# Infrared absorption in defect induced anharmonic solids

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**Abstract.** The infrared absorption in isotopically disordered anharmonic crystals is theoretically investigated using double time thermal Green's function technique. The Hamiltonian used in the study includes the cubic and quartic anharmonicities alongwith the terms associated with the crystal defects. The total i.r. absorption in impurity induced anharmonic crystals is obtained as the sum of diagonal and non-diagonal terms. The diagonal terms can be further separated into defect dependent, anharmonic and impurity-anharmonicity cross term contributions, the non-diagonal terms chiefly depend on mass change parameters and vanishes in the absence of impurities. The impurity-anharmonicity interactions involve defect and anharmonic parameters simultaneously and contribute significantly to the absorption coefficient. A brief description of impurity modes, phonon life times and strength of absorption is given with special reference to impurity-anharmonicity interactions to study the effects of temperature, frequency and impurity concentration on optical absorption.

**Keywords.** Impurity induced anharmonic i.r. absorption coefficient; impurity-anharmonicity interactions; impurity modes; phonon life times; renormalized restsrahl frequency; strength of absorption.

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## 1. Introduction

A large number of properties of real crystals, e.g. lattice thermal conductivity, phonon life times, thermal expansion, dielectric properties etc. as observed by infrared spectroscopy cannot be explained in the harmonic approximation. These properties can be investigated by considering the cubic and higher order terms in the expansion of potential energy, which couple the normal modes and give rise to phonon–phonon interactions. The presence of substitutional impurities in a crystal, on the other hand leads to the phonon interaction. The phonon field is localized around the defect sites, and removes the translational symmetry of crystal, leading to modifications in the phonon frequency spectrum. Consequently, the frequency and symmetry dependent physical properties of crystals are also altered [1–7]. Further there is possibility of interactions among the phonons present in anharmonic and localized fields. The study of various properties of impurity induced anharmonic crystals is thus essentially a many body problem.

The experimental observations on ionic crystals [8] exhibit a set of temperature dependent i.r. absorption bands consisting of a central maximum and several side bands on the shorter wavelength side of the central absorption peak. The phonon line width and the central frequency of main absorption line vary with temperature [9]. In the harmonic approximation, the nuclear displacements in the second quantized

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crystal Hamiltonian give rise to the temperature independent delta function peaks at long wavelength transverse optic mode frequencies [3, 10, 11] which are not in complete accord with the experimental results. The discrepancies between theory and experiments can be well understood by considering the anharmonic effects. The anharmonic terms cause the broadening of lattice absorption bands in the immediate vicinity of the peak and produce a set of temperature dependent absorption bands with the temperature dependent central frequency of main absorption line. Considering the defect and anharmonic terms in the crystal Hamiltonian simultaneously one finds that as a result of removal of translational symmetry not only the localized modes but the entire frequency spectrum of host crystal becomes i.r. active.

The aim of this paper is to investigate the behaviour of defect induced anharmonic crystal in the presence of external radiation and the effect of the interactions of anharmonic phonon fields with localized phonon fields on i.r. absorption. In §2 the general formulation of the problem is given and §3 deals with the defect induced anharmonic Hamiltonian and the evaluation of thermodynamic double time Green's functions (GF). Section 4 is devoted to the derivation of optical absorption coefficient and the strength of absorption with highlights on defect-anharmonicity interactions. The contribution of defect and anharmonicity to the impurity modes, phonon life times, central frequency of perturbed mode is evaluated in §5 followed by a brief discussion in §6.

## 2. Formulation of the problem

The optical absorption coefficient related to the displacement–displacement Green's function [12] can be written in the form

$$\alpha(\omega) = (4\pi\omega/\eta c) \operatorname{Im} \left[ \sum_{\alpha,\beta} \sum_{\substack{l,l' \\ i,j}} e_i(l) e_j(l') t_\alpha t_\beta (2\pi/\hbar) \langle\!\langle U_{i\alpha}(l,t); U_{j\beta}(l'O) \rangle\!\rangle_\omega \right], \quad (1)$$

where $\eta$ is the refractive index, $c$ is the velocity of electromagnetic radiation of frequency $\omega$, $e_i(l)$ is the charge on the $i$-th atom in the $l$-th unit cell, $t_\alpha$ is the polarization vector of the incident radiation and $\langle\!\langle \cdots \rangle\!\rangle_\omega$ stands for the Fourier transform of the thermodynamic double time GF. In diatomic crystal and a reduced mass $\mu^{-1} = M_1 M_2 (M_1 + M_2)^{-1}$, equation (1) becomes

$$\alpha(\omega) = (4\pi N e^2/\eta c)(\pi\mu\omega/\omega_0) \operatorname{Im} G_{kk'}(\omega), \quad (2)$$

where

$$G_{kk'}(\omega) = \langle\!\langle A_k(t); A_{k'}(0) \rangle\!\rangle_\omega, \quad (3)$$

and $\omega_0$ is the transverse optical mode frequency at $k = 0$ for the host lattice. Equation (2) suggests that the form of imaginary GF will exhibit the nature of absorption bands, thus the evaluation of GF becomes the essential part of the problem.

