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TEMPERATURE FUNCTIONS FOR FIRST & SECOND ORDER RAMAN SCATTERING IN ISOTOPICALLY DISORDERED AN HARMONIC CRYSTAL

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ABSTRACT

The temperature dependence of first and second order Raman Scattering tensors in investigated with the help of quantum dynamical approach for a defect induced anharmonic crystal. The help of quantum dynamical approach for a defect induced anharmonic crystal. The thermal gradients of Raman tensors reveal that the temperature dependence of Raman lines is extremely significant and can only be explained with the help of coupling of Raman active optical modes.

I INTRODUCTION

A wealth of experimental data on Raman scattering (RS) processes has come up during the past few decades[1-14]. It is observed that the various orders of RS processes, namely : first order (FORS) Second Order (SORS), third order Raman Scattering (TORS) etc. process (SORS, TORS etc are known as higher order Raman Scattering (HORS) processes) depict a characteristics temperature dependence[15].

The intensity, line centre and line width of Raman spectral lines is found to vary with temperature[16-19]. The Stokes components of FORS showed drastic changes at low temperatures whereas anti-Stokes components are found to be less sensitive towards temperature variations[20]. Attempts have been made but none succeeded to explain this temperature dependent nature of Raman lines, when one considers the most simple theory of harmonic approximation[12,20-21].

Going beyond the quadratic terms in the expansion of potential energy and electronic polarizability of the crystal the possibility of coupling of various phonon modes comes into picture which gives the idea of certain resisting terms (temperature dependent) and thereby giving rise to the anharmonic phonon processes. It is the crystal anharmonicity which explains the temperature dependence of Raman lines.

Some work has evidenced the anharmonic coupling of Raman optical modes just like infrared active modes[21]. Very limited number of articles[22] could undertake the problem of FORS, SORS and TORS on the basis of anharmonic theory for defect induced crystals. In recently[22] the concept of FORS and HORS defect induced crystalline solids is explained in which the possibility of coupling of anharmonic and localized phonons is also discussed which significantly contribute to HORS and show strong temperature dependence.

In the present chapter, the temperature dependence of HORS processes in an anharmonic crystal containing isotopically distributed impurities has been taken into account. The temperature gradients for HORS tensors have been discussed in details along with the temperature functions of various higher orders Raman processes.

II THE RAMAN TENSOR

The Raman tensor is given by

$$i_{\alpha\gamma,\beta\lambda}(\omega_R)=\left(\frac{1}{2\pi^2}\right)\int_{-\infty}^{\infty}dt\exp[-i\omega_R t]<P_{\beta\lambda}(t)P_{\alpha\gamma}(O)>_T$$

[1]

where $P_{\beta\lambda}(t)$ etc. defines the electronic polarizability the details of which are given in the reference[22]. Making the use of polarizability expansion and second quantized normal coordinate transformation, one can easily obtain.

$$i_{\alpha\gamma,\beta\lambda}(\omega_R)=i^{(1)}_{\alpha\gamma,\beta\lambda}(\omega_R)+i^{(2)}_{\alpha\gamma,\beta\lambda}(\omega_R)+i^{(3)}_{\alpha\gamma,\beta\lambda}(\omega_R),$$

[2]

where $i^{(1)}_{\alpha\gamma,\beta\lambda}(\omega_R), i^{(2)}_{\alpha\gamma,\beta\lambda}(\omega_R)$ and $i^{(3)}_{\alpha\gamma,\beta\lambda}(\omega_R)$ are the components of Raman tensor due to the fluctuations in first, second-and third-order electronic polarizability. Using the various order Green's functions with the help of defect induecd anharmonic Hamiltonian[22, 24] we can separate FORS tensor into its diagonal and non-diagonal parts as

$$i^{(1)}_{\alpha\gamma,\beta\lambda}(\omega_R)_{FOR}=i^{1,d}_{\alpha\gamma,\beta\lambda}(\omega_R)_{FOR}+i^{1,nd}_{\alpha\gamma,\beta\lambda}(\omega_R)_{FOR}$$

