad \times V_4\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2 & \mathbf{k}_3 & -\mathbf{k}\\ j_1 & j_2 & j_3 & j\end{pmatrix} V_4\begin{pmatrix}\mathbf{k}'_1 & \mathbf{k}'_2 & \mathbf{k}'_3 & -\mathbf{k}'\\ j'_1 & j'_2 & j'_3 & j'\end{pmatrix} G_3(\omega)
\end{aligned} \tag{24}$$

where

$$\begin{aligned}
R\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2\\ j_1 & j_2\end{pmatrix} &= \left[\omega\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}\Big/\omega\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\right] C\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2\\ j_1 & j_2\end{pmatrix} + D\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2\\ j_1 & j_2\end{pmatrix} \\
&\quad + 4\sum_{k'_2 j'_2} C\begin{pmatrix}-\mathbf{k}_1 & \mathbf{k}'_2\\ j_1 & j'_2\end{pmatrix} D\begin{pmatrix}-\mathbf{k}'_2 & \mathbf{k}_2\\ j'_2 & j_2\end{pmatrix}\Big/\omega\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}
\end{aligned} \tag{25}$$

An explicit expression for $P\left(\begin{smallmatrix}\mathbf{k} & \mathbf{k}'\\ j & j'\end{smallmatrix}, \omega\right)$ can be obtained in the form

$$P\left(\begin{matrix}\mathbf{k} & \mathbf{k}'\\ j & j'\end{matrix}, \omega + i\varepsilon\right) = \Delta_{kj}(\omega) - i\Gamma_{kj}(\omega) \tag{26}$$

where

$$\Delta_{kj}(\omega)=\Delta_{kj}^{D}(\omega)+\Delta_{kj}^{A}(\omega)+\Delta_{kj}^{AD}(\omega) \tag{27}$$

and

$$\Gamma_{kj}(\omega)=\Gamma_{kj}^{D}(\omega)+\Gamma_{kj}^{A}(\omega)+\Gamma_{kj}^{AD}(\omega) \tag{28}$$

with

$$\Delta_{kj}^{D}(\omega)=8P\sum_{k_1j_1}R\begin{pmatrix}\mathbf{k}_1 & -\mathbf{k}_1\\ j_1 & j_1\end{pmatrix}R\begin{pmatrix}-\mathbf{k}_1 & -\mathbf{k}\\ j_1 & j\end{pmatrix}\omega\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\left[\omega^2-\tilde{\omega}^2\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\right]^{-1} \tag{29a}$$

$$\Delta_{kj}^{A}(\omega)=\Delta_{kj}^{(3)}(\omega)+\Delta_{kj}^{(4)}(\omega) \tag{29b}$$

$$\begin{aligned}\Delta_{kj}^{(3)}(\omega)=18P&\sum_{k_1j_1,k_2j_2}\ \sum_{\mu=\pm1}V_3\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2 & -\mathbf{k}\\ j_1 & j_2 & j\end{pmatrix}V_3\begin{pmatrix}-\mathbf{k}_1 & -\mathbf{k}_2 & -\mathbf{k}\\ j_1 & j_2 & j\end{pmatrix}\eta_1\\ &\times\left[n\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}+\mu n\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\right]\left[\tilde{\omega}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}+\mu\tilde{\omega}\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}\right]\\ &\times\left[\omega^2-\left\{\tilde{\omega}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}+\mu\tilde{\omega}\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}\right\}^2\right]^{-1}\end{aligned} \tag{29c}$$

$$\begin{aligned}\Delta_{kj}^{(4)}(\omega)=48P&\sum_{k_1j_1,k_2j_2,k_3j_3}\ \sum_{\mu=\pm1}\left\{V_4\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2 & \mathbf{k}_3 & -\mathbf{k}\\ j_1 & j_2 & j_3 & j\end{pmatrix}\right.\\ &\times V_4\begin{pmatrix}-\mathbf{k}_1 & -\mathbf{k}_2 & -\mathbf{k}_3 & -\mathbf{k}\\ j_1 & j_2 & j_3 & j\end{pmatrix}\\ &\times\eta_2\left(\left[1+\mu n\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}n\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}+n\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}n\begin{pmatrix}\mathbf{k}_3\\ j_3\end{pmatrix}+\mu n\begin{pmatrix}\mathbf{k}_3\\ j_3\end{pmatrix}n\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\right]\right.\\ &\times\left[\tilde{\omega}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}+\mu\tilde{\omega}\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}+\mu\tilde{\omega}\begin{pmatrix}\mathbf{k}_3\\ j_3\end{pmatrix}\right]\\ &\times\left\{\omega^2-\left[\tilde{\omega}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}+\mu\tilde{\omega}\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}+\mu\tilde{\omega}\begin{pmatrix}\mathbf{k}_3\\ j_3\end{pmatrix}\right]^2\right\}^{-1}\\ &\left.\left.+\left\{\tilde{\omega}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\leftrightarrow\tilde{\omega}\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}\right\}+\left\{\tilde{\omega}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\leftrightarrow\tilde{\omega}\begin{pmatrix}\mathbf{k}_3\\ j_3\end{pmatrix}\right\}\right)\right\}\end{aligned} \tag{29d}$$

$$\Delta_{kj}^{AD}(\omega)=16P\sum_{k_1j_1}C\begin{pmatrix}-\mathbf{k} & \mathbf{k}_1\\ j & j_1\end{pmatrix}C\begin{pmatrix}-\mathbf{k} & -\mathbf{k}_1\\ j & j_1\end{pmatrix}\Delta_{k_1j_1}^{A}(\omega)\Big/\omega^2\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix} \tag{29e}$$

$$
\begin{aligned}
\Gamma^{D}_{kj}(\omega) = 8\pi\,\varepsilon(\omega) \sum_{k_1 j_1} & R\begin{pmatrix} -\mathbf{k} & \mathbf{k}_1 \\ j & j_1 \end{pmatrix} R\begin{pmatrix} -\mathbf{k} & -\mathbf{k}_1 \\ j & j_1 \end{pmatrix} \omega\begin{pmatrix} \mathbf{k}_1 \\ j_1 \end{pmatrix} \\
& \times \delta\left[\omega^2 - \tilde{\omega}^2\begin{pmatrix} \mathbf{k}_1 \\ j_1 \end{pmatrix} \right]
\end{aligned} \tag{30a}
$$

$$
\Gamma^{A}_{kj}(\omega) = \Gamma^{(3)}_{kj}(\omega) + \Gamma^{(4)}_{kj}(\omega) \tag{30b}
$$

