

Lattice dynamics of impurity clusters. Application to pairs

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Abstract. A general solution is obtained for the lattice dynamics of a cluster of n -impurity atoms using the double-time Green's function formalism. The cluster is characterized by n -mass defect and m -force constant change parameters. It is shown that this general solution for the Green's function for the n -impurity cluster can also be expressed in terms of the Green's function for the $(n-1)$ -impurity cluster. As an application, the cluster impurity modes for a pair are calculated using the Debye model for the host lattice dynamics. The splitting of the high frequency local modes and nearly zero frequency resonant modes due to pairs show an oscillatory behaviour on varying the distance of separation between the two impurity atoms. These oscillations are most prominent for two similar impurities and get damped for two dissimilar impurities or if one of the impurities produces a force constant change. The predictions of the calculation provide qualitative explanation of the data obtained from the infrared measurements of the resonant modes in mixed crystal system of $\text{KBr}_{1-c}\text{Cl}_c$: Li^+ and $\text{KBr}_{1-c}\text{I}_c$: Li^+ .

Keywords. Impurity modes; impurity clusters; pair modes.

1. Introduction

Recently there has been a lot of emphasis on the study of phonon modes associated with impurity clusters. Specially, it has become possible to identify experimentally local, gap and resonant modes associated with pairs (e.g. see Barker and Sievers 1975 for a review) and cluster of three impurities (Schneider 1973) using infrared and Raman scattering techniques on samples with high concentrations of impurities. The pair modes are identified by noting that the strength of absorption for these is proportional to the square of the concentration. The first observation of pair-local-modes was by Schaefer (1960) simultaneously with that of single impurity local modes due to U centres in NaCl. He observed a splitting of the U centre local mode on alloying NaCl with RbCl and attributed the new modes to $\text{Rb}^+ \text{H}^-$ pairs. Since then such splitting of U centre local modes in mixed crystals has also been reported by Mirlin and Reshina (1966) and Barth and Fritz (1967). However the most extensively studied pair local modes were those associated with B-Li pairs in Si (Barker and Sievers 1975). Subsequently, U centre pairs (pairs of similar impurities) were produced in KCl and local mode due to these were observed by de Souza *et al* (1970). Gap and resonant modes associated with pairs of Br^- and Cl^- in KI have been reported by Ward and Clayman (1974) and Ward *et al* (1974). There is one report by Schneider (1973) of production of three impurity clusters of $\text{H}^- \text{Na}^+ \text{H}^-$ in KCl and the observation of local modes due to these.

Many simplified three-dimensional model calculations have been attempted (summarised in Behera and Patnaik 1975) to determine the pair-mode frequencies. It has also been shown that pair (Behera and Patnaik 1975; Patnaik and Behera 1976; Behera and Patnaik 1976) and three impurity cluster (Nayak and Behera 1978) calculations within the diatomic linear chain framework give results in qualitative agreement with experimental data. Eventhough a general Green's function formalism and an exact solution for an n -mass-defect-impurity cluster had been given by Maradudin (1965), it has not been made use of for calculating cluster mode frequencies. Takeno (1965), using a simple model for the dynamics of the host crystal has shown that as the distance of separation between the two impurity atoms in a pair decreases the splitting of the single impurity degenerate local mode gradually increases, till the lower one enters into the continuum and gives rise to a high frequency resonant mode. He has dealt at length on the observation of this high frequency resonant mode by infrared absorption. On the other hand, Elliott and Pfeuty (1967) have stressed on the calculation of local modes in Si containing various kinds of pairs, namely (i) pair of two substitutional impurities (ii) a substitutional and an interstitial impurity pair and (iii) an interstitial pair. They have also considered various force constant change models for the above mentioned pairs and compared their results with the experimental data.

In what follows, we generalise the exact solution given by Maradudin (1965), to take into account m -nearest neighbour force constant changes produced by the n -impurities forming the cluster. The nearest-neighbour force constant changes are considered in the separable kernel approximation (Behera and Deo 1967; Tripathi and Behera 1974) and the general solution to the n -cluster problem obtained using the matrix Green's function formalism of Tripathi and Behera (1974). Further, it will be shown that the matrix Green's function for the n -impurity cluster can be expressed in terms of the Green's function for the $(n-1)$ -impurity cluster. As an example of this general theory the case of an impurity pair where one of the impurity atoms could produce a nearest neighbour force constant change is considered. Treating the host dynamics in the Debye model, analytic solutions for very high frequency local modes and nearly zero frequency resonant modes of the pair are obtained. The width of the resonant mode is also calculated. It was shown that contrary to the results of Takeno (1965) the pair local mode frequencies and splitting oscillates as the distance of separation between the two impurity atoms are varied. The results are used to analyse the experimental data on local and resonant modes due to impurity pairs in mixed crystal systems.

The organisation of the rest of the paper is as follows: The general theory is developed in §2. §3 is devoted to the application of the theory to pair calculations. In the concluding §(4) the results of §3 are compared with the experimental data on mixed crystal impurity systems.

2. The general solution

An exact solution to the problem of a crystal containing n -impurity atoms substituted at random sites $\{\mathbf{R}_i\}$ ($i=1, 2, \dots, n$) was obtained by Maradudin (1965). However, this solution will also correspond to a single cluster of n -impurity atoms if the impurity sites $\{\mathbf{R}\}$ are chosen to be those belonging to the cluster. It has been shown

by Maradudin (1965) that for this problem the Fourier transform of the Green's function obeys the integral equation

$$G_{kk'}(\omega) = \delta_{k,-k'} G_k^{(0)}(\omega) + G_k^{(0)}(\omega) \sum_{k_1} U(k, k_1) G_{k,k'}(\omega), \quad (1)$$

where $G_k^{(0)}(\omega)$ and $U(k, k')$ are respectively the Fourier transforms of the unperturbed (host) Green's function and the perturbation. If the perturbation $U(k, k')$ is of the separable form

$$U(k, k') = \sum_{i=1}^n \lambda_i u_i(k) u_i(k'), \quad (2)$$

then the solution of (1) can be written as

$$\begin{aligned} G_{kk'}(\omega) &= \delta_{k,-k'} G_k^{(0)}(\omega) + G_k^{(0)}(\omega) \sum_{i,j=1}^n \lambda_i u_i(k) \\ &\times [\hat{1} - \hat{M}(\omega)]_{ij}^{-1} u_j(-k') G_{k'}^{(0)}(\omega), \end{aligned} \quad (3)$$

where
$$M_{ij}(\omega) = \lambda_i \sum_k u_i(k) G_k^{(0)}(\omega) u_j(-k). \quad (4)$$