[3]

where superscripts 'd' and 'nd' stand for the diagonal and non-diagonal parts, respectively. After some simplifications the FORS tensor can be obtained in the form

$$i^{1,d}_{\alpha\gamma,\beta\lambda}(\omega_R)_{FOR} = 8\sum_{kj} P^{(1)}_{\alpha\gamma,\beta}\begin{pmatrix}\vec{k}-\vec{k}\\ j\ \ j\end{pmatrix} R^{*}\begin{pmatrix}\overrightarrow{-k}\,\vec{k}\\ j\ \ j\end{pmatrix} R\begin{pmatrix}\overrightarrow{-k}\,\vec{k}\\ j\ \ j\end{pmatrix}\left[\omega^{3} * \begin{pmatrix}\vec{k}\\ j\end{pmatrix} / \tilde{\omega}\begin{pmatrix}\vec{k}\\ j\end{pmatrix}\right]$$

$$\tilde{\omega}\begin{pmatrix}\vec{k}\\ j\end{pmatrix} D\left[\tilde{\omega}\begin{pmatrix}\vec{k}\\ j\end{pmatrix}, \overset{\approx}{\omega}\begin{pmatrix}\vec{k}\\ j\end{pmatrix}\right] \qquad [4a]$$

and

$$i^{1,nd}_{\alpha\gamma,\beta\lambda}(\omega_R)_{FOR} = 32\sum_{kj,k',j'} P^{(1)}_{\alpha\gamma,\beta\lambda}\begin{pmatrix}\vec{k}-\vec{k}'\\ j\ \ j'\end{pmatrix} C\begin{pmatrix}\vec{k}-\vec{k}'\\ j\ \ j'\end{pmatrix} R^{*}\begin{pmatrix}\overrightarrow{-k}\,\vec{k}'\\ j\ \ j'\end{pmatrix} R\begin{pmatrix}\overrightarrow{-k}-\vec{k}'\\ j\ \ j'\end{pmatrix}$$

$$\left[\omega^{2}\begin{pmatrix}\vec{k}\\ j\end{pmatrix} / \left(\tilde{\omega}\right)\right]\tilde{n}\begin{pmatrix}\vec{k}\\ j\end{pmatrix} D\left[\tilde{\omega}\begin{pmatrix}\vec{k}\\ j\end{pmatrix}, \overset{\approx}{\omega}\begin{pmatrix}\vec{k}\\ j\end{pmatrix}\right],, \qquad [4b]$$

with

$$\overset{\approx}{n}\begin{pmatrix}\vec{k}\\ j\end{pmatrix} = \left\{\exp\left[\beta\omega\begin{pmatrix}\vec{k}\\ j\end{pmatrix}\right] - 1\right\}^{-1} \qquad (4c)$$

The non-diagonal part depends on the mass difference parameter and hence is significant only in case of impure crystals.

The SORS tensor can also be written in the form

$$i_{\alpha\gamma,\beta\lambda}(\omega_R)_{SOR} = i^{1,d}_{\alpha\gamma,\beta\lambda}(\omega_R)_{SOR} + i^{1,nd}_{\alpha\gamma,\beta\lambda}(\omega_R)_{SOR} + i^{(2)}_{\alpha\gamma,\beta\lambda}(\omega_R)_{SOR} \qquad (5)$$

In the equation (5) first two terms arise due to the fluctuations in the first order electronic polarizatbilty, while the third term emerges due to the fluctuations in the second order polarizatbility and are given by

$$i^{1,d}_{\alpha\gamma,\beta\lambda'}(\omega_R)_{SOR} = 18\sum_{kj\ k_1j_1}\sum_{kj\ k_2j_2} P^{(1)}_{\alpha\gamma,\beta\lambda}\begin{pmatrix}\vec{k}-\vec{k}\\ j\ \ j\end{pmatrix}\omega^{2}\begin{pmatrix}\vec{k}\\ j\end{pmatrix}\left\{\xi^{(1)}_{k_1k_2k} S_1(\beta)\right\}, \qquad (6a)$$

$$i^{1,nd}_{\alpha\gamma,\beta\lambda'}(\omega_R)_{SOR} = 72\sum_{kj\ k_1j_1}\sum_{kj\ k_2j_2} P^{(1)}_{\alpha\gamma,\beta\lambda}\begin{pmatrix}\vec{k}-\vec{k}\\ j\ \ j\end{pmatrix} C\begin{pmatrix}\overrightarrow{-k}-\overrightarrow{k}\\ j\ \ j\end{pmatrix}\omega\begin{Bmatrix}\vec{k}\\ j\end{Bmatrix},$$

$$\xi^{(1)}_{k_1k_2k} S_1(\beta), \qquad (6b)$$

and

$$i^{(2)}_{\alpha\gamma,\beta\lambda},(\omega_R)_{SOR} = \left(\frac{1}{2\pi^2}\right)\sum_{k_1 j_1, k_2 j_2} P^{(2)}_{\alpha\gamma,\beta\lambda}\begin{pmatrix}\overrightarrow{k_1} & \overrightarrow{k_2} & \overrightarrow{-k_1} & \overrightarrow{-k_2} \\ j_1 & j_2 & j_1 & j_2\end{pmatrix} n_1$$
$$\left[S_{+\alpha}n_{+\alpha} + S_{-\alpha}n_{-\alpha}\right],$$

