

Anharmonic effects on lattice resonant modes of impure metallic crystals

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Abstract. The effect of lattice anharmonicity on the resonant modes of dilute impurities for Au–Cu, Au–Ag and W–Cr metallic systems are studied from the poles of the double time temperature dependent impure Green's function of these crystals. The third order force constants used in the present work are derived assuming the systems to obey the Lennard-Jones potential. The inclusion of lattice anharmonicity has been found to increase the resonant frequency which depends upon the mass defect, force constant change parameter and the impurity concentration terms. Some interesting features about the phase shift and the change in width of the vibrational spectrum are reported at room temperature for the isotopic defects and the defects interacting with host atoms. The results are found to be in qualitative agreement with the experiments on the systems considered.

Keywords. Resonant modes; mass defect; force constant; phase shift.

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1. Introduction

In the harmonic approximation, the normal modes of an impure lattice containing a heavy mass impurity consist of resonant mode and a set of other lattice modes. When the resonance occurs at low frequency as a sharp peak in the density of states, it is a reasonable approach to regard the resonance as being in a single mode (Alexander *et al* 1970, Barker and Sievers 1975).

When the potential energy is purely harmonic the spectrum consists of a sharp line at the resonance frequency. When the anharmonic terms are also included this line may shift, broaden and change in strength. In general the anharmonicity would also induce other lines to appear elsewhere in the spectrum. These are side bands and two phonon transitions which overlap the fundamental or the zero lattice phonon (ZLP) line. The effect of temperature on the impurity induced absorption line has been studied by many workers (Svensson *et al* 1965; Behera and Deo 1967; Weber and Siebert 1968). The contribution of anharmonic terms to the broadening and shifting of absorption lines due to impurity modes have also been discussed by many authors (Maradudin *et al* 1971; Bruesch 1982; Roy 1985; Roy and Kundu 1987) specially with reference to high frequency localized modes treating the anharmonic terms by perturbation theory. In the present work we adopt the Green's function technique (Zubarev 1960; Doniach and Sondheimer 1974) to evaluate the anharmonic effects on the lattice resonant modes for various impure metallic systems considering the effects of force constant change and the impurity concentration. Our calculations follow from simple assumption that the only lattice modes coupled to the resonant

mode could be represented by a Debye spectrum. This assumption, although was able to explain the width and shift data, where it was found that only low frequency lattice modes were effectively coupled to the resonant modes, gives only qualitative results on the changes in width and shift.

2. Theory

In the present work we propose to study the impurity resonant modes assuming the host atoms to obey the Lennard-Jones potential for simple cubic lattices containing impurities of mass M' which replace the host atoms of mass M .

The Hamiltonian of the impure system in second quantized notation using the well known normal mode transformations (Maradudin *et al* 1971) can be written as

$$H = \hbar \sum_k \omega_k a_k^\dagger a_k + \hbar \sum_{k,q} U(k,q) B_k B_q + \hbar \sum_{k,q} V(k,q) A_k A_q + \hbar \sum_{k,q,p} V'(k,q,p) A_k A_q A_p \quad (1)$$

where A_k and B_k are phonon field and momentum operators which can be written in terms of phonon creation and annihilation operators a_k^\dagger , a_k (Roy 1985) and

$$U(k,q) = \frac{\lambda}{4N} \sum_{\alpha,i=1}^{N_d} e_\alpha(k) e_\alpha(q) [\omega_k \omega_q]^{1/2} \exp [i(\mathbf{k} + \mathbf{q}) \cdot \mathbf{R}_i] \quad (2)$$

$$V(k,q) = \frac{\tau}{4N} \sum_{\alpha,i=1}^{N_d} e_\alpha(k) e_\alpha(q) [\omega_k \omega_q]^{1/2} \exp [i(\mathbf{k} + \mathbf{q}) \cdot \mathbf{R}_i] \quad (3)$$

$$V'(k,q,p) = \frac{\lambda'}{4N} \sum_{\alpha,i=1}^N \frac{e_\alpha(k) e_\alpha(q) e_\alpha(p)}{[\omega_k \omega_q \omega_p]^{1/2}} \exp [i(\mathbf{k} + \mathbf{q} + \mathbf{p}) \cdot \mathbf{R}_i] \quad (4)$$

where λ and τ are mass and force constant change parameters which can be given as

$$\lambda = (1 - M/M') \quad (5a)$$

$$\tau = \frac{\phi''(i) - \phi''(0)}{\phi''(0)} \quad (5b)$$

and

$$\lambda' = \frac{\phi'''(0)}{3M} (\hbar/2MN)^{1/2}. \quad (5c)$$

Here $\phi''(i)$, $\phi''(0)$ and $\phi'''(0)$ represent the nearest neighbour impurity-host, host-host second order force constants and host-host third order force constant respectively.