$$
\begin{aligned}
\Gamma^{(3)}_{kj}(\omega) = 18\pi\,\varepsilon(\omega) \sum_{k_1 j_1 k_2 j_2} & V_3\begin{pmatrix} \mathbf{k}_1 & \mathbf{k}_2 & -\mathbf{k} \\ j_1 & j_2 & j \end{pmatrix} V_3\begin{pmatrix} -\mathbf{k}_1 & -\mathbf{k}_2 & -\mathbf{k} \\ j_1 & j_2 & j \end{pmatrix} \eta_1 \\
& \times \left[n\begin{pmatrix} \mathbf{k}_2 \\ j_2 \end{pmatrix} + n\begin{pmatrix} \mathbf{k}_1 \\ j_1 \end{pmatrix} \right] \left[\tilde{\omega}\begin{pmatrix} \mathbf{k}_1 \\ j_1 \end{pmatrix} + \tilde{\omega}\begin{pmatrix} \mathbf{k}_2 \\ j_2 \end{pmatrix} \right] \\
& \times \delta\left[\omega^2 - \left\{ \tilde{\omega}\begin{pmatrix} \mathbf{k}_1 \\ j_1 \end{pmatrix} + \tilde{\omega}\begin{pmatrix} \mathbf{k}_2 \\ j_2 \end{pmatrix} \right\}^2 \right] \\
& \times \left[n\begin{pmatrix} \mathbf{k}_2 \\ j_2 \end{pmatrix} + n\begin{pmatrix} \mathbf{k}_1 \\ j_1 \end{pmatrix} \right] \left[\tilde{\omega}\begin{pmatrix} \mathbf{k}_1 \\ j_1 \end{pmatrix} - \tilde{\omega}\begin{pmatrix} \mathbf{k}_2 \\ j_2 \end{pmatrix} \right] \\
& \times \delta\left[\omega^2 - \left\{ \tilde{\omega}\begin{pmatrix} \mathbf{k}_1 \\ j_1 \end{pmatrix} - \tilde{\omega}\begin{pmatrix} \mathbf{k}_2 \\ j_2 \end{pmatrix} \right\}^2 \right]
\end{aligned} \tag{30c}
$$

$$
\begin{aligned}
\Gamma^{(4)}_{kj}(\omega) = 48\pi\,\varepsilon(\omega) \sum_{k_1 j_1, k_2 j_2, k_3 j_3} & V_4\begin{pmatrix} \mathbf{k}_1 & \mathbf{k}_2 & \mathbf{k}_3 & -\mathbf{k} \\ j_1 & j_2 & j_3 & j \end{pmatrix} \\
& \times V_4\begin{pmatrix} -\mathbf{k}_1 & -\mathbf{k}_2 & -\mathbf{k}_3 & -\mathbf{k} \\ j_1 & j_2 & j_3 & j \end{pmatrix} \\
& \times \eta_2 \Bigg(\left[1 + n\begin{pmatrix} \mathbf{k}_1 \\ j_1 \end{pmatrix} n\begin{pmatrix} \mathbf{k}_2 \\ j_2 \end{pmatrix} + n\begin{pmatrix} \mathbf{k}_2 \\ j_2 \end{pmatrix} n\begin{pmatrix} \mathbf{k}_3 \\ j_3 \end{pmatrix} + n\begin{pmatrix} \mathbf{k}_3 \\ j_3 \end{pmatrix} n\begin{pmatrix} \mathbf{k}_1 \\ j_1 \end{pmatrix} \right] \\
& \times \left[\tilde{\omega}\begin{pmatrix} \mathbf{k}_1 \\ j_1 \end{pmatrix} + \tilde{\omega}\begin{pmatrix} \mathbf{k}_2 \\ j_2 \end{pmatrix} + \tilde{\omega}\begin{pmatrix} \mathbf{k}_3 \\ j_3 \end{pmatrix} \right] \\
& \times \delta\left\{ \omega^2 - \left[\tilde{\omega}\begin{pmatrix} \mathbf{k}_1 \\ j_1 \end{pmatrix} + \tilde{\omega}\begin{pmatrix} \mathbf{k}_2 \\ j_2 \end{pmatrix} + \tilde{\omega}\begin{pmatrix} \mathbf{k}_3 \\ j_3 \end{pmatrix} \right]^2 \right\} \\
& + \left[1 - n\begin{pmatrix} \mathbf{k}_1 \\ j_1 \end{pmatrix} n\begin{pmatrix} \mathbf{k}_2 \\ j_2 \end{pmatrix} + n\begin{pmatrix} \mathbf{k}_2 \\ j_2 \end{pmatrix} n\begin{pmatrix} \mathbf{k}_3 \\ j_3 \end{pmatrix} - n\begin{pmatrix} \mathbf{k}_3 \\ j_3 \end{pmatrix} n\begin{pmatrix} \mathbf{k}_1 \\ j_1 \end{pmatrix} \right] \\
& \times \left[\tilde{\omega}\begin{pmatrix} \mathbf{k}_1 \\ j_1 \end{pmatrix} - \tilde{\omega}\begin{pmatrix} \mathbf{k}_2 \\ j_2 \end{pmatrix} - \tilde{\omega}\begin{pmatrix} \mathbf{k}_3 \\ j_3 \end{pmatrix} \right]
\end{aligned}
$$

$$\times\,\delta\left\{\omega^2-\left[\tilde{\omega}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}-\tilde{\omega}\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}-\tilde{\omega}\begin{pmatrix}\mathbf{k}_3\\ j_3\end{pmatrix}\right]^2\right\}$$

$$+\left\{\tilde{\omega}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\leftrightarrow\tilde{\omega}\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}\right\}+\left\{\tilde{\omega}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\leftrightarrow\tilde{\omega}\begin{pmatrix}\mathbf{k}_3\\ j_3\end{pmatrix}\right\}\Bigg) \tag{30d}$$

$$\Gamma_{kj}^{AD}(\omega)=16\sum_{k_1j_1}C\begin{pmatrix}-\mathbf{k} & \mathbf{k}_1\\ j & j_1\end{pmatrix}C\begin{pmatrix}-\mathbf{k} & -\mathbf{k}_1\\ j & j_1\end{pmatrix}$$

$$\times\,\Gamma_{k_1j_1}^{A}(\omega)\Big/\omega^2\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix} \tag{30e}$$

In equation (29), P denotes the principal value of the quantity and $\varepsilon(\omega)=1$ for $\omega>0$ and $=-1$ for $\omega<0$.