## 3. Hamiltonian and Green's functions

### 3.1 Defect induced anharmonic Hamiltonian

Let us consider a three-dimensional bravais crystal with total number of $N$ atoms, out of which $n$ lattice sites are occupied by the randomly distributed substitutional

impurity atoms each of mass $M'$, while the rest $(N - n)$ lattice sites are filled by the host atoms each of mass $M$. Let us consider the impurity concentration low enough to avoid the interaction among impurity atoms. The introduction of impurities greatly modifies the force constants between host and impurity along with the change of mass. In the present case we shall restrict the theory to the nearest neighbour force constants. The Hamiltonian for this problem can be written in the form

$$H = H_0 + H_D + H_A, \tag{4}$$

where $H_0$ is the unperturbed Hamiltonian and $H_D$ and $H_A$ are the defect and anharmonic parts of Hamiltonian, respectively. The various components of Hamiltonian are given by

$$H_0 = (\hbar/4)\sum_k \omega_k(A_k^* A_k + B_k^* B_k) \tag{5a}$$

$$H_D = -\hbar \sum_{k_1,k_2} [C(\mathbf{k}_1,\mathbf{k}_2)B_{k_1}B_{k_2} - D(\mathbf{k}_1,\mathbf{k}_2)A_{k_1}A_{k_2}], \tag{5b}$$

$$H_A = \sum_{s \geq 3} \sum_{k_1,\ldots,k_s} \hbar V_s(\mathbf{k}_1,\mathbf{k}_2,\ldots,\mathbf{k}_s)A_{k_1}A_{k_2},\ldots,A_{k_s}, \tag{5c}$$

where the parameters $C(\mathbf{k}_1,\mathbf{k}_2)$ and $D(\mathbf{k}_1,\mathbf{k}_2)$ account for the mass change and force constant change, respectively [13]. $V_s(\mathbf{k}_1,\mathbf{k}_2,\ldots,\mathbf{k}_s)$ are the Fourier transforms of the anharmonic force constants of the host lattice. They are completely symmetric with respect to the pair of indices $\mathbf{k}$ [14]. In the present analysis we shall use the cubic and quartic anharmonicities.

### 3.2 *Green's functions*

We now consider the evaluation of single particle Green's function

$$G_{kk'}(t,0) = \lang\!\langle A_k(t); A_{k'}(0) \rangle\!\rangle, \tag{6}$$

using Hamiltonian (4) and using the equation of motion method of Zubarev [15]. Following the technique of successive approximations [13,16] and some tedious algebra, the GF can be evaluated as

$$G_{kk'}(\omega + i\varepsilon) = \omega_k \eta_{kk'}/\pi[\omega^2 - \tilde{\omega}_k^2 + 2i\omega_k\Gamma_k(\omega)], \tag{7}$$

with

$$\eta_{kk'} = \delta_{kk'} + 4C(-\mathbf{k},\mathbf{k}')\omega_k^{-1}, \tag{8}$$

and

$$\tilde{\omega}_k^2 = \bar{\omega}_k^2 + 2\omega_k\Delta_k(\omega), \tag{9}$$

where $\Gamma_k(\omega)$, $\Delta_k(\omega)$ and $\bar{\omega}_k$ describe the phonon half width, phonon frequency shift and the phonon frequency of renormalized mode, respectively.

$$\bar{\omega}_k^2 = \omega_k^2 + (\omega_k/2\pi)\{\langle [F_k(t), B_{k'}^*(t')]^0 \rangle + (4/\omega_k)\sum_{k_1}C(\mathbf{k},-\mathbf{k}_1)$$

$$\langle [F_k(t), B_{k'},(t')]^0 \rangle + 8(\omega^2 - \omega_k^2)C(-\mathbf{k},\mathbf{k})/\omega_k\}_{t=t'}, \tag{10}$$

$$\Delta_k(\omega) = \Delta_k^D(\omega) + \Delta_k^A(\omega) + \Delta_k^{AD}(\omega) \tag{11}$$

and

$$\Gamma_k(\omega) = \Gamma_k^D(\omega) + \Gamma_k^A(\omega) + \Gamma_k^{AD}(\omega), \tag{12}$$

where the superscripts D, A and AD stand for the defect, anharmonic and defect-anharmonicity cross term contributions, respectively. The various terms appearing in (10) to (12) are given by

$$F_k(t) = F_k^{(1)}(t) + F_k^{(2)}(t) + F_k^{(3)}(t), \tag{13a}$$

with

$$F_k^{(1)}(t) = 4\pi \sum_{k_1} [D(-\mathbf{k}, \mathbf{k}_1) + (\omega_{k_1}/\omega_k)C(-\mathbf{k}, \mathbf{k}_1)]A_{k_1}$$

$$+ 16\pi \sum_{k_1,k_2} [C(-\mathbf{k}, \mathbf{k}_1)D(-\mathbf{k}_2, \mathbf{k}_1)\omega_k^{-1}A_{k_1}, \tag{13b}$$

$$F_k^{(2)}(t) = 2\pi \sum_{s \geqslant 3} \sum_{k_1,\dots,k_{s-1}} sV_s(\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_{s-1}, -\mathbf{k})A_{k_1}A_{k_2}\cdots A_{k_{s-1}}, \tag{13c}$$

$$F_k^{(3)}(t) = 16\sum_{k_1} |C(\mathbf{k}_1, -\mathbf{k})\omega_k^{-1}|^2 F_{k_1}^{(2)}(t), \tag{13d}$$

$$\Delta_k^D(\omega) = 8P\sum_{k_1} R(-\mathbf{k}, \mathbf{k}_1)R^*(-\mathbf{k}, \mathbf{k}_1)\omega_{k_1}(\omega^2 - \tilde{\omega}_{k_1}^2)^{-1} \tag{14a}$$