It may be noted that in writing (4) we have neglected the anharmonic contribution arising due to impurity part of the potential for it will be negligibly small. The information about the impurity modes can be obtained from the denominator of the fourier transformed impurity Green's function in the matrix form (Tripathi and Behera 1974).

$$\mathbf{G}_{\mathbf{k},q}(\omega) = \delta_{k,-q} \mathbf{G}_{\mathbf{k}}^{(0)}(\omega) + \delta_{k,-q} \mathbf{G}_{\mathbf{k}}^{(0)}(\omega) \sum_h \chi(-k,h) \mathbf{G}_{\mathbf{h},q}(\omega) \quad (6)$$

where $G_k^{(0)}(\omega)$ is the unperturbed Green's function and $\chi(-k, h)$ is the kernel in matrix form (Roy and Kundu 1987). The matrix Green's function can be written in the characteristic form of Dyson's equation by iteration of (6) as (Doniach and Sondheimer 1974)

$$\mathbf{G}_{k,q}(\omega) = \delta_{k,-q} \mathbf{G}_k^{(0)}(\omega) + \delta_{k,-q} \mathbf{G}_k^{(0)}(\omega) \Lambda(\omega) \mathbf{G}_k^{(0)}(\omega) \quad (7)$$

where $\Lambda(\omega)$ is the modified vertex function given by

$$\Lambda(\omega) = \sum_k \chi(-k, k) [\hat{1} - \mathbf{G}_k^{(0)}(\omega) \chi(-k, h)]^{-1}. \quad (8)$$

3. Impurity resonant modes

For random non interacting impurities at the lattice sites, the Green's function (7) has to be averaged over all possible configurations of the impurities. Following the Langer's method (1961) for averaging of the vertex function in (8) and then solving (7) we get

$$\langle G_{k,q}(\omega) \rangle = \frac{G_k^{(0)}(\omega)}{[\hat{1} - \langle \Lambda q \rangle G_k^{(0)}(\omega)]}. \quad (9)$$

The physically measurable quantities are related to the imaginary part of the impure Green's function $\langle G_{k,q}(\omega + i\varepsilon) \rangle$: which usually gives the observed line shape—a peak distribution around a frequency $\omega = \omega_k$. The impurity modes can be determined by equating to zero the real part of the denominator of (9) considering the cubic anharmonic part and the effect of concentration of the defects in addition to mass and force constant changes. It may be noted that for dilute impurity case we only consider up to the terms linear in concentration ($C_d = N_d/N$) where N_d is the number of impurities in N number of hosts. The ratio of the impurity resonant frequency to the Debye frequency ($\omega_R/\omega_D = X$) may be obtained from the following

$$f_h(x) + f_{ch}(x) + f_{h'}(x) + f_{ch'}(x) = (1 - \lambda)(1 + \tau) \quad (10)$$

where

$$f_h(x) \simeq 3x^2(\lambda - \tau + \frac{5}{4}\lambda\tau) - 3x^3[\frac{1}{2}(\lambda - \tau) + \lambda\tau] \ln\left(\frac{1+x}{1-x}\right) \quad (11a)$$

$$f_{ch}(x) \simeq \frac{9}{8}(\tau^2 + \lambda^2)C_d \left[1/3 + 2x^2 + \frac{7}{4}x^3 \ln\left(\frac{1+x}{1-x}\right) \right] - 2\lambda\tau C_d \left[x^2 - \frac{3}{4}x^3 \ln\left(\frac{1+x}{1-x}\right) \right] \quad (11b)$$

$$f_{h'}(x) \simeq k_\beta T(1 - \lambda/3)K \left[\frac{(1-\lambda)}{48} + \frac{(5-7\lambda)}{96}x^2 - \frac{\lambda}{32}x^3 \ln\left(\frac{1+x}{1-x}\right) \right] \quad (11c)$$

$$f_{ch'}(x) \simeq k_\beta T(1 - \lambda/3)K\lambda(1 + C_d)x^2$$

where

$$K = [\phi_{(0)}''' / \phi_{(0)}''^3].$$

The third order force constant appearing in (11c) and (11d) may be obtained by choosing a suitable potential for the system. In this work the third order force constant is evaluated from elastic constants and Bulk moduli using the Lennard-Jones potential for the host impurity systems mentioned, as has been done earlier (Dobrzynski and Maradudin 1973). Equations (11a, b, c, d) represent the harmonic, harmonic with effect of impurity concentration, anharmonic and anharmonic with effect of impurity concentration terms respectively. The above equations together may therefore be taken as the general expression for the impurity resonant mode solution. Equation (11a, b) for isotopic defect ($\tau=0$) together lead to a well known result (Behera and Deo 1967) on the resonant frequency in the limit of long wave length phonons

$$X^2 \simeq \frac{1 - \frac{3}{5} C_d \lambda \varepsilon}{3\varepsilon(1 + \frac{6}{5} \lambda C_d)} \quad (12)$$

where

$$\varepsilon = \lambda/(1 - \lambda).$$

The consideration of the impurity concentration therefore reduces the resonant frequency of the heavy impurities vibrating in light hosts.