The various correlation functions appearing in $i_{\alpha\gamma,\beta\lambda}(\omega_\mathrm{R})$ can be evaluated from (Zubarev, 1960; Plakida and Ivanov, 1980; Plakida and Siklós, 1978; Morita and Tanaka, 1965; Lee and Hui, 1967)

$$F_{kjk'j'}^{(i)}(t,t')=\int_{-\infty}^{\infty}J_{kjk'j'}^{(i)}(\omega)\exp[-i\omega(t-t')]\,d\omega \tag{31}$$

where

$$F_{kjk'j'}^{(i)}(t,t')=\langle A_{k_1j_1}A_{k_2j_2}\ldots A_{k_ij_i}A_{k'_1j'_1}A_{k'_2j'_2}\ldots A_{k'_ij'_i}\rangle \tag{32}$$

and $J_{kjk'j'}^{(i)}(\omega)$ are known as spectral density functions, given by

$$J_{kjk'j'}^{(i)}(\omega)=-\{2/[\exp(\beta\hbar\omega)-1]\}\,\mathrm{Im}\,G_i(\omega+i\varepsilon) \tag{33}$$

4. FIRST-ORDER RAMAN SCATTERING

The use of equations (31)–(33) in equation (7a) yields

$$i_{\alpha\gamma,\beta\lambda}^{(1)}(\omega_\mathrm{R})=(2/\pi)\sum_{k_1j_1,k'_1j'_1}\int_{-\infty}^{\infty}dt\,\exp(-i\omega t)$$

$$\times\,P_{\alpha\gamma,\beta\lambda}^{(1)}\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}'_1\\ j_1 & j'_1\end{pmatrix}\int_{-\infty}^{\infty}d\omega\;\eta_{kjk'j'}\,\omega^2\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\exp(i\omega t)\,\Gamma_{kj}(\omega)$$

$$\times\left\{\left[\omega^2-\tilde{\tilde{\omega}}^2\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\right]^2+4\omega^2\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\Gamma_{kj}^2(\omega)\right\}^{-1} \tag{34}$$

The integrand

$$(2/\pi)\omega^2\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\Gamma_{kj}(\omega)\left\{\left[\omega^2-\tilde{\tilde{\omega}}^2\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\right]^2+4\omega^2\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\Gamma^2_{kj}(\omega)\right\}^{-1}$$

describes the phonon frequency spectrum in the whole range of frequency. If the linewidth is vanishingly small, the integrand tends to a delta shape distribution $\omega\binom{\mathbf{k}}{j}\ \delta[\omega^2-\tilde{\tilde{\omega}}^2\binom{\mathbf{k}}{j}]$ in the Breit–Wigner expansion. In the limiting cases where the linewidth is small enough but finite, $\Gamma_{kj}(\omega)\ll\omega\binom{\mathbf{k}}{j}$, the integrand has a steep maximum at $\omega=\tilde{\tilde{\omega}}\binom{\mathbf{k}}{j}$, provided that $\partial\Gamma_{kj}(\omega)/\partial\omega\ll 1$ and $\partial\Delta_{kj}(\omega)/\partial\omega\ll 1$. If it is assumed that in the vicinity of $\omega\simeq\tilde{\tilde{\omega}}\binom{\mathbf{k}}{j}$ the linewidth varies slowly with ω, i.e., $\Gamma_{kj}(\omega)=\Gamma_{kj}[\tilde{\tilde{\omega}}\binom{\mathbf{k}}{j}]$, then the integrand exhibits a Lorentzian line shape distribution with its maximum at $\omega=\tilde{\tilde{\omega}}\binom{\mathbf{k}}{j}$. If the variation of widths and shifts with ω is taken into account, then, apart from the nature of combination bands arising as a result of anharmonicities, new delta-function peaks will appear and the band shape will be changed. For values of ω in the immediate neighborhood of $\tilde{\tilde{\omega}}\binom{\mathbf{k}}{j}$ with small enough $\Gamma_{kj}(\omega)$ the integrand may be written as

$$2\omega^2\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\Gamma_{kj}(\omega)D\left[\omega,\tilde{\tilde{\omega}}\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\right]$$

where

$$D\left[\omega,\tilde{\tilde{\omega}}\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\right]=\pi^{-1}\left[\omega^2-\tilde{\tilde{\omega}}^2\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\right]^{-2} \tag{35}$$

The first-order Raman tensor can be separated into diagonal and nondiagonal parts as

$$i^{(1)}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})=i^{1,\mathrm{d}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})+i^{1,\mathrm{nd}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}}) \tag{36}$$

where the superscripts d and nd indicate the diagonal and nondiagonal parts, respectively, and these are given by

$$i^{1,\mathrm{d}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})=(2/\pi)\sum_{kj}P^{(1)}_{\alpha\gamma,\beta\lambda}\begin{pmatrix}\mathbf{k} & -\mathbf{k}\\ j & j\end{pmatrix}\omega^2\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}I_1 \tag{37}$$

and

$$i^{1,\mathrm{nd}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})=(8/\pi)\sum_{\substack{kj,k'j'\\ kj\neq k'j'}}P^{(1)}_{\alpha\gamma,\beta\lambda}\begin{pmatrix}\mathbf{k} & \mathbf{k}'\\ j & j'\end{pmatrix}C\begin{pmatrix}-\mathbf{k} & \mathbf{k}'\\ j & j'\end{pmatrix}\omega\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}I_1 \tag{38}$$

Here the integral

$$I_1=\int_{-\infty}^{\infty} n(\omega)D\left[\omega,\ \tilde{\tilde{\omega}}\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\right]\Gamma_{kj}(\omega)\,d\omega \tag{39}$$

describes the order of scattering as per the nature of $\Gamma_{kj}(\omega)$. Making use of equation (30a), we can obtain the FOR tensor in the form

$$i^{(1)}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{FOR}}=i^{1,\mathrm{d}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{FOR}}+i^{1,\mathrm{nd}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{FOR}} \tag{40}$$

where

$$\begin{aligned}i^{1,\mathrm{d}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{FOR}}={}&8\sum_{kj}P^{(1)}_{\alpha\gamma,\beta\lambda}\begin{pmatrix}\mathbf{k} & -\mathbf{k}\\ j & j\end{pmatrix}R\begin{pmatrix}-\mathbf{k} & \mathbf{k}\\ j & j\end{pmatrix}R\begin{pmatrix}-\mathbf{k} & -\mathbf{k}\\ j & j\end{pmatrix}\\ &\times\left[\omega^3\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\Big/\tilde{\omega}\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\right]\tilde{n}\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}D\left[\tilde{\omega}\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix},\ \tilde{\tilde{\omega}}\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\right]\end{aligned} \tag{41a}$$