(6c)

with

$$\xi^{(1)}_{k_1 k_2 k} = V_3\begin{pmatrix}\overrightarrow{k_1} & \overrightarrow{k_2} & \overrightarrow{-k} \\ j_1 & j_2 & j\end{pmatrix} V_3\begin{pmatrix}\overrightarrow{-k_1} & \overrightarrow{-k_2} & \overrightarrow{-k} \\ j_1 & j_2 & j\end{pmatrix} n_1 \tag{7a}$$

$$S_1(\beta) = S_{+\alpha}n_{+\alpha}\left\{D\left[\omega_{+\alpha}, \tilde{\omega}\begin{pmatrix}\vec{k} \\ j\end{pmatrix}\right] + \zeta^{(1)}_{kk_1} D\left[\omega_{+\alpha}, \tilde{\omega}\begin{pmatrix}\overrightarrow{k_1} \\ j_1\end{pmatrix}\right]\right\}$$

$$+ S_{-\alpha}n_{-\alpha}\left\{D\left[\omega_{+\alpha}, \tilde{\omega}\begin{pmatrix}\vec{k} \\ j\end{pmatrix}\right] + \zeta^{(1)}_{kk_1} D\left[\omega_{-\alpha}, \tilde{\omega}\begin{pmatrix}\overrightarrow{k_1} \\ j_1\end{pmatrix}\right]\right\} \tag{7b}$$

$$\zeta^{(1)}_{kk_1} = C\begin{pmatrix}\overrightarrow{-k} & \overrightarrow{k_1} \\ j & j_1\end{pmatrix} C\begin{pmatrix}\overrightarrow{-k} & \overrightarrow{-k_1} \\ j & j_1\end{pmatrix} / \omega^2\begin{Bmatrix}\vec{k} \\ j\end{Bmatrix}, \tag{7c}$$

$$\omega_{\pm\alpha} = \overset{\approx}{\omega}\begin{pmatrix}\overrightarrow{k_1} \\ j_1\end{pmatrix} \pm \begin{pmatrix}\overrightarrow{k_1} \\ j_1\end{pmatrix} \tag{7d}$$

$$S_{\pm\alpha} = S_{\pm 1}n_{\pm a} \quad and \quad S_{\pm 1} = n\begin{pmatrix}\overrightarrow{k_1} \\ j_1\end{pmatrix} \pm \begin{pmatrix}\overrightarrow{k_1} \\ j_1\end{pmatrix} \tag{7e}$$

III TEMPERATURE FUNCTIONS FOR DIFFERENT ORDER RAMAN SCATTERING

Experimental observations reveal that Raman processes are heavily influenced by temperature. In SOR tensor S_1 (β) is the term which explicitly revels the temperature dependence. This term can be rearranged as

$$S_1(\beta) = F_1(T)\theta_1 + F_2(T)\theta_2 \tag{8}$$

$$F_1(T)=\left[Coth\left(\frac{\theta_2}{T}\right)+Coth\left(\frac{\theta_1}{T}\right)\right]\left[\exp\{2(\vartheta_1+\vartheta_2)/T\}-1\right]^2 \qquad \textbf{(8a)}$$

And

$$F_2(T)=\left[Coth\left(\frac{\theta_2}{r}\right)--Coth\left(\frac{\theta_1}{T}\right)\right]\left[\exp\left\{\frac{2\theta_1-\theta_2}{T}\right\}-1\right]^{-2} \qquad \textbf{(8b)}$$

With

$$\theta_i=\left(\frac{K}{2K_B}\right)\tilde{\omega}\begin{pmatrix}\vec{k}_i\\ j_i\end{pmatrix} \qquad \textbf{(9 a)}$$

$$\theta_1=D\left[\omega_{+a},\overset{\approx}{\omega}\begin{pmatrix}\vec{k}_i\\ j_i\end{pmatrix}\right]+\zeta\begin{matrix}(1)\\ kk_1\end{matrix}D\left[\omega_{+a},\overset{\approx}{\omega}\begin{pmatrix}\vec{k}_1\\ j_1\end{pmatrix}\right] \qquad \textbf{(9 b)}$$

and

$$\theta_2=D\left[\omega_{-a},\overset{\approx}{\omega}\begin{pmatrix}\vec{k}\\ j\end{pmatrix}\right]+\zeta\begin{matrix}(1)\\ kk_1\end{matrix}D\left[\omega_{-a},\overset{\approx}{\omega}\begin{pmatrix}\vec{k}_1\\ j_1\end{pmatrix}\right] \qquad \textbf{(9c)}$$

Fig. 1 shows the variation of F_1 (T) and F_2 (T) with temperature where frequency data taken from experimental value of Benoit et al are ω_1 = 45 cm^{-1} and ω_2 = 88 cm^{-1}. It is evident from the plot that values of F_1 (T) and F_2(T) increase with rising temperature and both the terms show nearly the similar slope with different magnitudes. Thus SORS is significantly affected by the temperature and is prominent in the higher temperature region.