$$\Delta_k^A(\omega) = 18P \sum_{k_1,k_2} |V_3(\mathbf{k}_1, \mathbf{k}_2, -\mathbf{k})|^2\eta_1[S_{+1}\omega_{+\alpha}(\omega^2 - \omega_{+\alpha}^2)^{-1}$$

$$+ S_{-1}\omega_{-\alpha}(\omega^2 - \omega_{-\alpha}^2)^{-1}] + 48P \sum_{k_1,k_2,k_3} |V_4(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, -\mathbf{k})|^2$$

$$\eta_2[S_{+2}\omega_{+\beta}(\omega^2 - \omega_{+\beta}^2)^{-1} + 3S_{-2}\omega_{-\beta}(\omega^2 - \omega_{-\beta}^2)^{-1}], \tag{14b}$$

$$\Delta_k^{AD}(\omega) = 16P\sum_{k_1} |C(-\mathbf{k}, \mathbf{k}_1)\omega_k^{-1}|^2 \Delta_{k_1}^A(\omega), \tag{14c}$$

$$\Gamma_k^D(\omega) = 8\pi\varepsilon(\omega)\sum_{k_1} R(-\mathbf{k}, \mathbf{k}_1)R^*(-\mathbf{k}, \mathbf{k}_1)\omega_{k_1}\delta(\omega^2 - \tilde{\omega}_{k_1}^2) \tag{15a}$$

$$\Gamma_k^A(\omega) = 18\pi\varepsilon(\omega) \sum_{k_1,k_2} |V_3(\mathbf{k}_1, \mathbf{k}_2, -\mathbf{k})|^2\eta_1[S_{+1}\omega_{+\alpha}\delta(\omega^2 - \omega_{+\alpha}^2)$$

$$+ S_{-1}\omega_{-\alpha}\delta(\omega^2 - \omega_{-\alpha}^2)] + 48\pi\varepsilon(\omega) \sum_{k_1,k_2,k_3} |V_4(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, -\mathbf{k})|^2$$

$$\eta_2[S_{+2}\omega_{+\beta}\delta(\omega^2 - \omega_{+\beta}^2) + 3S_{-2}\omega_{-\beta}\delta(\omega^2 - \omega_{-\beta}^2)], \tag{15b}$$

and

$$\Gamma_k^{AD}(\omega) = 16\sum_{k_1} |C(-\mathbf{k}, \mathbf{k}_1)\omega_k^{-1}|^2 \Gamma_{k_1}^A(\omega) \tag{15c}$$

with

$$R(\mathbf{k}_1, \mathbf{k}_2) = (\omega_{k_2}/\omega_{k_1})C(\mathbf{k}_1, \mathbf{k}_2) + D(\mathbf{k}_1, \mathbf{k}_2)$$

$$+ 4\sum_{k_2'} \omega_{k_1}^{-1} C(\mathbf{k}_1, \mathbf{k}_2')D(-\mathbf{k}_2', \mathbf{k}_2), \tag{15d}$$

Here $F_{k_1}^{(2)}(t)$, $\Delta_{k_1}(\omega)$ and $\Gamma_{k_1}^A(\omega)$ are obtained after replacing $\mathbf{k}$ by $\mathbf{k}_1$ in $F_k^{(2)}(t)$, $\Delta_k^A(\omega)$ and $\Gamma_k^A(\omega)$, respectively. In the above equations $P$ stands for the principle value and

some undefined terms have the forms

$$\eta_1 = \omega_{k_1}\omega_{k_2}/\tilde{\omega}_{k_1}\tilde{\omega}_{k_2}; \quad \eta_2 = \omega_{k_1}\omega_{k_2}\omega_{k_3}/\tilde{\omega}_{k_1}\tilde{\omega}_{k_2}\tilde{\omega}_{k_3}, \tag{16}$$

$$S_{\pm 1} = n_{k_2} \pm n_{k_1}; \quad S_{\pm 2} = 1 \pm n_{k_1}n_{k_2} + n_{k_2}n_{k_3} \pm n_{k_3}n_{k_1}, \tag{17}$$

$$\omega_{\pm\alpha} = \tilde{\omega}_{k_1} \pm \tilde{\omega}_{k_2}; \quad \omega_{\pm\beta} = \tilde{\omega}_{k_1} \pm \tilde{\omega}_{k_2} \pm \tilde{\omega}_{k_3}, \tag{18}$$

and

$$n_k = \coth(\beta\hbar\omega_k/2) \tag{}$$

## 4. Infrared lattice absorption

### 4.1 *The absorption coefficient*

The linear i.r. absorption coefficient $\alpha(\omega)$ can easily be obtained on substitution of imaginary part of GF given by (7) into (2) as

$$\alpha(\omega) = (8\pi Ne^2\mu/\eta c)\omega_k\eta_{kk'}\Gamma_k(\omega)[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2\Gamma_k^2(\omega)]^{-1}. \tag{19}$$