and

$$\begin{aligned}i^{1,\mathrm{nd}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{FOR}}={}&32\sum_{\substack{kj,k'j'\\ kj\neq k'j'}}P^{(1)}_{\alpha\gamma,\beta\lambda}\begin{pmatrix}\mathbf{k} & \mathbf{k}'\\ j & j'\end{pmatrix}C\begin{pmatrix}-\mathbf{k} & \mathbf{k}'\\ j & j'\end{pmatrix}\\ &\times R\begin{pmatrix}-\mathbf{k} & \mathbf{k}'\\ j & j'\end{pmatrix}R\begin{pmatrix}-\mathbf{k} & -\mathbf{k}'\\ j & j'\end{pmatrix}\\ &\times\left[\omega^2\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\Big/\tilde{\omega}\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\right]\tilde{n}\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}D\left[\tilde{\omega}\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix},\ \tilde{\tilde{\omega}}\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\right]\end{aligned} \tag{41b}$$

with

$$\tilde{n}\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}=\left\{\exp\left[\beta\hbar\tilde{\omega}\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\right]-1\right\}^{-1}$$

The nondiagonal part is significant in impure crystals because this term chiefly depends on the mass difference parameter and vanishes in the case of pure crystals. In obtaining equation (41), only the phonon frequency shift $\Gamma^{D}_{kj}(\omega)$ generated by the localized interactions is used. The other frequency shifts cannot produce a FORs and will be discussed in the following sections. Before going into the details of impurity-induced FORs, let us examine the possibilities of FORs in pure crystals.

In diatomic polar crystals (NaCl, etc.) the vibrational modes are of two types, namely: the even-parity or symmetric modes and the odd-parity or antisymmetric modes. In the former the motion of only one kind of ion is involved and these modes are designated by A_g (nondegenerate), E_g (doubly degenerate), and F_g (triply degenerate) symmetric modes, while in the latter the motion of both kinds of ions is allowed and these odd-parity modes are designated by A_u, E_u, and F_u antisymmetric modes with respect to the center of inversion. In the case of pure crystals the selection rule $\mathbf{k}=0$ must inevitably be followed. The FORs for pure crystals cannot be studied with the help of the present formulation without some substantial approximation. The GF for this case should be developed by retaining only the unperturbed (harmonic) Hamiltonian H_0 in H. This formulation based on the harmonic approximation can be found in the literature (Born and Huang, 1954; Benedek and Mulazzi, 1969; Negi and Ram, 1984; Cowley, 1966). The use of harmonic GFs in equation (7a) shows the presence of Stokes and anti-Stokes lines with Raman shift ω_R, i.e., $[\omega_0-\omega\binom{0}{j}]$ gives the Stokes lines and $[\omega_0+\omega\binom{0}{j}]$ produces the anti-Stokes (Raman) lines. It is notable here that the nature of even- or odd-parity modes changes the form of harmonic GFs.

The diagonal term (41a) can be studied in more detail for isotopically disordered crystals. The FOR spectrum consists of spectral lines with frequencies of anti-Stokes lines $\omega_0+\omega\binom{0}{j}$ and of Stokes lines $\omega_0-\omega\binom{0}{j}$. Here the wave vector selection rule $\mathbf{k}=0$ is not a necessity, due to the removal of the symmetry of the crystals. Since $\mathbf{k}=0$, optical modes are no longer exact eigenstates of the crystal Hamiltonian; the incident light radiation then couples to all the modes of the host crystal. The FOR scattering therefore produces a continuous spectrum rather than a line spectrum as for perfect crystals (Maradudin, 1966; Yacoby and Yust, 1972). Also, according to the present formulation, the FORs appears only due to the localized modes, which do not exist in the pure crystals. The local mode frequency may even lie in the acoustic band of the host crystal, depending on the nature of the impurity (Behra and Deo, 1967; Tripathi and Behra, 1974; Behra and Tripathi, 1974; Borovik-Romonov *et al.*, 1976). Evidently, the FORs in doped crystals may be observed even in the acoustic region of the host crystal with some specifically defined even- or odd-parity modes (Negi and Ram, 1984; Mills *et al.*, 1969; Pershan and Lacina, 1969; Harley *et al.*, 1971; Hoff and Irwin, 1974; Mokross *et al.*, 1977). In all crystals where the impurity substitutes for one of the host ions without generating any vacancy, the even-parity modes A_{1g}, E_g, and F_{2g} give rise to the FORs in the usually forbidden region (Kravitz, 1970; Harley and Walker, 1970), e.g., KCl : Tl$^+$, RbCl : F-centers. If the impurity does not go to the substitutional site and create a vacancy, then both the translational and inversion symmetries are broken. In such cases (Radhakrishna and Sai, 1971) even the odd-parity modes contribute to the FORs. For example, in RbCl : Cu and KI : Pb the A_g, E_g, and F_{2g} symmetric modes and F_{1u} antisymmetric modes give rise to FORs.

The general trend of temperature and frequency variation of the first-order Raman tensor is contained in the functions (hereafter called the Raman intensity factors)

$$I(\omega)_{\mathrm{AS}} = \left[n\begin{pmatrix} \mathbf{k} \\ j \end{pmatrix} + 1 \right] F(\omega) \tag{42a}$$

$$I(\omega)_{\mathrm{S}} = n\begin{pmatrix} \mathbf{k} \\ j \end{pmatrix} F(\omega) \tag{42b}$$

where

$$F(\omega) = f\omega^2[A_1(1-f)\omega^2 + A_2]\left[\omega^2 - \tilde{\omega}^2\begin{pmatrix} \mathbf{k} \\ j \end{pmatrix} \right]^{-2} \tag{42c}$$

Here A_1 and A_2 are parameters and f is the impurity concentration. The subscripts AS and S stand for anti-Stokes and Stokes components, respectively. Equations (42) are obtained from equation (39) after evaluating $\Gamma^D_{kj}(\omega)$ in the form (Indu, 1990)

$$\begin{aligned} \Gamma^D_{kj}(\omega) = {} & (2NV/\pi v^3) f \left[\omega^2\begin{pmatrix} \mathbf{k} \\ j \end{pmatrix} \Big/ \omega\begin{pmatrix} -\mathbf{k} \\ j \end{pmatrix} \tilde{\omega}\begin{pmatrix} \mathbf{k} \\ j \end{pmatrix} \right] \\ & \times \left[(M_0/4N\mu)^2 \omega^4\begin{pmatrix} \mathbf{k} \\ j \end{pmatrix}(1-f) + \omega^2\begin{pmatrix} \mathbf{k} \\ j \end{pmatrix} \sum_{\substack{ll' \\ \alpha\beta}} \Delta\phi_{ll'} \cos(\mathbf{k} \cdot \mathbf{R}_{ll'}) \right] \end{aligned} \tag{43}$$

To indicate the continuous nature of the FORs, we have calculated the Raman intensity factor (Russell and Loudon, 1965) for $CaWO_4$. The coefficients A_1, A_2, and f are taken as parameters due to the lack of various constants. Sharp peaks are found at B_g 86 cm^{-1}, E_g 118 cm^{-1}, F_g 196 cm^{-1}, A_g 210 cm^{-1}, E_g 281 cm^{-1}, A_g 334 cm^{-1}, etc., and the continuous spectrum is shown in Figure 1. It is evident from Figure 1 that the intensity and broadening of Stokes lines is more persistent than that of anti-Stokes lines. The temperature dependence of the Raman intensity factor is shown in Figure 2. It is clear that the Stokes components show a drastic variation at low temperature, whereas the anti-Stokes components are comparatively less sensitive.