If the impurities are considered as only mass defects then the separability of the kernel $U(k, k')$ as given by (2) is exact. Hence the derivation of (3) does not involve any approximations. We wish to generalise this solution to the case where the n -impurity atoms produce m -force constant changes. Thus there will be two different kinds of perturbation namely (i) the change in the mass due to impurity substitution which will perturb the kinetic energy and the Fourier transform of which will be denoted by $U(k, k')$ and (ii) the changes in the force constants due to impurity substitution which perturb the harmonic potential the Fourier transform of which will be denoted by $V(k, k')$. In general the kernel $V(k, k')$ is not of a separable form (equation (2)). However, it has been demonstrated by Behera and Deo (1967) and Behera and Tripathi (1974) that one can get reasonably good agreement with experimental data by assuming a simple separable form for the kernel $V(k, k')$, i.e.

$$V(k, k') = \sum_{j=1}^m \tau_j v_j(k) v_j(k'). \quad (5)$$

The mass (λ_i) and force constant (τ_j) change parameters entering (4) and (5) are defined as

$$\lambda_i = (M - M_I^{(i)})/M_I^{(i)} \text{ and } \tau_j = (\Phi_j - \Phi_0)/\Phi_0, \quad (6)$$

where $M_I^{(i)}$ and M are respectively the masses of the i th impurity and that of the host atoms. Similarly Φ_j and Φ_0 are the j th modified force constant resulting from the substitution of an impurity atom and the host force constant respectively. It has been shown by Tripathi and Behera (1974) that the Green's function equations for this generalised problem reduces in form to that of (1) if one works with the matrix

Green's function given below. Here we follow the paper of Tripathi and Behera (1974) with slightly altered notations.

$$\hat{G}_{kk'}(t) = \begin{pmatrix} G_{kk'}^{AA}(t) & G_{kk'}^{AB}(t) \\ G_{kk'}^{BA}(t) & G_{kk'}^{BB}(t) \end{pmatrix} = \begin{pmatrix} \langle A_k(t); A_{k'}(0) \rangle & \langle A_k(t); B_{k'}(0) \rangle \\ \langle B_k(t); A_{k'}(0) \rangle & \langle B_k(t); B_{k'}(0) \rangle \end{pmatrix}, \quad (7)$$

where the notation on the r.h.s. of (7) is the same as that used by Zubarev (1960), and

$$A_k = a_k + a_{-k}^\dagger; \quad B_k = a_k - a_{-k}^\dagger, \quad (8)$$

a_k (a_k^\dagger) being the phonon annihilation (creation) operator. The Green's function (1) simply corresponds to the BB element of (7). The Fourier transformed matrix Green's function $\hat{G}_{kk'}(n, m; \omega)$ for the n -impurity cluster, producing m -force constant changes, is determined from the equation

$$\hat{G}_{kk'}(n, m; \omega) = \delta_{k,-k'} \hat{G}_k^{(0)}(\omega) + \hat{G}_k^{(0)}(\omega) \sum_{k_1} \hat{W}(k, k_1) \hat{G}_{k,k'}(n, m; \omega), \quad (9)$$

where

$$G_k^{(0)}(\omega) = \frac{1}{\pi(\omega^2 - \omega_k^2)} \begin{pmatrix} \omega_k - \omega \\ \omega - \omega_k \end{pmatrix} = \begin{pmatrix} G_k^{(0)AA}(\omega) & -G_k^{(0)AB}(\omega) \\ G_k^{(0)BA}(\omega) & -G_k^{(0)BB}(\omega) \end{pmatrix}, \quad (10)$$

is the host Green's function, and

$$\hat{W}(k, k_1) = \begin{pmatrix} V(k, k_1) & 0 \\ 0 & U(k, k_1) \end{pmatrix} = \sum_{i=1, j=1}^{n, m} \hat{\phi}_i^j(k) \hat{\phi}_i^j(k_1) \hat{\Lambda}_i^j, \quad (11a)$$

$$\hat{\Lambda}_i^j = \begin{pmatrix} \pi \tau_j & 0 \\ 0 & -\pi \lambda_i \end{pmatrix}, \quad (11b)$$

$$\hat{\phi}_i^j(k) = \begin{pmatrix} v_j(k) & 0 \\ 0 & u_i(k) \end{pmatrix}. \quad (11c)$$

At this stage it is worth pointing out that it is not possible to obtain an equation similar to (9) for a single element of the matrix Green's function \hat{G} as was explicitly demonstrated by Tripathi and Behera (1974). Instead one gets a set of four coupled equations, which only when written in the matrix form reduce to the single equation (9). Noting that the structure of (9) is identical to that of (1), one can immediately write down the solution to (9) in analogy with (3); i.e.

$$\begin{aligned} \hat{G}_{kk'}(n, m, \omega) &= \delta_{k,-k'} \hat{G}_k^{(0)}(\omega) + \hat{G}_k^{(0)}(\omega) \sum_{j=1}^m \sum_{p=1}^n \hat{\Lambda}_i^j \\ &\times \hat{\phi}_i^j(k) [\hat{1} - \hat{G}_0(\omega) \hat{\Lambda}]_{ip}^{-1} \hat{\phi}_p^i(-k') \hat{G}_k^{(0)}(\omega). \end{aligned} \quad (12)$$

In (12) each element of $\hat{G}_0(\omega)$ and $\hat{\Lambda}$ are 2×2 matrices and are given by

$$[\hat{G}_0]_{ip}^{jl} = \sum_k \hat{\phi}_i^j(k) \hat{G}_k^{(0)}(\omega) \hat{\phi}_p^l(-k), \quad (13)$$

and
$$[\hat{\Lambda}]_{ip}^{jl} = \hat{\Lambda}_i^j \delta_{jl} \delta_{ip}. \quad (14)$$

Thus (12) provides the most general solution to the impurity cluster problem.

In an earlier paper (Chandralekha Devi and Behera 1978) it has been shown that for an impurity producing local distortion of the lattice, the general solution for the Green's function with m force constant changes (which represent the lattice distortion) can be expressed in terms of a Green's function involving $(m-1)$ force constant changes. Following a similar procedure one can show (the derivation of the result is given in Chandralekha Devi and Behera 1977) that the n -cluster Green's function (12) can be expressed in terms of the $(n-1)$ cluster Green's function as

$$\begin{aligned} \hat{G}_{kk'}(nm; \omega) &= \hat{G}_{kk'}(n-1, m-1; \omega) + \sum_{k_1 k_2} \hat{G}_{kk_1}(n-1, m-1; \omega) \\ &\times \hat{\Lambda}_n^m \hat{\phi}_n^m(k_1) [\hat{1} - \hat{G}(n, m; \omega) \hat{\Lambda}_n^m]^{-1} \hat{\phi}_n^m(k_2) \hat{G}_{k_2 k'}(n-1, m-1; \omega), \end{aligned} \quad (15a)$$

where
$$\hat{G}(n, m; \omega) = \sum_{q_1 q_2} \hat{\phi}_n^m(q_1) \hat{G}_{q_1 q_2}(n-1, m-1; \omega) \hat{\phi}_n^m(q_2). \quad (15b)$$

It can be shown that the impurity denominator appearing in (15a) is equivalent to the $\begin{pmatrix} m & m \\ n & n \end{pmatrix}$ th element of that of (12) (see Chandralekha Devi and Behera 1977 for the proof). In (15) the reference crystal which acts as the host for the n th impurity atom producing the m th force constant change is the one with $(n-1)$ impurity atoms with $(m-1)$ force constant changes. The solution in the form of (15) is very convenient for generalising the present single cluster theory to the case of an alloy where multipole scattering from clusters (see Elliott *et al* 1974) is taken into account. Equations analogous to (15) have been written down by Kumar and Joshi (1975) and later on derived by Bloom and Mattis (1977) for the electronic systems in connection with the cluster theory of the alloys.