Let us examine (19) in more detail. $\alpha(\omega)$ can be separated into diagonal and non-diagonal components as

$$\alpha(\omega) = \alpha_d(\omega) + \alpha_{nd}(\omega), \tag{20}$$

where

$$\alpha_d(\omega) = P_c\omega_k\Gamma_k(\omega)[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2\Gamma_k^2(\omega)]^{-1}, \tag{21}$$

and

$$\alpha_{nd}(\omega) = 4P_cC(-\mathbf{k},\mathbf{k}')\Gamma_k(\omega)[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2\Gamma_k^2(\omega)]^{-1}|_{k \neq k'} \tag{22}$$

with

$$P_c = (8\pi Ne^2\mu/\eta c). \tag{}$$

The non-diagonal contribution $(\mathbf{k} \neq \mathbf{k}')$ chiefly depends on the mass change parameter $C(-\mathbf{k},\mathbf{k}')$ and is significant only in impure crystals and vanishes for pure crystals. The Lorentzian line shape distribution appearing in (21) and (22) can be simplified under reasonable approximations for the small value of $\Gamma_k(\omega)$ far from the fundamental absorption peak $\omega = \omega_k$, to give

$$\alpha_d(\omega) = P_c\omega_k\Gamma_k(\omega)(\omega^2 - \tilde{\omega}_k^2)^{-2}, \tag{23}$$

and

$$\alpha_{nd}(\omega) = 4P_cC(-\mathbf{k},\mathbf{k}')\Gamma_k(\omega)(\omega^2 - \tilde{\omega}_k^2)^{-2}|_{k \neq k'} \tag{24}$$

The diagonal contribution to absorption coefficent can be separated into three contributions, namely defect contribution $\alpha_d^D(\omega)$; anharmonic contribution $\alpha_d^A$ and defect anharmonic contribution $\alpha_d^{AD}(\omega)$. These contributions can be arranged as

$$\alpha_d(\omega) = \alpha_d^D(\omega) + \alpha_d^A(\omega) + \alpha_d^{AD}(\omega), \tag{25}$$

$$\alpha_d^D(\omega) = P_c\omega_k\Gamma_k^D(\omega)(\omega^2 - \tilde{\omega}_k^2)^{-2}, \tag{26a}$$

$$\alpha_d^A(\omega) = P_c\omega_k\Gamma_k^A(\omega)(\omega^2 - \tilde{\omega}_k^2)^{-2}, \tag{26b}$$

and

$$\alpha_d^{AD}(\omega) = P_c\omega_k\Gamma_k^{AD}(\omega)(\omega^2 - \tilde{\omega}_k^2)^{-2}. \tag{26c}$$

The defect dependent diagonal contribution to the absorption coefficient can be

obtained on deriving an explicit relation for $\Gamma_k^D(\omega)$, thus

$$\alpha_d^D(\omega) = (VP_c/8\pi v^3)(M_0/N\mu)^2(\omega_k\omega_{k_1}/\omega_0)(\omega^2 - \tilde{\omega}_k^2)^{-2}(1-f)$$
$$+ [(1-f)\omega_{k_1}^4 - 2\omega_{k_1}^2(\mu/M_0^2)\gamma], \tag{27}$$

where $\gamma$ is some sort of force constant change parameter and $f$ is the defect concentration. The first term in the square bracket describes the mass change contribution while the second describes the force constant change effects. For low concentration of impurities $\alpha_d^D(\omega)$ varies linearly with $f$. For the heavy impurity case, (27) describes the resonant band mode absorption at $\omega_R = \omega_k$ within the frequency band of host crystal. This contribution is, however, a temperature independent contribution and describes the sharp absorption peaks around $\tilde{\omega}_{k_1} = \pm \tilde{\omega}_k$ if one reasonably approximates $\tilde{\omega}_k$ as temperature independent. The temperature dependent contribution to $\alpha_d(\omega)$ is due to the anharmonic part $\alpha_d^A(\omega)$ and is of the form

$$\alpha_d^A(\omega) = [(\lambda P_c V\omega_0^2/16\pi N\beta\hbar a_0 c^2) + (\hbar P_c/48M)(a_0\hbar\lambda'\phi_4 V/4\pi^2\beta\phi_2 c^3)^2$$
$$+ (\omega_R^2 + \tilde{\omega}_{k_1}^2)]\omega_k(\omega^2 - \tilde{\omega}_k^2)^{-2}, \tag{28}$$

Here $\lambda$ and $\lambda'$ are some parameters and $\phi_2$ and $\phi_4$ are second and fourth order force constants, respectively. The first term in the square bracket describes the cubic-anharmonic contribution to $\alpha_d^A(\omega)$ and varies linearly with temperature. The second term shows the quartic-anharmonic contribution and exhibits $T^2$ dependence on absorption coefficient.

The phonons present in the anharmonic fields definitely interact with the phonons of localized fields giving rise to the impurity-anharmonicity interactions. This interaction can be described by the phonon half width $\Gamma_k^{AD}(\omega)$ and shows the linear dependence on impurity concentration but linear $(T)$ as well as non-linear $(T^2)$ dependence on temperature. This contribution gives rise to an additional absorption $\alpha_d^{AD}(\omega)$ which can take place as a result of coupling of anharmonic coefficients with defect parameters and is given by

$$\alpha_d^{AD}(\omega) = [0.0394 P_c M_0 f V/\pi\mu\phi_2\beta c^2]\{[MM_0(1-f)\lambda/N^2\hbar a_0\mu]$$
$$+ \lambda' a_0\hbar^2\phi_4/\pi\phi_2\beta c\}\omega_k^5(\omega^2 - \tilde{\omega}_k^2)^{-2}, \tag{29}$$

$\alpha_d^{AD}(\omega)$ is of the finite magnitude, because the cross term $\Gamma_k^{AD}(\omega)$ shows the dependence of the form $(b_1 + b_2 T)f(1-f)\omega^4 T$, where $b_1$ and $b_2$ are cubic and quartic anharmonic interaction parameters with defects, respectively. The magnitudes of $b_1$ and $b_2$ remain always comparable with the individual defect or anharmonic contribution.