After substitution of equation (41) into equation (9) with appropriate simplifications, one can very easily obtain the FORs differential cross section

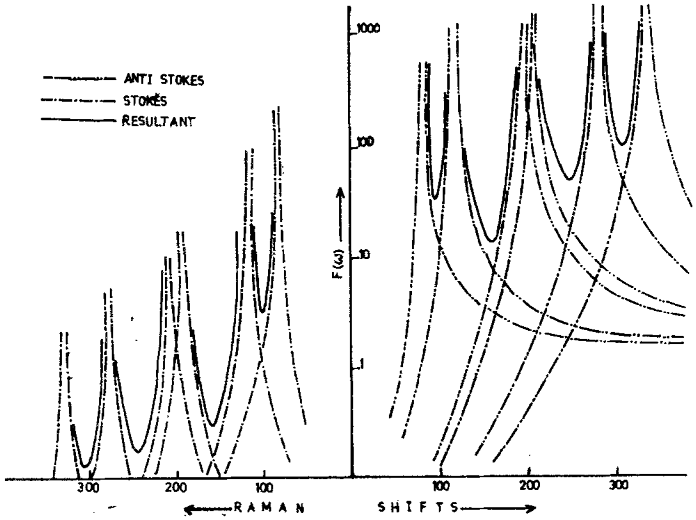

Fig. 1. Variation of Raman intensity factor with Raman shift.

in the form

$$(d^2\sigma/d\Omega\, d\omega_{\mathrm{R}}) = (d^2\sigma/d\Omega\, d\omega_{\mathrm{R}})^{1,\mathrm{d}} + (d^2\sigma/d\Omega\, d\omega_{\mathrm{R}})^{1,\mathrm{nd}} \tag{44}$$

where

$$(d^2\sigma/d\Omega\, d\omega_{\mathrm{R}})^{1,\mathrm{d}} = (\omega/c)^4 \sum_{\alpha\beta\gamma\lambda} n_\alpha n_\beta m_\gamma m_\lambda i^{1,\mathrm{d}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{FOR}} \tag{45a}$$

and

$$(d^2\sigma/d\Omega\, d\omega_{\mathrm{R}})^{1,\mathrm{nd}} = (\omega/c)^4 \sum_{\alpha\beta\gamma\lambda} n_\alpha n_\beta m_\gamma m_\lambda i^{1,\mathrm{nd}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{FOR}} \tag{45b}$$

5. SECOND-ORDER RAMAN PROCESSES

The second-order Raman tensor is given by

$$i_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{SOR}} = i^{1,\mathrm{d}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{SOR}} + i^{1,\mathrm{nd}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{SOR}} + i^{(2)}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{SOR}} \tag{46}$$

where the first and second terms of the SOR tensor are obtained from equation (34) for these processes in which two phonons contribute in the inelastic scattering processes via $\Gamma^{(3)}_{kj}(\omega)$ and are given by

$$i^{1,\mathrm{d}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{SOR}}$$

$$= 18 \sum_{kj,k_1j_1,k_2j_2} P^{(1)}_{\alpha\gamma,\beta\lambda}\begin{pmatrix}\mathbf{k} & -\mathbf{k}\\ j & j\end{pmatrix}\omega^2\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\mathscr{C}^{(1)}_{k_1k_2k}S_1(\beta) \tag{47}$$

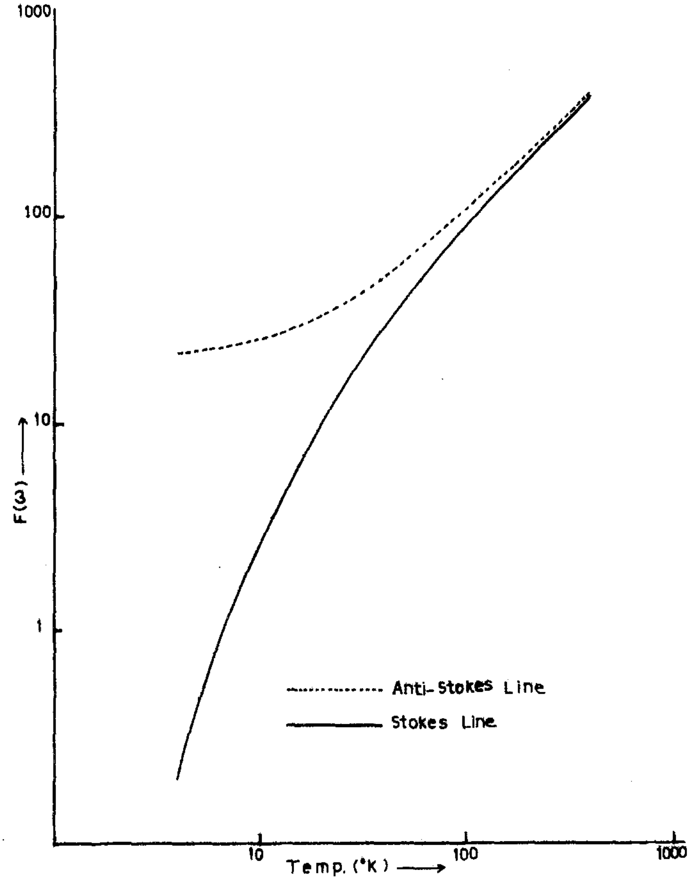

Fig. 2. Temperature dependence of Raman intensity factor.