It is clear from (12) and (15) that the frequencies of the modes associated with the cluster of n -impurity atoms can be calculated from the condition

$$\det [\hat{1} - \hat{G}_0(\omega) \hat{\Lambda}] = 0. \quad (16)$$

Furthermore, it can be easily verified that in the limiting case of an n -mass-defect impurity cluster, one can set all $\tau_j = 0$ and recover Maradudin's result for the component Green's function $G_{kk}^{BB}(\omega)$. However, the equation for $G_{kk}^{AA}(\omega)$ does not reduce to the form of (3).

3. Application to pairs

We shall use the results obtained in § 2 to calculate the local and resonant mode frequencies associated with the vibrations of a cluster consisting of a pair of impurities. The results thus obtained will be compared with those obtained in the pair calculations of Takeno (1965) and Elliott and Pfeuty (1967). In order to compare the results with the experimental data on local and resonant modes in mixed crystal systems, we shall consider a pair where one of the impurity atoms produces a change in the nearest neighbour force constants, whereas the other impurity atom is a simple mass defect. The modes of vibration of such a pair can be calculated from (16) by setting the impurity denominator for $n=2$ and $m=1$ equal to zero, i.e.

$$\begin{aligned} & \{1 - \pi\tau_1 [G_0^{AA}(\omega)]_{11}\} D_2(\omega) - \pi\tau_1 \{ \pi\lambda_1 [G_0^{AB}(\omega)]_{11} D_1^{(2)}(\omega) [G_0^{BA}(\omega)]_{11} \\ & + \pi\lambda_2 [G_0^{AB}(\omega)]_{12} D_1^{(1)}(\omega) [G_0^{AB}(\omega)]_{21} + 2(\pi\lambda_1)(\pi\lambda_2) [G_0^{AB}(\omega)]_{11} \\ & \times [G_0^{BB}(\omega)]_{12} [G_0^{BA}(\omega)]_{21} \} = 0, \end{aligned} \quad (17)$$

where $D_2(\omega)$ and $D_1^{(i)}(\omega)$ which are the impurity denominators for the case of a mass-defect pair, and that for the i th single impurity respectively are given by

$$\begin{aligned} D_2(\omega) &= (1 - \pi\lambda_1 [G_0^{BB}(\omega)]_{11})(1 - \pi\lambda_2 [G_0^{BB}(\omega)]_{22}) \\ &\quad - (\pi\lambda_1)(\pi\lambda_2) [G_0^{BB}(\omega)]_{12} [G_0^{BB}(\omega)]_{21}, \end{aligned} \quad (18)$$

$$\text{and} \quad D_1^{(i)}(\omega) = 1 - \pi\lambda_i [G_0^{BB}(\omega)]_{ii}. \quad (19)$$

It is easily seen that (17) reduces to (18) when $\tau_1=0$ and it reproduces the result for a single impurity with nearest neighbour force constant changes (Behera and Tripathi 1974) when $\lambda_2=0$. The various host Green's function matrix elements entering (17)–(19) are given by (13). In order to evaluate these elements we make the following simplifying assumptions. (i) The forms of $u_i(k)$ and $v_j(k)$ are taken to be the same as those given in Tripathi and Behera (1974). (ii) The Debye model is assumed for the host lattice dynamics, and (iii) it is assumed that the local mode frequency $\omega_L \gg \omega_D$ and the resonant mode frequency $\omega_R \rightarrow 0$ for the evaluation of the \mathbf{k} integrals. Here $\omega_D (=ck_D)$ is the Debye cut off frequency, $k_D (=2\pi/\lambda_D)$ is the Debye wave vector and λ_D is the Debye wavelength. These parameters are different for different hosts. These assumptions permit us to evaluate the local and resonant mode frequencies analytically.

3.1. Local modes

For the high frequency local mode the real and imaginary parts of the Green's function matrix elements can be evaluated, and are given by

$$\text{Re} [G_0^{BB}(\omega)]_{ii} = \frac{3}{5\pi} \left(\frac{\omega_D}{\omega} \right)^2, \quad \text{Im} [G_0^{BB}(\omega)]_{ii} = 0, \quad (20a)$$

$$\operatorname{Re} [G_0^{BB}(\omega)]_{ij} = \frac{3}{\pi} \left(\frac{\omega_D}{\omega} \right)^2 f(k_D a_{ij}), \quad \operatorname{Im} [G_0^{BB}(\omega)]_{ij} = 0, \quad (20b)$$

$$\operatorname{Re} [G_0^{AB}(\omega)]_{ii} = \frac{3}{4\pi} \left(\frac{\omega_D}{\omega} \right), \quad \operatorname{Im} [G_0^{AB}(\omega)]_{ii} = 0, \quad (20c)$$

$$\operatorname{Re} [G_0^{AB}(\omega)]_{ij} = \frac{3}{\pi} \left(\frac{\omega_D}{\omega} \right) f_1(k_D a_{ij}), \quad \operatorname{Im} [G_0^{AB}(\omega)]_{ij} = 0, \quad (20d)$$

where

$$f(k_D a_{ij}) = \frac{1}{(k_D a_{ij})^2} \left\{ \left[\frac{6}{(k_D a_{ij})^2} - 1 \right] \cos(k_D a_{ij}) - \frac{3}{(k_D a_{ij})} \left[\frac{2}{(k_D a_{ij})^2} - 1 \right] \times \sin(k_D a_{ij}) \right\}, \quad (21a)$$

$$f_1(k_D a_{ij}) = \frac{1}{(k_D a_{ij})^2} \left\{ \left[1 - \frac{2}{(k_D a_{ij})^2} \right] \cos(k_D a_{ij}) + 2 \frac{\sin(k_D a_{ij})}{(k_D a_{ij})} \right\} \quad (21b)$$

are oscillatory functions of a_{ij} and $a_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$ is the magnitude of the distance of separation between the two atoms in the pair. Besides the values of the Green's function matrix elements given by (20), these have the following symmetry properties in the model considered, i.e.

$$[G_0^{AA}(\omega)]_{ij} = [G_0^{BB}(\omega)]_{ij} \text{ and } [G_0^{AB}(\omega)]_{ij} = [G_0^{BA}(\omega)]_{ij}. \quad (22)$$