4. Frequency shift and the line width

The frequency shift $\Delta(\omega)$ and the line width $\Gamma(\omega)$ are evaluated from (9) by separating the real and imaginary parts and are given by the following expressions (Fetter and Walecka 1971)

$$\Delta(\omega) = \frac{[1 - \text{Re } D_k(\omega + i\varepsilon)]}{[1 - \text{Re } D_h(\omega + i\varepsilon)]^2 + [\text{Im } D_h(\omega + i\varepsilon)]^2} \quad (13)$$

and

$$\Gamma(\omega) = \frac{2|\text{Im } D_k(\omega + i\varepsilon)|_{\omega = \omega_R}}{\left. \frac{d}{d\omega} [1 - \text{Re } D_k(\omega + i\varepsilon)] \right|_{\omega = \omega_R}} \quad (14)$$

for heavier impurities in lighter solids, the resonant modes lie within the maximum frequency of the host crystal. Although the Debye approximation fails for band edge resonance, one can compare the low frequency resonant modes with the Debye cut off frequency using the Debye approximation for the host. Within the bands of the allowed frequencies of the host crystal the singular points in the frequency spectrum of three dimensional crystal occur and depending upon the impurity mass, the bond shortening and the impurity concentration a critical frequency can be defined at which the frequency spectrum itself is continuous. The typical values of the ratio of line width to the Debye cut off frequency at resonance without and with anharmonicity are 0.30 and 0.312 for Au-Cu system with impurity concentration $C_d = 0.93$ At. % and $\tau = 0.45$. The τ and ω_D values in our calculations have been selected from the reported results of Grow *et al* 1978 (for Au-Cu, $\omega_D = 2.078 \times 10^{13}$ rad/s). At very low frequency the half width goes to zero and the resonance degenerates into a delta function. For the resonance near the band edge the spectrum of mode gives a finite width because of large damping effect whereas above the maximum frequency the

modes become localized. Many workers (Maradudin 1966; Elliott *et al* 1965) suggested that the resonant mode properties are influenced by lattice anharmonicity to a much larger extent than the local modes. The contribution of the local anharmonicity is neglected from the fact that the local anharmonicity appears as due to the change in third order force constant which has been found to be much smaller than the lattice anharmonicity. Although the contribution of the quartic anharmonic term to the line width and shift would have given a better physical result but because of problems of decoupling the impure Green's function and involvement of heavy computation, the contribution of quartic term to the width and shift are not considered in the present case (Jindal and Kalus 1983).

5. Discussion

The effects of inclusion of anharmonic terms in the potential energy, to the broadening and shifting of the absorption lines due to localized and resonant modes have been widely discussed particularly with reference to high frequency localized modes for ionic crystals (Maradudin 1966; Lowndes 1972). The present calculations are performed for impure metallic crystals where the impurity masses and the impurity-host force constant changes are such that the impurities generate the resonant modes.

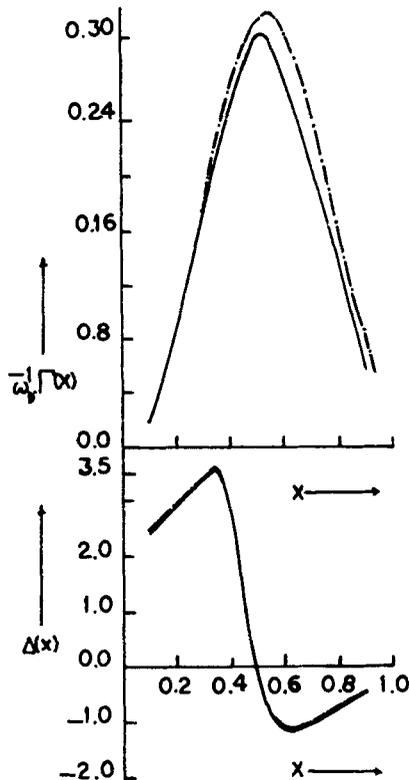


Figure 1. Plot of resonant width and shift for Au-Cu System ($\lambda = 0.68$, $\tau = 0.45$ and $K = 0.18 \times 10^{14} \text{ erg}^{-1}$, $C_d = 0.93 \text{ At. \%}$). (—) Harmonic effect; (---) total effect including anharmonicity.