and

$$i^{1,\mathrm{nd}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{SOR}} = 72 \sum_{\substack{kj,k'j' \\ kj \neq k'j'}} P^{(1)}_{\alpha\gamma,\beta\lambda}\begin{pmatrix} \mathbf{k} & \mathbf{k}' \\ j & j' \end{pmatrix} C\begin{pmatrix} -\mathbf{k} & \mathbf{k}' \\ j & j' \end{pmatrix} \omega\begin{pmatrix} \mathbf{k} \\ j \end{pmatrix} \mathscr{C}^{(1)}_{k_1k_2k} S_1(\beta) \tag{48}$$

with

$$\mathscr{C}^{(1)}_{k_1k_2k} = V_3\begin{pmatrix} \mathbf{k}_1 & \mathbf{k}_2 & -\mathbf{k} \\ j_1 & j_2 & j \end{pmatrix} V_3\begin{pmatrix} -\mathbf{k}_1 & -\mathbf{k}_2 & -\mathbf{k} \\ j_1 & j_2 & j \end{pmatrix} \eta_1 \tag{49a}$$

$$S_1(\beta)=S_{+\alpha}\tilde{n}_{+\alpha}\left\{D\left[\omega_{+\alpha},\tilde{\tilde{\omega}}\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\right]+\mathscr{E}^{(1)}_{kk_1}D\left[\omega_{+\alpha},\tilde{\tilde{\omega}}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\right]\right\}$$

$$+S_{-\alpha}\tilde{n}_{-\alpha}\left\{D\left[\omega_{-\alpha},\tilde{\tilde{\omega}}\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\right]+\mathscr{E}^{(1)}_{kk_1}D\left[\omega_{-\alpha},\tilde{\tilde{\omega}}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\right]\right\} \tag{49b}$$

$$\mathscr{E}^{(1)}_{kk_1}=C\begin{pmatrix}-\mathbf{k} & \mathbf{k}_1\\ j & j_1\end{pmatrix}C\begin{pmatrix}-\mathbf{k} & -\mathbf{k}_1\\ j & j_1\end{pmatrix}\Big/\omega^2\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix};\qquad \omega_{\pm\alpha}=\tilde{\omega}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\pm\tilde{\omega}\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix} \tag{49c}$$

$$S_{\pm\alpha}=S_{\pm 1}\tilde{n}_{\pm\alpha}\qquad\text{and}\qquad S_{\pm 1}=n\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}\pm n\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix} \tag{49d}$$

The third term $i^{(2)}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{SOR}}$ emerges from equation (7b) due to the fluctuations in the second-order electronic polarizability and can be obtained as

$$i^{(2)}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{SOR}}=(1/2\pi^2)\sum_{k_1j_1k_2j_2}P^{(2)}_{\alpha\gamma,\beta\lambda}\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2 & -\mathbf{k}_1 & -\mathbf{k}_2\\ j_1 & j_2 & j_1 & j_2\end{pmatrix}\eta_1$$

$$\times(S_{+1}\tilde{n}_{+\alpha}+S_{-1}\tilde{n}_{-\alpha}) \tag{50}$$

Loudon (1964) inferred that SOR scattering can be divided into two classes, i.e., the line spectrum and the continuous spectrum. The line spectrum occurs due to the processes in which light suffers two successive FORs, while the continuous spectrum occurs due to the processes in which the light interacts with a pair of phonons in a single event. Also, the scattering efficiencies for SOR scattering increase with the crystal size. Born and Bradburn (Born and Bradburn, 1947) state that SOR scattering takes place due to the involvement of second-order terms in the electronic polarizability. Several authors (Agrawal *et al.*, 1975; Laplaze, 1979; Liarokapis *et al.*, 1985) have studied the SOR scattering in the same framework. They found that SOR spectra are continuous since they involve the excitations of all possible combinations of two phonons with equal and opposite wave vectors. The intensity of any given combination is weighted by a coefficient which is expressible in terms of a second derivative of $P_{\beta\lambda}(t)$ with respect to the pairs of nuclear displacements. These arguments can be modified here. The SOR scattering not only depends on the second derivative of electronic polarizability, but also on its first derivative, i.e., the SOR tensor consists of three terms, $i^{1,\mathrm{d}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{SOR}}$, $i^{1,\mathrm{nd}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{SOR}}$, and $i^{(2)}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{SOR}}$, of which the first two terms come from the FOR-type excitations, while the third term appears from pure SOR excitations [involvement of second derivative of $P_{\beta\lambda}(t)$]. The $i^{(2)}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{SOR}}$ term is purely anharmonic and is mainly influenced by the temperature-dependent distribution function contained in $S_{\pm\alpha}\tilde{n}_{\pm\alpha}$-type terms. The use of wave vector selection rules shows that this term displays continuous structure. At the same time the diagonal and nondiagonal parts $i^{1,\mathrm{d}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{SOR}}$ and $i^{1,\mathrm{nd}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{SOR}}$ appear as a result of the cubic anharmonicities involved in the fluctuations of the first-order electronic polarizability and the interfering cubic anharmonicities in the localized fields. For this case the wave vector selection rules exhibit a line spectrum. These terms are heavily influenced by the temperature term $S_1(\beta)$, mass difference terms, and cubic force constants. The uncertainty involved in the forms of

$$P^{(1)}_{\alpha\gamma,\beta\lambda}\begin{pmatrix}\mathbf{k} & -\mathbf{k}\\ j & j\end{pmatrix} \quad \text{and} \quad P^{(2)}_{\alpha\gamma,\beta\lambda}\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2 & -\mathbf{k}_1 & -\mathbf{k}_2\\ j_1 & j_2 & j_1 & j_2\end{pmatrix}$$

does not cause any significant source of error, but an approximate evaluation of the two-phonon density of states (Loudon, 1964; Russell, 1966) will cause severe alterations in the results. It has been observed (Indu, 1990) that the density of states is no longer independent of temperature, and the SOR spectra are automatically affected by it. The general theory of crystal spectra including anharmonic effects predicts no selection rules for the overtones or combination and difference bands. However, factor group analysis can be regarded (Born and Bradburn, 1947; Born and Blackman, 1933) as a very rough guide for the higher-order spectra, and predicts that:

(a) The first overtone (which occurs approximately at the double of a fundamental frequency) of any normal mode is Raman-active, irrespective of the fundamental's activity.
(b) Any infrared-active and Raman-active fundamental combining with a Raman-active mode gives rise to an infrared-active combination tone.
(c) Any Raman-active mode combining with any of the even-parity modes always produces a Raman mode.

These rules are very applicable to the present theory under wave vector selection rules. In the case of a chemically pure crystal $i^{1,\mathrm{nd}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{SOR}}$ disappears. All the overtones, combination, and difference bands have different frequency and temperature dependences and are dependent on the two-phonon density of states, in agreement with earlier results with some modifications.