The non-diagonal absorption coefficients also add up some features to the impurity-anharmonicity interactions. The mass difference parameters couple with $\Gamma_k(\omega)$, i.e., mass change interference with $\Gamma_k(\omega)$ giving a multiplying effect to the $\Gamma_k^D(\omega)$, $\Gamma_k^A(\omega)$ and $\Gamma_k^{AD}(\omega)$ and fractionally increases the absorption in the immediate vicinity of absorption peaks at the frequencies $\pm \tilde{\omega}_{k_1}$, $\pm \omega_{+\alpha}$ and $\pm \omega_{\pm\beta}$. The configuration of GF shows that $\omega_{-\beta}$ has three frequencies, namely: $\tilde{\omega}_{k_1} - \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3}$, $\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} - \tilde{\omega}_{k_3}$, and $-\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3}$. Equation (26) reveals that the i.r. absorption coefficient consistently depends on $\Gamma_k(\omega)$, hence, the general trend of variation of $\alpha(\omega)$ with impurity concentration, frequency and temperature can be studied from the nature of $\Gamma_k(\omega)$. The frequency dependence of $\Gamma_k(\omega)$ is depicted in figures 1 and 2. Due to
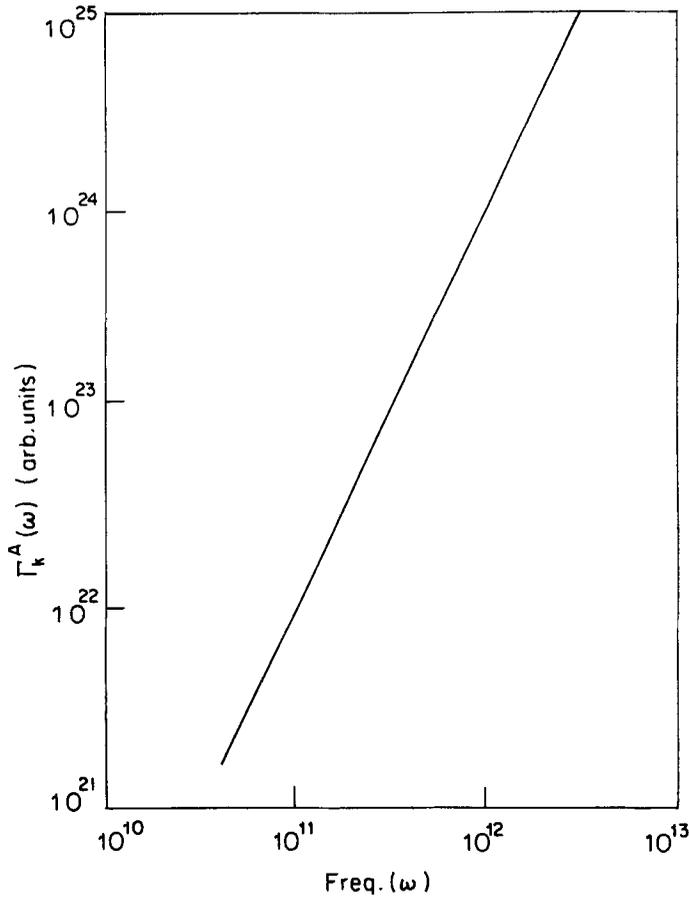
**Figure 1.** Variation of $\Gamma_k^A(\omega)$ with frequency $\omega$.