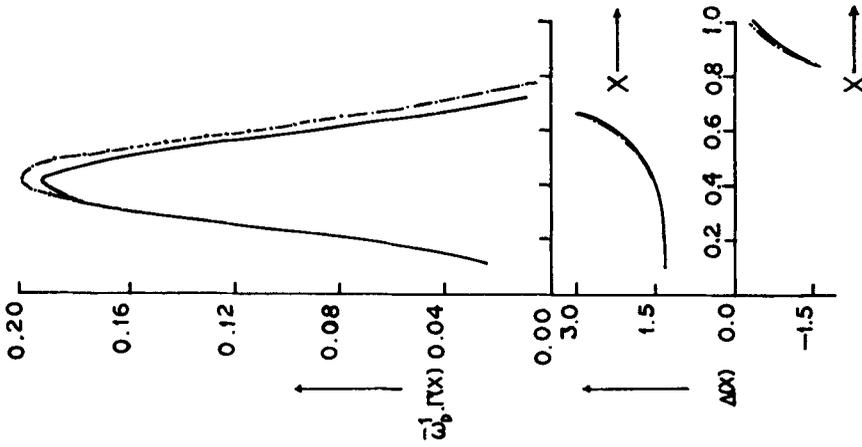


Figure 2. Curves showing the variations of width and shift for Au-Ag System ($\lambda = 0.45$, $\tau = 0.47$ and $K = 0.17 \times 10^{14} \text{ erg}^{-1}$, $C_d = 1.0$ At. %). (—) Harmonic effect; (---) Total effect including anharmonicity.

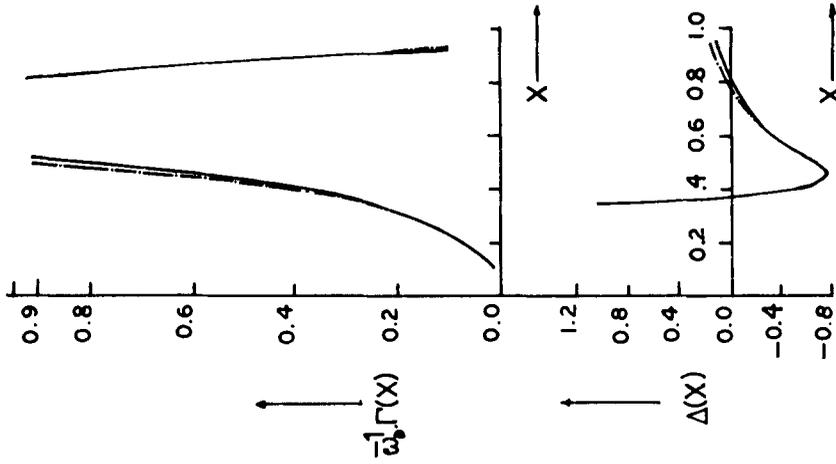


Figure 3. Variations of resonant width and shift for W-Cr System ($\lambda = 0.72$, $\tau = 0$ and $K = 0.16 \times 10^{14} \text{ erg}^{-1}$, $C_d = 0.3$ At. %). (—) Harmonic effect; (---) Total effect including anharmonicity.

The resonance frequency values are obtained by solving (10) numerically with the help of (11a-d). The numerical results obtained for three systems Au-Cu, Au-Ag and W-Cr are shown in figures 1 to 3. The results shown for the line widths in different systems are in qualitative agreement with those reported earlier (Svensson *et al* 1965). The inclusion of anharmonic term and the impurity concentrations significantly change the resonant frequencies in different Debye solids which may be attributed to the damping of resonant modes. The damping may be given by the shift of the maxima in each case from the resonance point. The widths corresponding to resonance are represented by the dotted lines in the curves. It is interesting to note that the effect of inclusion of anharmonic term shifts both the line width and the frequency shift to the higher side.

We therefore conclude from calculations on lattice anharmonic effects of the resonant frequency of the impure metallic systems for a definite small concentration of impurity in a metallic system that the anharmonic term increases the line width by a considerable amount and lowers the resonant frequency and also depends on the impurity concentration. Also there is a phase shift between the host and the impurity motion which alters the width of the vibrational spectra. The shift depends on the mass and force constant parameters.

However, the correct temperature dependence of these metallic crystals can be obtained and compared with the experimental data by considering a rather real crystal potential with impurity-impurity interactions. At large impurity concentration one has in general a mixed crystal behaviour in which the characteristic absorption of mixed crystals will show concentration dependence. Therefore the theory on impure crystals should be able to provide a criterion to predict one, two or mixed mode behaviour and reproduce the correct concentration dependence of the mode frequencies as well as that of the absorption strength. However, a quantitative comparison can be made by further improving the theory introducing proper metallic crystal potential and also applying the symmetry behaviours of the crystals.

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