In the classical high temperature limit

$$F_1(T)=\left[2\tilde{\omega}\begin{pmatrix}\vec{k}_1\\ j_1\end{pmatrix}\tilde{\omega}\begin{pmatrix}\vec{k}_2\\ j_2\end{pmatrix}\left\{\tilde{\omega}\begin{pmatrix}\vec{k}_1\\ j_1\end{pmatrix}+\tilde{\omega}\begin{pmatrix}\vec{k}_2\\ j_2\end{pmatrix}\right\}\right]^{-1}(2K_BT/h)^3 \qquad \textbf{(10 a)}$$

$$F_2(T)=\left[2\tilde{\omega}\begin{pmatrix}\vec{k}_1\\ j_1\end{pmatrix}\tilde{\omega}\begin{pmatrix}\vec{k}_2\\ j_2\end{pmatrix}\left\{\tilde{\omega}\begin{pmatrix}\vec{k}_1\\ j_1\end{pmatrix}-\tilde{\omega}\begin{pmatrix}\vec{k}_2\\ j_2\end{pmatrix}\right\}\right]^{-1}(2K_BT/h)^3 \qquad \textbf{(10 b)}$$

IV CONCLUSIONS

These expression very clearly exhibit that the theory of Raman scattering discussed by earlier workers in the harmonic approximation suffers severe inadequacies and it is not reasonable to consider the Raman scattering processes independent of temperatures. In the present theory, in addition to the traditional temperature term (which appears in the phonon occupation number only) a large number of temperature dependent terms are invoked as a result of phonon-phonon interactions which, intern, cause the fluctuations in the electronic polarizability to give rise the higher order Raman scattering processes. The HORS depend categorically on one-, two- and three phonon density of states via phonon line widths of impure anharmonic crystals. It is seen that the density of states depend on the temperature also, hence the temperature dependent study of Raman scattering becomes more and more significant. The advent of very high power laser sources may show up these theoretical finding in near future.

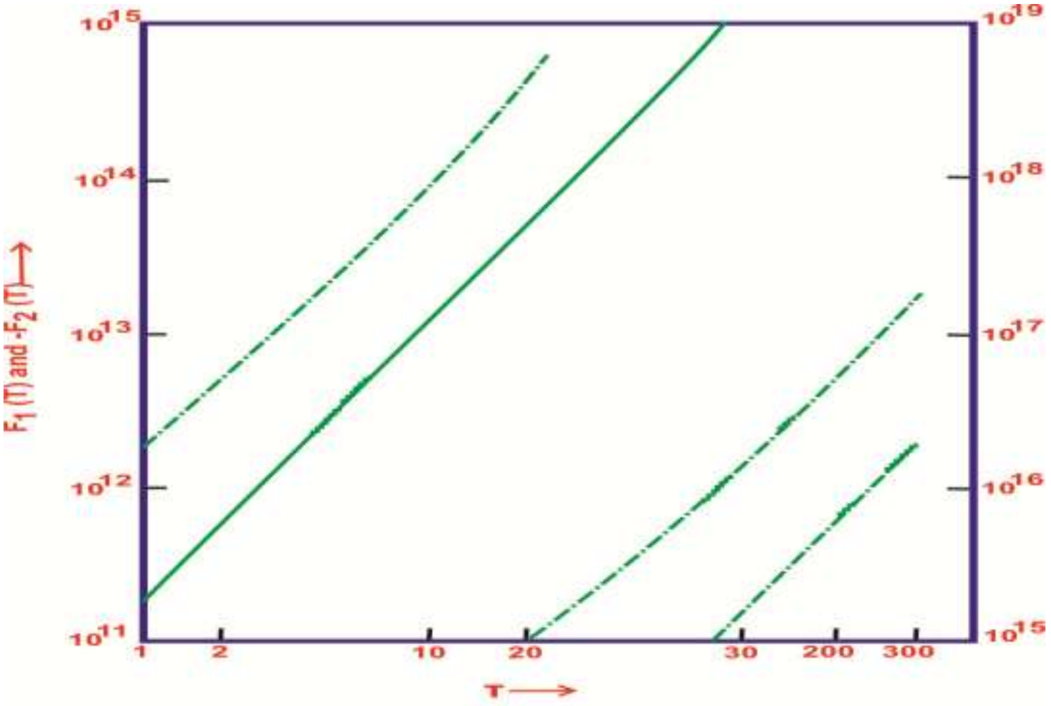

Fig. 1 Variation of F_1 (T) and F_2 (T) With Temperature

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