The real part of (17) can be solved for the pair local mode frequencies making use of (20)–(22) to yield,

$$\frac{5}{3} \left(\frac{\omega}{\omega_D} \right)^2 = \frac{1}{2} b \pm \frac{1}{2} (b^2 - 4c)^{1/2}, \quad (23)$$

$$\text{where } b = \lambda_1 + \lambda_2 + \tau_1 + 15\tau_1 \left[\frac{1}{16} \lambda_1 + \lambda_2 f_1^2(k_D a_{ij}) \right], \quad (24a)$$

$$\text{and } c = \tau_1(\lambda_1 + \lambda_2) + \lambda_1 \lambda_2 (1 - 25f^2(k_D a_{ij})) + 15\lambda_1 \lambda_2 \tau_1 \left[\frac{1}{16} + f_1^2(k_D a_{ij}) - \frac{5}{2} f(k_D a_{ij}) f_1(k_D a_{ij}) \right]. \quad (24b)$$

The imaginary part of the r.h.s. of (17) which is proportional to the width of the pair modes is obviously zero for the case of the local modes, as is expected for the harmonic theory. As is obvious from (23) and (24) together with (21), the pair mode frequencies vary as the distance of separation a_{ij} varies. A monotonous increase in the splitting

of the two local mode frequencies as a_{ij} decreases from ∞ was predicted earlier by Takeno (1965). However, the oscillatory nature of (21) in our case clearly shows that the splitting will oscillate. One can consider the various limiting cases of (23): (i) if $\lambda_2=0$, i.e. there exists a single impurity atom characterised by a change in mass (λ_1) and a change in the nearest neighbour force constant (τ_1), then (17) yields

$$\left(\frac{\omega_L}{\omega_D}\right)^2 = \frac{3}{5} \left[\lambda_1 + \tau_1 + \frac{15}{16} \lambda_1 \tau_1 \right], \quad (25)$$

which reduces to the well known single mass defect result when $\tau_1=0$. (ii) If the two impurities are infinitely separated then $a_{ij} \rightarrow \infty$ and hence $f(k_D a_{ij})$ and $f_1(k_D a_{ij})$ go to zero, thus reducing (23) to two frequencies

$$\left(\frac{\omega_L}{\omega_D}\right)^2 = \begin{cases} \frac{3}{5} \left[\lambda_1 + \tau_1 + \frac{15}{16} \lambda_1 \tau_1 \right] \\ \frac{3}{5} \lambda_2 \end{cases} \quad (26)$$

corresponding to two independent single impurities (iii) If $\tau_1=0$, then (23) becomes

$$\frac{5}{3} \left(\frac{\omega_L}{\omega_D}\right)^2 = \frac{1}{2} (\lambda_1 + \lambda_2) \pm \frac{1}{2} [(\lambda_1 - \lambda_2)^2 + 100 \lambda_1 \lambda_2 f^2(k_D a_{ij})]^{1/2}. \quad (27)$$

For two similar mass defect impurities ($\lambda_1=\lambda_2$), the local mode frequency is degenerated for $a_{ij} \rightarrow \infty$ as can be seen from (27). For a finite distance of separation the splitting as given by (27) is

$$\Delta \left(\frac{\omega_L}{\omega_D}\right)^2 = 6 \lambda f(k_D a_{ij}), \quad (28)$$

which shows that the splitting oscillates as a_{ij} is varied. The amplitude and the period of this oscillation will be dependent on $k_D (=2\pi/\lambda_D)$ or on the property of the host crystal. Of course, the larger the λ , the larger will be the splitting.

These oscillations are depicted in figure 1. For the purpose of the numerical calculations we have expressed the distance of separation a_{ij} as well as λ_D (Debye wavelength) in terms of the lattice constant as

$$k_D a_{ij} = \frac{2\pi}{\lambda_D} n a = \frac{2\pi}{100} n, \quad (29)$$

where a is the lattice constant, n is an integer and λ_D is taken to be $100 a$. It can be seen from figure 1 that the local mode frequencies oscillate as n varies. These oscillations are most pronounced when $\tau_1=0$. However for a finite value of τ_1 , there is a splitting in the local mode frequencies for large n ; and the oscillations get highly damped. However, one can see very strong oscillations when $n \rightarrow 0$ or when the two impurity atoms tend to be close to each other. These oscillations are further damped

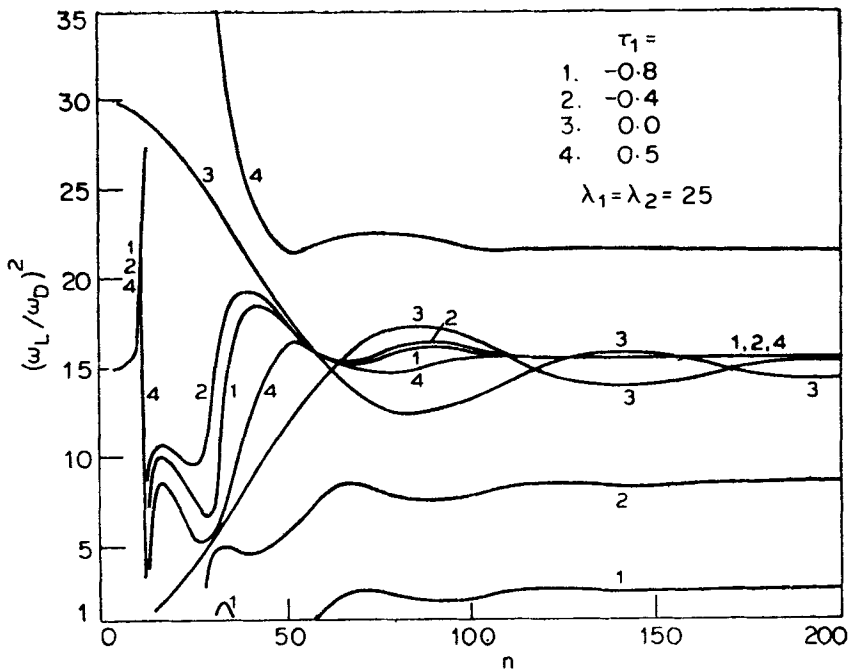


Figure 1. Variation of the square of the local mode frequency $(\omega_L/\omega_D)^2$ with increasing distance of separation between the two similar impurity atoms for various values of the force constant change parameters is shown. Relation of n to the distance of separation is defined in the text. The two local mode frequencies never cross.