the lack of several constants we have taken the forms of $\Gamma_k(\omega)$ as

$$\Gamma_k^D(\omega) = A_1 f(1-f)\omega^4 + A_2 f\omega^2, \tag{30a}$$

$$\Gamma_k^{(3)}(\omega) = B_1 \omega^2 T, \tag{30b}$$

$$\Gamma_k^{(4)}(\omega) = B_2 \omega^2 T^2, \tag{30c}$$

$$\Gamma_k^{3D}(\omega) = b_1 f(1-f)\omega^4 T, \tag{30d}$$

$$\Gamma_k^{4D}(\omega) = b_2 f(1-f)\omega^4 T^2, \tag{30e}$$

where $A$, $B$ and $b$ are parameters. It should be noted here that the frequencies given in the above equations are taken independent of temperature. In general, in the anharmonic approximation the renormalized frequencies are temperature dependent and show strong impurity dependence in impure crystals. The temperature and impurity concentration dependence of $\Gamma_k(\omega)$ is shown in figures 3 and 4, respectively. The figures show that $\alpha(\omega)$ shows strong frequency temperature and impurity concentration dependence, for different phonon bound states.
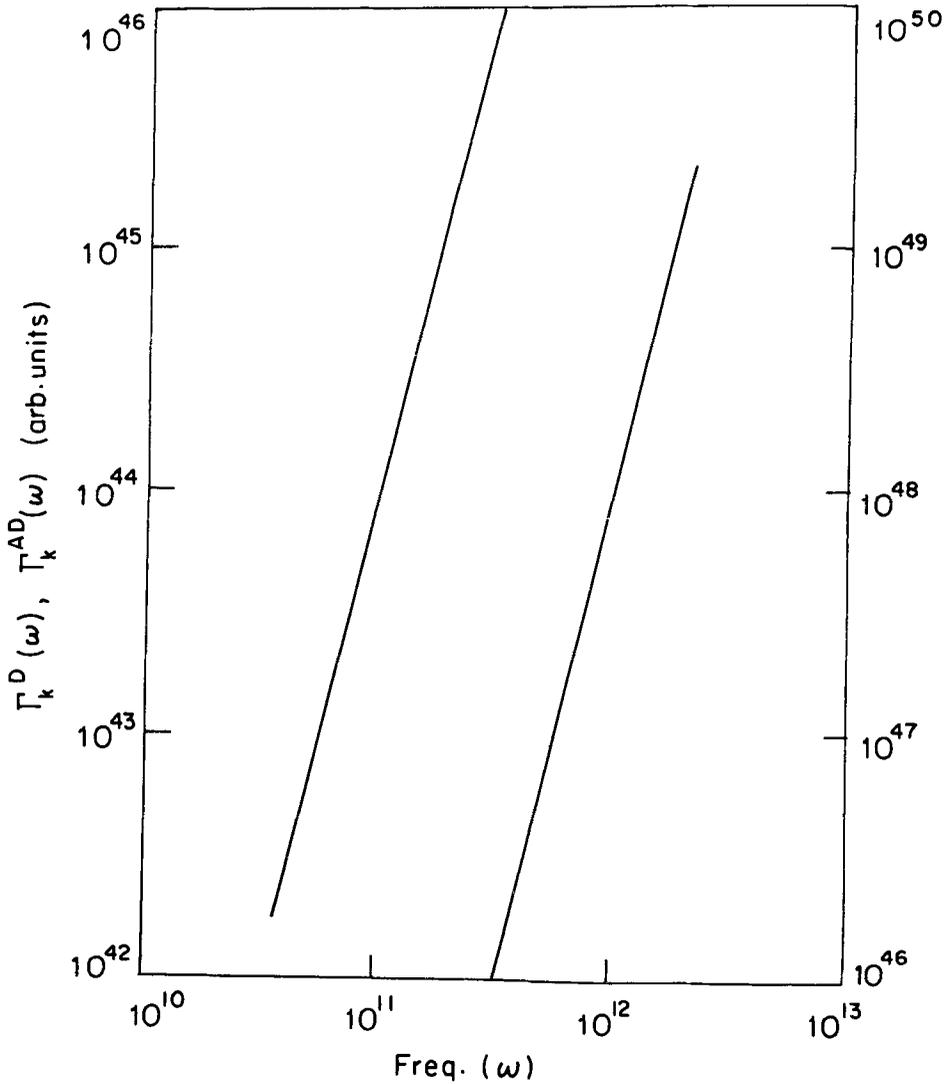
**Figure 2.** Variation of $\Gamma_k^D(\omega)$ and $\Gamma_k^{AD}(\omega)$ with frequency $\omega$.

### 4.2 The strength of absorption

For small values of phonon frequency widths the i.r. absorption coefficient will simply be a delta function peak (impurity case) and the strength of the delta function can be given by [12],

$$\alpha(\omega)|_{G,L} = 2\pi\omega_{G,L}\{2\omega - [(\partial/\partial\omega)\Delta_k(\omega)]\}|\omega_k = \tilde{\omega}_0, \qquad (31)$$
$$\omega = \omega_{G,L}$$

and is the fraction of the absorption at the local or gap mode. Here the subscripts G and L stand for gap and localized modes, respectively. The fractional contribution to the strength of absorption by the simultaneous involvement of interacting anhar-
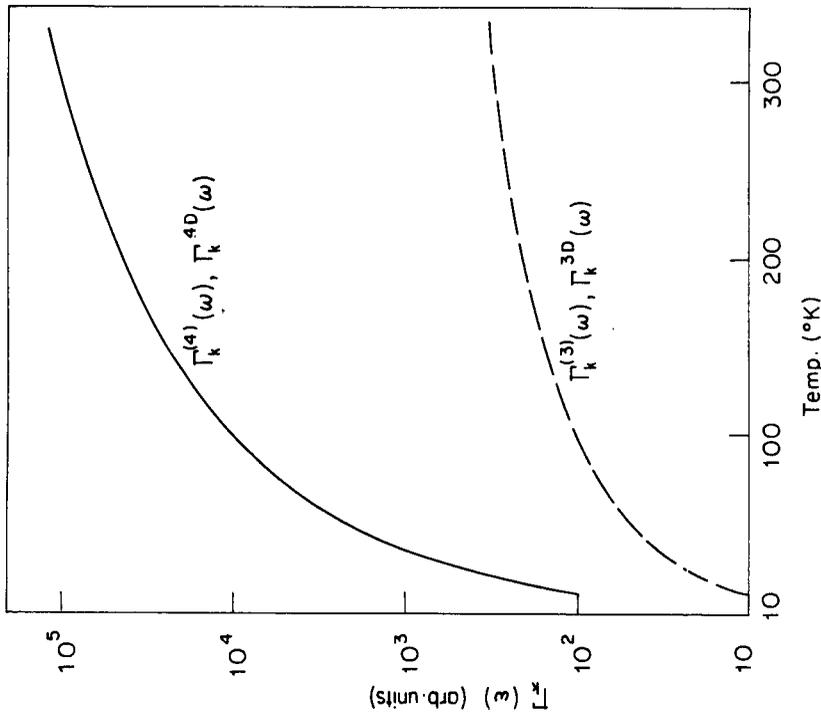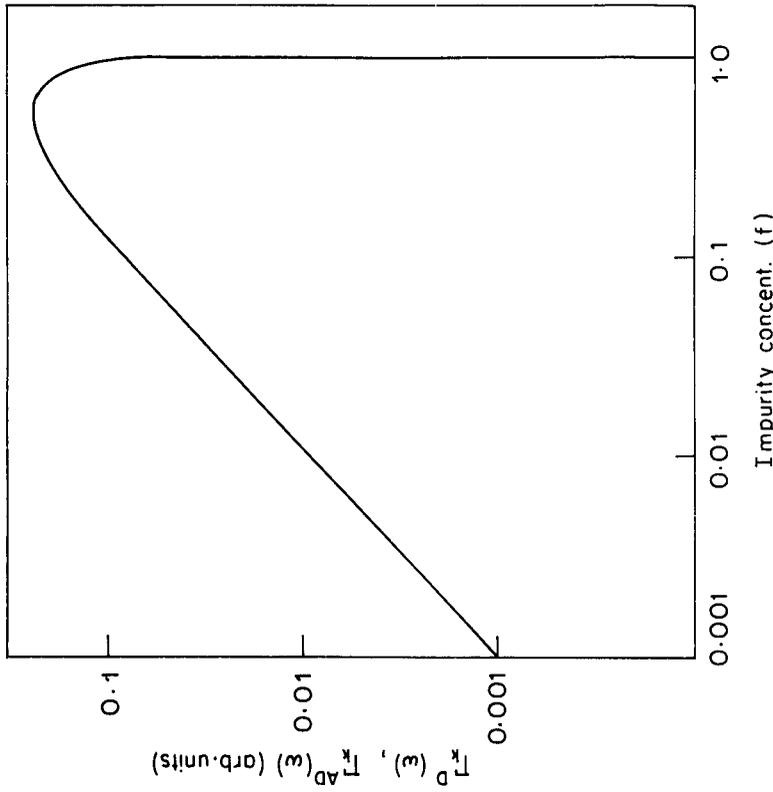
**Figure 4.** Variation of $\Gamma_k^D(\omega)$ and $\Gamma_k^{AD}(\omega)$ with impurity concentration $f$.