The SOR differential cross section can be obtained in the form

$$(d^2\sigma/d\Omega\, d\omega_{\mathrm{R}})_{\mathrm{SOR}} = (\omega/c)^4 \sum_{\alpha\beta\gamma\lambda} n_\alpha n_\beta [i^{1,\mathrm{d}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{SOR}} + i^{1,\mathrm{nd}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{SOR}} + i^{(2)}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{SOR}}] \tag{51}$$

which can be easily studied with the temperature variations for various frequencies, namely:

$$\pm 2\tilde{\omega}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}, \qquad \pm 2\tilde{\omega}\begin{pmatrix}-\mathbf{k}_1\\ j_2\end{pmatrix}, \qquad \pm 2\tilde{\omega}\begin{pmatrix}-\mathbf{k}_1\\ j_1\end{pmatrix}$$

$$\pm\left[\tilde{\omega}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix} \pm \tilde{\omega}\begin{pmatrix}-\mathbf{k}_1\\ j_2\end{pmatrix}\right], \qquad \pm\left[\tilde{\omega}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix} \pm \tilde{\omega}\begin{pmatrix}-\mathbf{k}_1\\ j_1\end{pmatrix}\right]$$

6. THIRD-ORDER RAMAN SCATTERING

After certain simplifications the TOR scattering tensor takes the form

$$i_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{TOR}} = i^{1,\mathrm{d}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{TOR}} + i^{1,\mathrm{nd}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{TOR}} + i^{(3)}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{TOR}} \tag{52}$$

where in the first two terms the first-order electronic polarizability is involved, but the third term appears due to the fluctuations of the electronic polarizability in its third-order derivative; these terms are given by

$$i^{1,\mathrm{d}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{TOR}} = 48 \sum_{kj} \sum_{k_1j_1,\ldots,k_3j_3} P^{1,\mathrm{d}}_{\alpha\gamma,\beta\lambda}\begin{pmatrix}\mathbf{k} & -\mathbf{k}\\ j & j\end{pmatrix} \omega^2\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix} \times \mathscr{C}^{(2)}_{k_1k_2k_3k} S_2(\beta) \tag{53}$$

$$i^{1,\mathrm{nd}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{TOR}} = 192 \sum_{\substack{kj,K'j'\\ kj\neq k'j'}} \sum_{k_1j_1,\ldots,k_3j_3} P^{1,\mathrm{nd}}_{\alpha\gamma,\beta\lambda}\begin{pmatrix}\mathbf{k} & \mathbf{k}'\\ j & j'\end{pmatrix} \times C\begin{pmatrix}-\mathbf{k} & \mathbf{k}'\\ j & j'\end{pmatrix} \omega\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix} \mathscr{C}^{(2)}_{k_1k_2k_3k} S_2(\beta) \tag{54}$$

and

$$i^{(3)}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{TOR}} = (1/2\pi^2) \sum_{k_1j_1,\ldots,k_3j_3} P^{(3)}_{\alpha\gamma,\beta\lambda}\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2 & \mathbf{k}_3 & -\mathbf{k}_1 & -\mathbf{k}_2 & -\mathbf{k}_3\\ j_1 & j_2 & j_3 & j_1 & j_2 & j_3\end{pmatrix} \times \eta_2(S_1\tilde{n}_1 + S_2\tilde{n}_2 + S_3\tilde{n}_3 + S_4\tilde{n}_4) \tag{55}$$

where

$$\mathscr{C}^{(2)}_{k_1k_2k_3k} = V_4\begin{pmatrix}\mathbf{k}_1 & \mathbf{k}_2 & \mathbf{k}_3 & -\mathbf{k}\\ j_1 & j_2 & j_3 & j\end{pmatrix} V_4\begin{pmatrix}-\mathbf{k}_1 & -\mathbf{k}_2 & -\mathbf{k}_3 & -\mathbf{k}\\ j_1 & j_2 & j_3 & j\end{pmatrix}\eta_2 \tag{56a}$$

$$\begin{aligned} S_2(\beta) = {} & S_1\tilde{n}_1\left\{D\left[\omega_1, \tilde{\tilde{\omega}}\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\right] + \mathscr{E}^{(1)}_{kk_1}D\left[\omega_1, \tilde{\tilde{\omega}}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\right]\right\}\\ & + S_2\tilde{n}_2\left\{D\left[\omega_2, \tilde{\tilde{\omega}}\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\right] + \mathscr{E}^{(1)}_{kk_1}D\left[\omega_2, \tilde{\tilde{\omega}}\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}\right]\right\}\\ & + S_3\tilde{n}_3\left\{D\left[\omega_3, \tilde{\tilde{\omega}}\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\right] + \mathscr{E}^{(1)}_{kk_1}D\left[\omega_3, \tilde{\tilde{\omega}}\begin{pmatrix}\mathbf{k}_3\\ j_3\end{pmatrix}\right]\right\}\\ & + S_4\tilde{n}_4\left\{D\left[\omega_4, \tilde{\tilde{\omega}}\begin{pmatrix}\mathbf{k}\\ j\end{pmatrix}\right] + \mathscr{E}^{(1)}_{kk_1}D\left[\omega_4, \tilde{\tilde{\omega}}\begin{pmatrix}\mathbf{k}_4\\ j_4\end{pmatrix}\right]\right\} \end{aligned} \tag{56b}$$

with

$$S_{\begin{pmatrix}1\\2\\3\\4\end{pmatrix}} = 1\begin{pmatrix}+\\-\\-\\+\end{pmatrix} n\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix} n\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}\begin{pmatrix}+\\+\\-\\-\end{pmatrix} n\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix} n\begin{pmatrix}\mathbf{k}_3\\ j_3\end{pmatrix}\begin{pmatrix}+\\-\\+\\-\end{pmatrix} n\begin{pmatrix}\mathbf{k}_3\\ j_3\end{pmatrix} n\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix} \tag{56c}$$

$$\omega_{\begin{pmatrix}1\\2\\3\\4\end{pmatrix}} = \begin{pmatrix}+\\-\\+\\+\end{pmatrix}\tilde{\omega}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\begin{pmatrix}+\\+\\-\\+\end{pmatrix}\tilde{\omega}\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}\begin{pmatrix}+\\+\\+\\-\end{pmatrix}\tilde{\omega}\begin{pmatrix}\mathbf{k}_3\\ j_3\end{pmatrix} \tag{56d}$$

and

$$\tilde{n}_{\begin{pmatrix}1\\2\\3\\4\end{pmatrix}} = \left[\exp\left(\beta\hbar\omega_{\begin{pmatrix}1\\2\\3\\4\end{pmatrix}}\right) - 1\right]^{-1} \tag{56e}$$