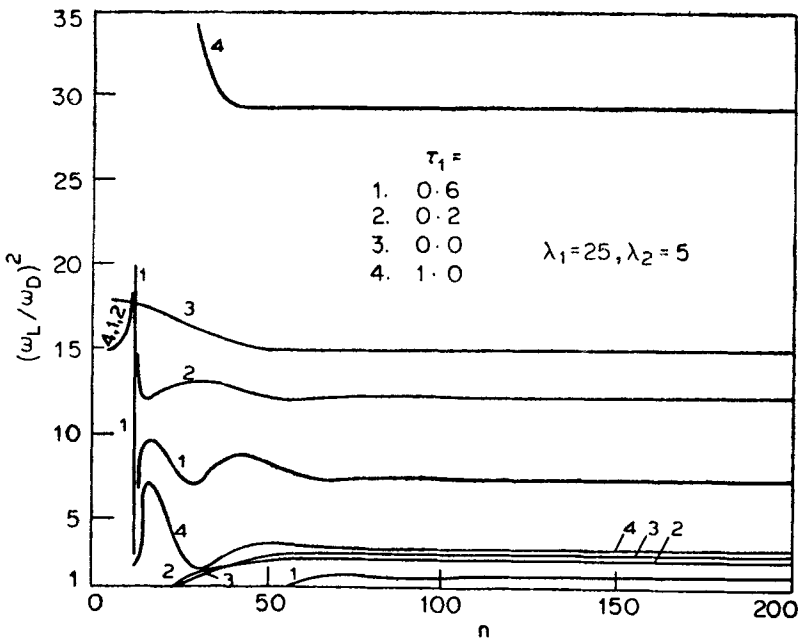


Figure 2. This shows the same variation as in figure 1, but for two dissimilar impurities.

for two dissimilar impurities as can be seen from figure 2. It is also clear from figure 1 that one of the local mode frequencies is lowered (raised) when the force constant is softened (hardened). This oscillatory behaviour of the local mode frequencies clearly demonstrates that the force between two impurity atoms is a truly long range one, as is expected in an elastic continuum or Debye model (Eshelby 1956). In figure 3, we show the variation of the local mode frequencies with increasing mass defect parameter $\epsilon_1 (= \epsilon_2) = (M - M_1)/M$ for two similar impurities when the distance of separation between the two atoms is fixed. Similarly figure 4 shows the variation of local mode frequencies for two dissimilar impurities as a function of the mass defect parameter ϵ_2 of the second impurity atom for fixed a_{ij} . In both figures 3 and 4 $\tau_1 = 0$. It is worthwhile comparing figures 3 and 4 with corresponding figures 6 and 7 of Elliott and Pfeuty (1967) and noting that in both the cases the nature of variations is similar. This shows that a simple Debye model calculation preserves the essential features of an exact calculation qualitatively. Figure 5 shows the variation of the pair local mode frequencies as the force constant change parameter is varied, keeping the distance of separation constant. Again figure 5 is similar in nature to figure 19 of Elliott and Pfeuty (1967).

3.2. Resonant modes

The frequencies of the pair-resonant modes can also be calculated from (17). The Green's function matrix elements can be evaluated analytically in the limit of the

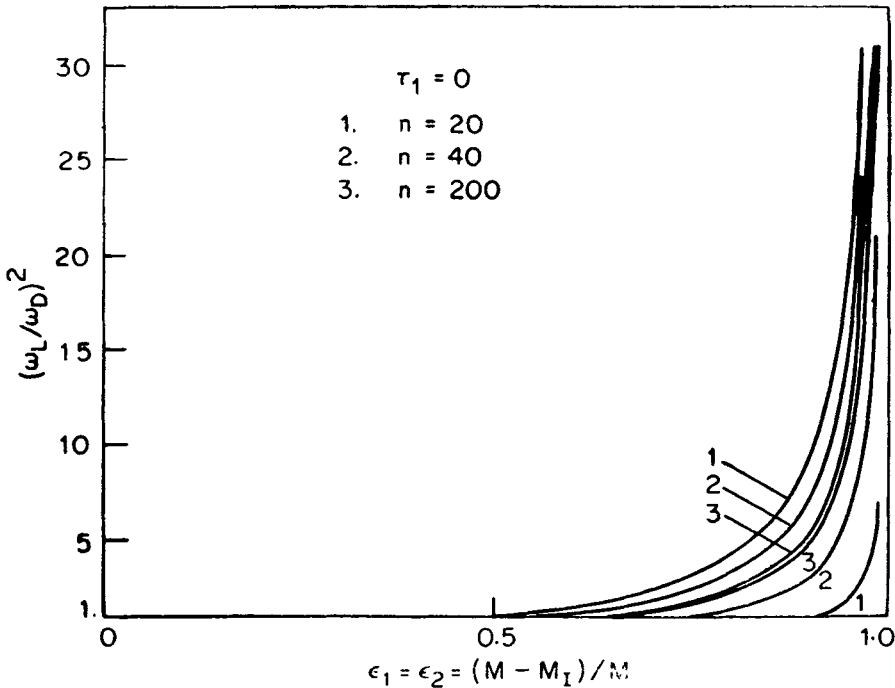


Figure 3. Variation of $(\omega_L/\omega_D)^2$ for two similar impurities as a function of the mass-defect parameter $\epsilon_l = (M - M_l^{(i)})/M$ when the distance of separation between the two impurities is fixed.

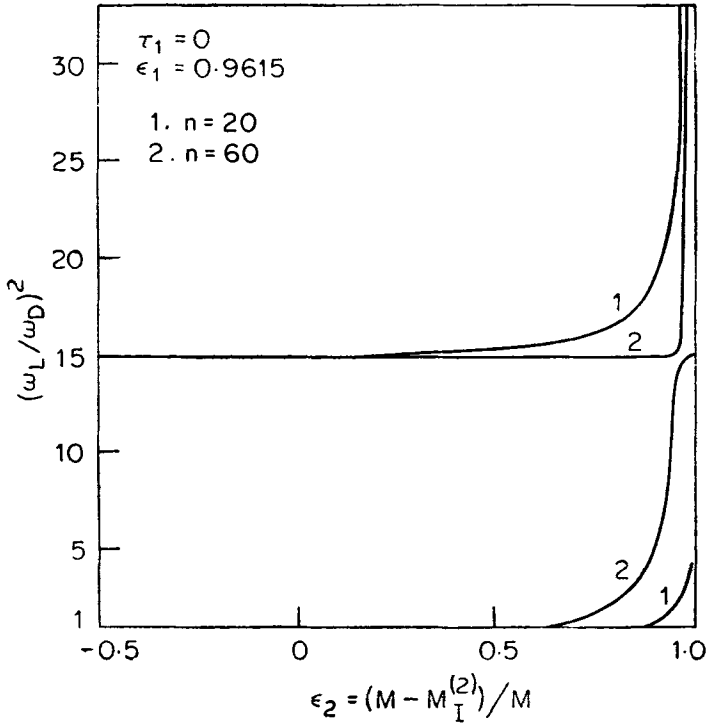


Figure 4. Variation of $(\omega_L/\omega_D)^2$ as the mass-defect-parameter $\epsilon_i = (M - M_I^{(i)})/M$ of the second impurity atom is varied keeping ϵ_1 fixed at 0.9615. Again the distance of separation between the two impurities is kept fixed.

resonant mode frequency going to zero, when the Green's function matrix elements can be expanded in a Taylor series as

$$[\hat{G}_0(\omega^2)]_{ij} = [\hat{G}_0(o)]_{ij} + \omega^2 [\hat{G}_0'(o)]_{ij} + \dots \quad (30)$$