**Figure 3.** Variation of $\Gamma_k(\omega)$ with temperature $T$.

monicity and defects will be due to the $\Delta_k^{AD}(\omega)$. Thus

$$\alpha^{-1}(\omega_{G,L}) = (1/\pi)\left[1 + 192\sum_{k_1}|C(\mathbf{0},\mathbf{k}_1)\omega_{k_1}^{-1}|^2\left\{3\sum_{k_2}|V_3(\mathbf{k}_1,\mathbf{k}_2,-\mathbf{k}_1)|^2\right.\right.$$

$$\eta_1[S_{+1}\omega_{+\alpha}(\omega_{G,L}^2 - \omega_{+\alpha}^2)^{-1} + S_{-1}\omega_{-\alpha}(\omega_{G,L}^2 - \omega_{-\alpha}^2)^{-1}]$$

$$+ 8\sum_{k_1,k_2,k_3}|V_4(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,-\mathbf{k}_1)|^2\eta_2[S_{+2}\omega_{+\beta}(\omega_{G,L}^2 - \omega_{+\beta}^2)^{-1}$$

$$\left.\left.+ 3S_{-2}\omega_{-\beta}(\omega_{G,L}^2 - \omega_{-\beta}^2)^{-1}]\right\}\right]^{-1}. \qquad (32)$$

This expression obviously shows that $\alpha^{-1}(\omega_{G,L})$ depends on the interacting mass difference parameter $C(\mathbf{0},\mathbf{k}_1)$ and anharmonic terms simultaneously. The mass difference parameter gives the linear impurity concentration dependence while the cubic and quartic anharmonic terms reveal, at the same time, $T$ and $T^2$ dependence, respectively.

## 5. Impurity modes and renormalized frequency

If $\Delta_k(\omega)$ is a smooth function of $\omega$ then the solutions of the equation

$$\omega^2 - \tilde{\omega}_k^2 - 2\omega_k\Delta_k(\omega) = 0, \qquad (33)$$

are simply the perturbed modes of the host crystal. But in the present analysis $\Delta_k(\omega)$ is a large valued function and no longer remains a smooth function of $\omega$. This nature corresponds to the nature of impurity modes such as localized, resonance or gap modes. The frequency of these modes can be determined by the relation according to the nature of impurity

$$\Delta_k(\omega) = 0. \qquad (34)$$

The optical absorption for a perfect harmonic crystal takes place at $\mathbf{k} = 0$ or $\omega = \omega_0$ the reststrahl frequency of zero phonon width. For impurity case this condition is no longer true and i.r. absorption takes place by impurity modes even in the acoustical branch (charged impurity case). The gap or localized mode frequency can be evaluated from (33) in the form

$$\omega_{G,L}^2 = [\tilde{\omega}_0^2 + 2\omega_0\Delta_0(\tilde{\omega}_0) - 16\omega_0 I_1(\tilde{\omega}_{k_1})][1 + 16\omega_0 I_2(\tilde{\omega}_{k_1})]^{-1}, \qquad (35)$$

with

$$\Delta_0(\tilde{\omega}_0) = [\Delta_0^A(\omega) + \Delta_k^{AD}(\omega)]\Big|_{\substack{\omega=\tilde{\omega}_0 \\ k=0}}, \qquad (36)$$

$$I_1(\tilde{\omega}_{k_1}) = [V/(2\pi)^3]\int R(\mathbf{0},\mathbf{k}_1)R^*(\mathbf{0},\mathbf{k}_1)(\omega_{k_1}/\tilde{\omega}_{k_1}^2)k_1^3\sin\theta\,dk_1\,d\theta\,d\phi, \qquad (37a)$$

and

$$I_2(\tilde{\omega}_{k_1}) = [V/(2\pi)^3]\int R(\mathbf{0},\mathbf{k}_1)R^*(\mathbf{0},\mathbf{k}_1)(\omega_{k_1}/\tilde{\omega}_{k_1}^4)k_1^3\sin\theta\,dk_1\,d\theta\,d\phi. \qquad (37b)$$