It is evident from equation (52) that the third-order Raman scattering is induced by three types of terms, two of which, namely $i^{1,\mathrm{d}}_{\alpha\gamma,\beta\lambda}(\omega_\mathrm{R})_\mathrm{TOR}$ and $i^{1,\mathrm{nd}}_{\alpha\gamma,\beta\lambda}(\omega_\mathrm{R})_\mathrm{TOR}$, appear due to processes in which light suffers three successive FORs; the remaining term, $i^{(3)}_{\alpha\gamma,\beta\lambda}(\omega_\mathrm{R})_\mathrm{TOR}$, appears due to the processes in which the third-order derivative of the electronic polarizability is encountered. It is notable that no second-order derivative is involved in the TOR scattering. High-power laser beams will make it possible to observe a large number of Raman lines along with a continuous spectrum. The intensity of TOR lines is also affected by the temperature, force constant changes, and interfering processes. The various TOR lines with different temperature functions may be obtained at the frequencies

$$\pm 3\tilde{\omega}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix},\quad \pm 3\tilde{\omega}\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix},\quad \pm 3\tilde{\omega}\begin{pmatrix}\mathbf{k}_3\\ j_3\end{pmatrix},\quad \pm\tilde{\omega}\begin{pmatrix}-\mathbf{k}_1\\ j_2\end{pmatrix},\quad \pm\tilde{\omega}\begin{pmatrix}-\mathbf{k}_1\\ j_3\end{pmatrix},$$

$$\pm\left[\begin{pmatrix}+\\-\\+\\-\end{pmatrix}\tilde{\omega}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\begin{pmatrix}+\\+\\-\\+\end{pmatrix}\tilde{\omega}\begin{pmatrix}\mathbf{k}_2\\ j_2\end{pmatrix}\begin{pmatrix}+\\+\\+\\-\end{pmatrix}\tilde{\omega}\begin{pmatrix}\mathbf{k}_3\\ j_3\end{pmatrix}\right],$$

$$\pm\left[\begin{pmatrix}+\\-\\+\\+\end{pmatrix}\tilde{\omega}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\begin{pmatrix}+\\+\\-\\+\end{pmatrix}\tilde{\omega}\begin{pmatrix}-\mathbf{k}_1\\ j_2\end{pmatrix}\begin{pmatrix}+\\+\\+\\-\end{pmatrix}\tilde{\omega}\begin{pmatrix}-\mathbf{k}_1\\ j_1\end{pmatrix}\right],$$

$$\pm\left[\begin{pmatrix}+\\-\\+\\+\end{pmatrix}\tilde{\omega}\begin{pmatrix}\mathbf{k}_1\\ j_1\end{pmatrix}\begin{pmatrix}+\\+\\-\\+\end{pmatrix}\tilde{\omega}\begin{pmatrix}-\mathbf{k}_1\\ j_2\end{pmatrix}\begin{pmatrix}+\\+\\+\\-\end{pmatrix}\tilde{\omega}\begin{pmatrix}-\mathbf{k}_1\\ j_2\end{pmatrix}\right]$$

The third-order Raman scattering cross section can also be obtained in the form

$$(d^2\sigma/d\Omega\, d\omega_{\mathrm{R}})_{\mathrm{TOR}} = (\omega/c)^4 \sum_{\alpha\beta\gamma\lambda} n_\alpha n_\beta[i^{1,\mathrm{d}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{TOR}} + i^{1,\mathrm{nd}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{TOR}} + i^{(3)}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{TOR}}] \tag{57}$$

The quartic-phonon frequency linewidth is involved in all the evaluations of TOR scattering, which reveals the thermal dependence as (Indu, 1990)

$$\Gamma^{(4)}_{kj}(\omega) \sim \omega^2 T^2 \tag{58}$$

7. CONCLUSIONS

We have developed the theory of higher-order Raman scattering (including first-order Raman scattering) for an isotopically disordered anharmonic crystal. It is observed that the FOR scattering provides only one Stokes component and one anti-Stokes component and is induced due to processes in which fluctuations in the first-order electronic polarizability are encountered. This scattering is governed by the defect terms only. The frequencies no longer remain harmonic but become quasiharmonic. The mass difference as well as force constant changes contribute significantly and the temperature term exhibits the general nature of the FOR spectrum.

The SOR scattering is governed by two principal types of terms; the first category of terms contribute due to the fluctuations in the first-order electronic polarizability influenced by the cubic anharmonic and interference terms. These terms are separable into diagonal and nondiagonal parts just like the FOR terms. Precisely speaking, these terms arise as a result of two successive FOR scatterings of phonons. These terms can again be separated into two terms, namely terms involved in purely cubic anharmonic interactions and those appearing due to the simultaneous involvement of cubic and defect terms, i.e., interference terms. The nondiagonal terms vanish throughout in case of chemically pure crystals, as they are chiefly contributed by the mass difference terms interacting with anharmonicities. The next class of terms contribute to the SOR events solely due to the second derivative of the electronic polarizability. The SOR terms display a continuous spectrum as well as a line spectrum and all the terms (overtones, summation, and difference bands) are heavily influenced by the temperature and show different temperature dependence via finite frequency linewidths. These inferences regarding line and continuous spectra are in agreement with Loudon (1964). The SOR spectrum simultaneously depends on the one-phonon density of states via $i^{1,\mathrm{d}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{SOR}}$ and $i^{1,\mathrm{nd}}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{SOR}}$ and on the two-phonon density of states via $i^{(2)}_{\alpha\gamma,\beta\lambda}(\omega_{\mathrm{R}})_{\mathrm{SOR}}$.

The TOR spectra can also be divided into two classes. The first category of TOR scattering appears due to the involvement of first-order polarizability which fluctuates due to the quartic anharmonic phonon fields. These terms can be separated into diagonal and nondiagonal terms and the former can be separated again into two terms: terms arising from the quartic anharmonic frequency widths and those arising due to the phonons interacting with local fields. The temperature and defect dependencies of these terms cause them to persist in the classical regime, and can be assumed as the result of three successive FOR collisions. The second class of terms appear as a result of the fluctuations in the third-order electronic polarizability. A large number of TOR lines may be obtained in this case, but only with the help of a very high-power laser source. The TOR results from the three-phonon and single-phonon densities of states. Appropriate experimental effort with laser sources should display TOR scattering and reveal new structural aspects of crystal physics.

ACKNOWLEDGMENTS

The authors are indebted to Prof. A. Mookerjee and Prof. Bal K. Agrawal for their useful suggestions. This work was supported by the Department of Science and Technology, New Delhi vide grant HCS/DST/1209/81.

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