The real and imaginary parts of the various matrix elements entering the expansion of (30) are given by

$$\text{Re}[G_0^{BB}(o)]_{ii} = -\frac{1}{\pi}, \quad \text{Re}[G_0^{BB'}(o)]_{ii} = -\frac{3}{\pi\omega_D^2}, \quad (31a)$$

$$\text{Re}[G_0^{BB}(o)]_{ij} = \frac{1}{\pi} g(k_D a_{ij}), \quad \text{Re}[G_0^{BB'}(o)]_{ij} = -\frac{3}{2\omega_D^2} \frac{1}{(k_D a_{ij})}, \quad (31b)$$

$$\text{Re}[G_0^{AB}(o)]_{ii} = -\frac{3}{2\pi} \left(\frac{\omega}{\omega_D}\right), \quad \text{Re}[G_0^{AB}(o)]_{ij} = \frac{3}{\pi} \left(\frac{\omega}{\omega_D}\right) \frac{[1 - \cos(k_D a_{ij})]}{(k_D a_{ij})^2} \quad (31c)$$

$$\text{and} \quad \text{Im}[\hat{G}_0(o)]_{ij} = 0, \quad (31d)$$

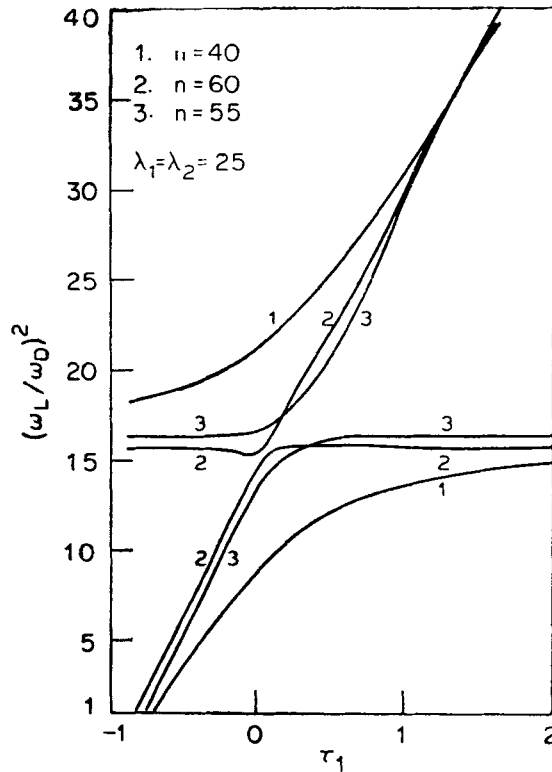


Figure 5. Variation of $(\omega_L/\omega_D)^2$ is shown for two similar impurity atoms at a fixed distance of separation, as the force constant change parameters τ_1 is varied.

where
$$g(k_D a_{ij}) = \frac{3}{(k_D a_{ij})^3} [(k_D a_{ij}) \cos(k_D a_{ij}) - \sin(k_D a_{ij})]. \quad (32)$$

Equations (30)–(32) together with (22) when substituted into (17) yield a quadratic equation for $(\omega/\omega_D)^2$ whose solution can be written as

$$3 \left(\frac{\omega}{\omega_D} \right)^2 = \{-b_1 \pm [b_1^2 - 4a_1c_1]^{1/2}\} / 2a_1, \quad (33)$$

where
$$a_1 = \lambda_1 \lambda_2 \left[1 - \frac{1}{4} \frac{1}{(k_D a_{ij})^2} \right], \quad (34a)$$

$$b_1 = \lambda_1 + \lambda_2 + 2\lambda_1 \lambda_2 + \lambda_1 \lambda_2 \frac{g(k_D a_{ij})}{(k_D a_{ij})}, \quad (34b)$$

and
$$c_1 = 1 + \lambda_1 + \lambda_2 + \lambda_1 \lambda_2 [1 - g^2(k_D a_{ij})]. \quad (34c)$$

Various limiting cases of (33) can be considered now. (i) If $\lambda_2 = 0$, then the problem

reduces to that of a single impurity producing mass change. In this case the resonant mode frequency reduces to

$$\left(\frac{\omega_R}{\omega_D}\right)^2 = -\frac{(1+\lambda_1)}{3\lambda_1}, \quad (35)$$

which is the well known mass defect result (Behera and Deo 1967). (ii) In the limit of $a_{ij} \rightarrow \infty$ (33) reproduces the two independent single impurity resonant modes. It is obvious from (31) and (32) that the pair-resonant mode frequencies too are oscillatory functions of the distance of separation between the two impurity atoms.

As pointed out earlier the imaginary part of the impurity denominator given by (17) will be proportional to the width (γ) of the resonant mode. The imaginary parts of the host Green's function matrix elements, are given by

$$\text{Im} [G_0^{BB}(\omega)]_{ii} = \text{Im} [G_0^{AB}(\omega)]_{ii} = -\frac{3}{2} \left(\frac{\omega}{\omega_D}\right)^3, \quad (36a)$$

$$\text{Im} [G_0^{BB}(\omega)]_{ij} = \text{Im} [G_0^{AB}(\omega)]_{ij} = -\frac{3}{2} \left(\frac{\omega}{\omega_D}\right)^2 \frac{\sin\left[\left(\frac{\omega}{\omega_D}\right)k_D a_{ij}\right]}{(k_D a_{ij})}. \quad (36b)$$

Thus (36) together with (31), (32) and (22) when used to evaluate the imaginary part of the left hand side of (17) in the limit $\tau_1=0$ yields for the width

$$\gamma\left(\frac{\omega}{\omega_D}\right) = \frac{3\pi}{2} \left(\frac{\omega}{\omega_D}\right)^3 \left\{ \lambda_1 + \lambda_2 + 2\lambda_1\lambda_2 \left[1 + g(k_D a_{ij}) \frac{\sin\left(\frac{\omega}{\omega_D} k_D a_{ij}\right)}{\left(\frac{\omega}{\omega_D} k_D a_{ij}\right)} \right] \right\}. \quad (37)$$

If $\lambda_2 = 0$, (37) gives the width of the single impurity resonant mode, i.e.

$$\gamma\left(\frac{\omega}{\omega_D}\right) = \frac{3\pi}{2} \left(\frac{\omega}{\omega_D}\right)^3 \lambda_1. \quad (38)$$

The width $\gamma(\omega/\omega_D)$ is also an oscillatory function of a_{ij} .