In (35) $\tilde{\omega}_0$ is known as 'renormalized reststrahl frequency' and can be obtained in

the form

$$\tilde{\omega}_0^2 = \omega_0^2 + 4\omega_0[C(\mathbf{O},\mathbf{k}_1) + D(\mathbf{O},\mathbf{k}_1)] + 20\sum_{k_1} C(\mathbf{O},\mathbf{k}_1)D(\mathbf{O},\mathbf{k}_1)$$

$$+ 4[\omega_0 + 4C(\mathbf{O},\mathbf{k}_1)R(\mathbf{O},\mathbf{k}') + 4\omega_0[1 + C(\mathbf{O},\mathbf{k}_1)]\omega_0^A, \tag{38}$$

with

$$\omega_0^A = 6\left[-3\sum_{k_1} V_3(\mathbf{k}',\mathbf{k}',\mathbf{O})\, V_3(-\mathbf{k},\mathbf{k}_1,-\mathbf{k}_1)\mathbf{N}_{k_1}/\omega_0\right]$$

$$+ V_4(\mathbf{k}',\mathbf{k}',\mathbf{k}',O)N_{k'}. \tag{39}$$

These expressions show that the renormalized reststrahl frequency is heavily influenced by defects, anharmonicities and cross terms. If we make a reasonable approximation to evaluate the frequency in the immediate vicinity of $\omega_k$, the $N_k$ function can be replaced by $[2n(\omega) + 1]$, where $n(\omega)$ is the Planck's distribution function. Hence the inclusion of anharmonic terms leaves the renormalized mode frequency and the reststrahl frequency no more temperature independent but they vary as $\{a + b[\exp(\beta\hbar\omega_k/2) - 1]^{-1}\}$ for various temperatures. The impurity concentration also affects the frequency. These evaluations, thus support the experimentally observed facts about the temperature dependence of frequency and appearance of side bands in the absorption spectra with temperature dependent widths.

## 6. Discussion

We have obtained general expressions for the i.r. absorption coefficient, strength of absorption, renormalized reststrahl frequency and gap or localized mode frequency for an anharmonic crystal containing randomly distributed substitutional impurities of low concentration. We have taken into account the cubic and quartic anharmonicities along with the mass difference and force constant change terms arising due to the defects. The absorption coefficient obtained in the present study can be expressed as a sum of two terms, $\alpha_d(\omega)$ and $\alpha_{nd}(\omega)$. The diagonal term can be written as a sum of three terms $\alpha_d^D(\omega)$, $\alpha_d^A(\omega)$ and $\alpha_d^{AD}(\omega)$. $\alpha_d^D(\omega)$ gives the dominant contribution arising due to the interacting defects and is independent of temperature but varies linearly with impurity concentration. However, a very weak non-linear impurity concentration $(f^2)$ also appears in the same expression. This term is also responsible for weak band mode absorption and makes the entire perturbed mode i.r. active. The second term $\alpha_d^A(\omega)$ arises due to the anharmonic effects. Anharmonic contribution appears as a sum of cubic and quartic contributions. The temperature enters the $\alpha_d(\omega)$ due to the anharmonicities and shows linear $T$-dependence for the third order and non-linear $T^2$-dependence for the fourth order anharmonic terms.

The third contribution to $\alpha_d(\omega)$ is $\alpha_d^{AD}(\omega)$ and occurs due to the simultaneous involvement of anharmonic and defect parameters. This term arises as a result of interference among the phonons present in the localized fields and that in anharmonic fields. This term chiefly depends on both mass difference parameters and temperature and varies as $\sim(b_1 T + b_2 T^2)$. This contribution is certainly of non-vanishing and finite magnitude comparable to either of $\alpha_d^D(\omega)$ or $\alpha_d^A(\omega)$ and is an incremental absorption at the same frequencies of anharmonic contributions. The impurity anharmonicity interaction effects are also dominant for the non-vanishing non-diagonal contribution, which chiefly depend on the mass difference parameter and vanishes in

the absence of impurities. The non-diagonal term remains significant for all sorts of impurities and shows nearly similar temperature variation as that of $\alpha_d^{AD}(\omega)$.

The reststrahl frequency, normal mode frequencies and gap or local mode frequencies has also been obtained in renormalized forms. These frequencies are found dependent on temperature and impurity concentration.

It emerges from the present study that all the salient features of optical absorption and perturbed mode frequencies can be discussed by considering the presence of both defects and anharmonic terms in the crystal Hamiltonian. The impurity-anharmonicity interactions and non-diagonal terms are the new features of the theory incorporating the impurity concentration as well as temperature. In this paper we have not evaluated the various contributions to the absorption coefficient due to the great complexity of computation, which mainly arises due to the involvement of a broad range of phonon frequencies and anharmonicities. But a general trend in the variation of $\Gamma_k(\omega)$ shows with changing frequency, temperature and impurity concentration, on which the i.r. absorption coefficient depends.

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