The variation of pair-resonant mode frequencies and their corresponding widths are shown in figures 6 and 7 respectively. The oscillations in these are quite evident from these figures. One can see from these figures (curves 1, 2 and 3) that for a given distance of separation (n) the resonant mode frequency shifts to higher values than that of the single impurity frequency and the width increases if the second impurity happens to be a light mass impurity. In fact the lighter the mass of the impurity

the larger are the shift and the width. On the other hand, if the second impurity happens to be a heavy mass impurity then the resonant frequency as well as the width decreases as can be seen from curves 4 and 5. Again the heavier the mass of the

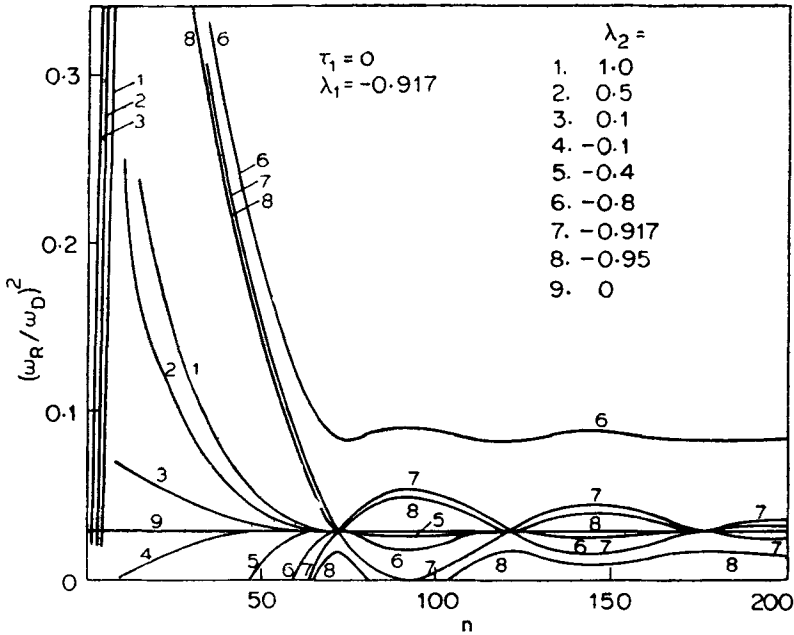


Figure 6. Variation of the square of the resonant mode frequency $(\omega_R/\omega_D)^2$ for a pair of heavy impurities as a function of their distance of separation n . The two resonant mode frequencies never cross.

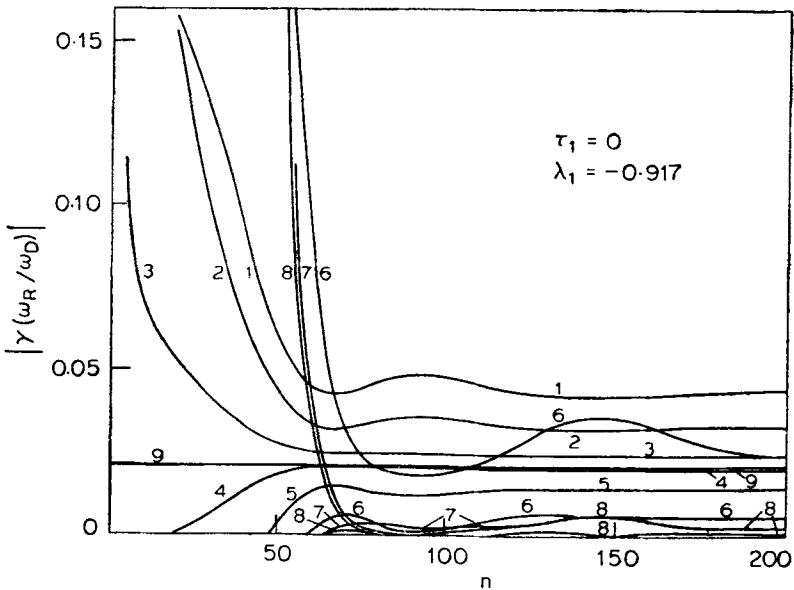


Figure 7. Variation of the width of the pair modes with the distance of separation between the pair. The parameters 1, 2, ..., 9 correspond to the same values of λ_2 as given in figure 6.

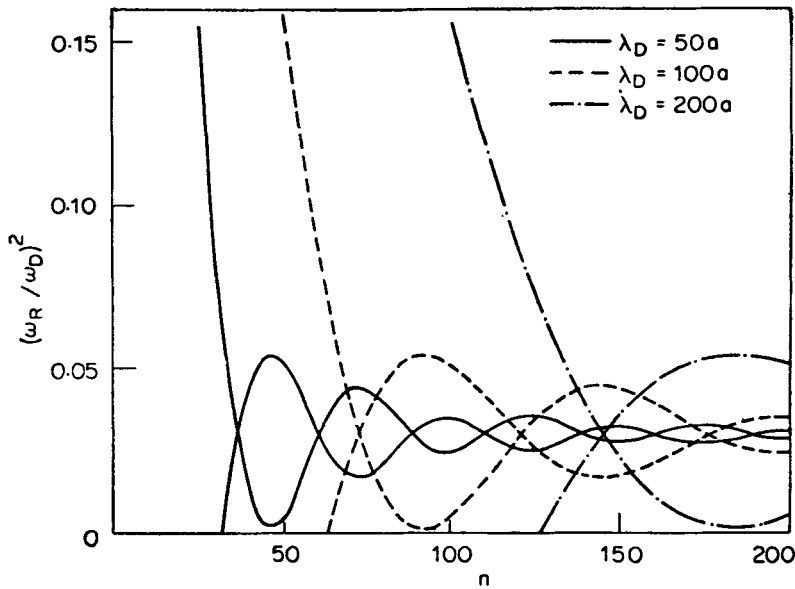


Figure 8. Variation of $(\omega_R/\omega_D)^2$ as a function of the distance of separation n for various values of the Debye wavelength (λ_D) of the host crystal. Note that both the period and amplitude of oscillation increases with increasing λ_D . There is no crossing between the two frequencies.

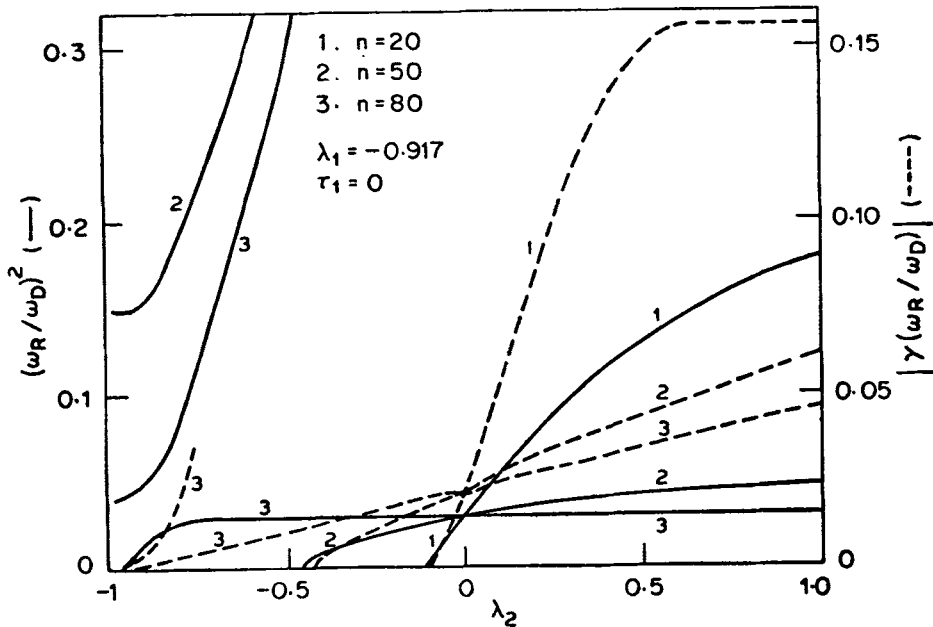


Figure 9. Variation of $(\omega_R/\omega_D)^2$ and $|\gamma(\omega_R/\omega_D)|$ as a function of the variation of the second mass defect parameter λ_2 for fixed distances of separation between the two impurity atoms. The mass defect parameter λ_2 is defined in the text.

second impurity the larger is the decrease. As can be seen from these curves the amplitudes of the oscillations are very small and a single pair resonant mode exists. This happens so long as the mass of the second impurity atom is not heavy enough to produce a second resonant mode, (see curves 6, 7 and 8). As soon as such a critical mass is reached two resonant modes appear one with a frequency and width lower than that of the single impurity mode and the other with higher frequency and larger width. For this case the oscillations are more prominent. The amplitude of oscillation is the largest for two similar heavy mass impurities and increases as $\lambda_1 = \lambda_2$ tend to -1 or the masses tend to infinity. Just as in the case of local modes, here also the period and amplitude of oscillation depend on λ_D . This is shown in figure 8. Figure 9 shows the variation of the pair resonant mode frequencies and their corresponding widths for a fixed distance of separation as the mass of the second impurity atom varies from half the host mass to infinity ($-1 < \lambda_2 < 1$). There exists no other calculation of the general features of pair resonant modes in the literature.

4. Conclusion

In concluding we shall consider some infrared measurements in mixed crystal systems the result of which could be qualitatively explained in terms of the pair mode discussions of § 3. Clayman and Sievers (1968) have studied the effect of alloying KBr with KCl and KI; on the narrow (width 1.1 cm^{-1}) low lying 16.2 cm^{-1} resonance line of $\text{KBr} : \text{Li}^+$. They have found that on alloying with KCl the resonance frequency shifts to higher values ($\omega_R = 24 \text{ cm}^{-1}$) the width (10.4 cm^{-1}) increases and the integrated strength of absorption remains constant. On the other hand, alloying with KI shifts the resonance to lower frequencies ($\omega_R = 11.2 \text{ cm}^{-1}$) the width (5 cm^{-1}) again increases and the strength of absorption decreases drastically. The width of $\text{KBr}_{1-c}\text{Cl}_c : \text{Li}^+$ resonance is much larger than that of the $\text{KBr}_{1-c}\text{I}_c : \text{Li}^+$ resonance. The authors had explained the shifts in the frequencies, as due to the change in the lattice constant because of alloying. However, they offer no explanation for the changes in the widths and the strengths of absorption. Similar measurements on U centre local modes in KCl alloyed with RbCl (Barth and Fritz 1967 and Mirlin and Reshina 1966) had resulted in the appearance of new local modes which were attributed to nearest neighbour pairs of Rb^+H^- , which are formed on alloying. Hence we propose to interpret the results of Clayman and Sievers (1968) as due to the formation of pairs of Li^+Cl^- and Li^+I^- on alloying. In order to apply the results of § 3 to these systems we consider a model, where the corresponding diatomic ionic crystals are considered to be monoatomic crystals, with the respective reduced masses. This we believe will be a good approximation to the system under consideration because, the experimental data concern the resonant mode of Li^+ in KBr which lies deep inside the acoustic band. Hence as far as this mode is concerned the Br^- ions can be thought of as static while the K^+ ions execute vibrations in the acoustic band. Such an analysis was shown to be quite successful in explaining qualitatively the Resstrahl absorption data of mixed crystals of $\text{LiH}_{1-c}\text{D}_c$ by Behera and Tripathi (1974) and $\text{Zn}_c\text{Cd}_{1-c}\text{Te}$ by Behera (1974). These authors used an Einstein model for the optic band. Besides we further assume that the $\text{KBr} : \text{Li}^+$ resonance is caused by an equivalent heavy mass impurity atom, whose mass defect parameter λ_1 can be estimated from (35) and turns out to be -0.917 . In doing so the Debye frequency (ω_D)

is taken to be 94 cm^{-1} (Bauerle 1973) which is the maximum frequency of the acoustic band of KBr. On alloying with KCl, pairs of $\text{Li}^+ \text{Cl}^-$ will be formed and Cl^- has $\lambda_2=0.44$ in terms of the reduced masses of KCl and KBr. Similarly alloying with KI will give rise to Li^+I^- pairs where $\lambda_2=-0.13$ for I^- . It can be clearly seen from figure 9 that for $\lambda_2>0$ (light mass impurity) the resonance frequency shifts to higher values and the width of the resonance increases enormously as compared to the single Li^+ resonance. On other hand for $\lambda_2<0$ the resonance frequency shifts to lower values and width decreases. It should be noted that the value of $\lambda_2=-0.13$ (corresponding to I^-) is not sufficient to produce two resonant modes for the Li^+I^- pair. However, if the resonance frequencies are shifted on alloying, then in principle one should experimentally observe two lines, one corresponding to the unpaired Li^+ impurities and the other corresponding to the pairs. But experimentally these two lines are not resolved, which clearly indicates that the two impurity atoms forming the pair are far apart and are not nearest neighbour pairs. That is why the shifts are small and the experimental resolution is not high enough to show two lines. Because of the composite nature of the resonance lines in the alloys, the lines are broadened in both the cases contrary to the prediction of the present theory. Finally, the loss of the strength of absorption on alloying with KI remains to be explained. It has been pointed out by Behera and Tripathi (1974) (their equation (35)) that for a single impurity the strength of absorption is equal to (M/M_I) times the concentration. Hence the strength of absorption due to a heavy mass impurity will be lowered by the ratio (M/M_I) . If in analogy with the single impurity result one assumes that the strength of absorption due to a pair will be given by

$$\left(M/M_I^{(1)} \right) C_1 \left(M/M_I^{(2)} \right) C_2,$$

where $M_I^{(i)}$, $C_i(i=1, 2)$ are respectively the mass and concentration of the two impurities forming the pair then it is clear that the strength of absorption for Li^+I^- will decrease, and that of Li^+Cl^- will increase for the same values of C_1 and C_2 . Thus the observed decrease in the integrated strength of absorption for $\text{KBr}_{1-c}\text{I}_c:\text{Li}^+$ system is understandable.

Similar analysis can also be used to qualitatively explain the U centre local modes in $\text{K}_{1-c}\text{Rb}_c \text{Cl}$ as observed by Mirlin and Reshina (1966) and Barth and Fritz (1967). It should be pointed out that it is impossible to experimentally observe the oscillations in the local and resonant mode frequencies, simply because, one cannot produce crystals with given distance of separation between two impurities. However the distribution of the impurity pairs with varying distances of separation in a sample could give rise to a statistical width of the local mode which is observed experimentally. These results are the subject matter of a separate communication (Behera and Chandrakhya Devi 1978).

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