

## Coherent potential approximation for a disordered diatomic linear chain having diagonal and off-diagonal randomness

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**Abstract.** A coherent potential approximation (CPA) for a mixed diatomic linear chain including both mass and force constant changes has been developed. In this case an impurity atom substituted at a particular site in one of the sublattices couples with two nearest neighbour atoms in the other sublattices. The diatomic linear chain is therefore considered as a tetratomic linear chain, the size of the unit cell being twice the original. The CPA density of states and the dielectric susceptibility have been calculated. The numerical values of the later have been calculated in the ATA (average  $t$ -matrix approximation) limit. Comparison of these results with the experimental and other computer calculations show a qualitative agreement.

**Keywords.** Mixed crystals; impurity modes; lattice dynamics; coherent potential approximation; average  $t$ -matrix approximation; diatomic linear chain.

### 1. Introduction

The mixed crystals of the type  $AB_{1-x}C_x$  or  $A_{1-x}B_xC$  show varied behaviour in infrared absorption and Raman scattering experiments (Chang and Mitra 1971; Barker and Sievers 1975). Typically these behaviours can be classified into three distinct types namely one-mode, two-mode and mixed-mode systems. The systems showing one-mode behaviour have only one absorption peak which varies continuously with composition from the characteristic frequencies of one end member to frequencies of the other end member, with strength of the absorption peak remaining approximately constant. In systems exhibiting two-mode behaviour, there are two absorption peaks at  $x=0$ , out of which the strength of one, corresponding to the rest strahl absorption, is much larger than that of the one corresponding to impurity mode. With increasing concentration, the strength of the impurity mode increases and tends to one while that of the other decreases and goes to zero as the concentration approaches unity. The final type of mixed crystal is that in which it appears to switch from one-mode to two-mode systems as the concentration is changed from 0 to 1 (Behera *et al* 1977).

Many theoretical models are available (Chang and Mitra 1971) to study the different mode behaviours. Some of these (Chang and Mitra 1968; Lucovsky *et al* 1970) also possess certain criteria for the general occurrence of these three types of mode behaviours. However, the models and the criterion they determine, are all based on the nature of low concentration limit, thereby showing that the theories that exist are all concentration-independent. Since mixed crystals appear to switch from

one-mode to two-mode behaviour as the concentration changes, it would be difficult therefore, to predict the concentration at which this transition occurs.

So it is necessary to develop a theory which will be valid for the whole concentration range. Coherent potential approximation (CPA) is perhaps the best available method to consider this line. This, being a mean field theory, is valid for all concentration range. This method was first applied to disordered problems, particularly to phonons, by Taylor (1967) and to electrons by Soven (1967). An excellent review of this is given by Elliot *et al* (1974). Almost all calculations carried out on CPA so far are confined mainly to monoatomic lattices. However, Sen and Hartman have reported a deviation and have tried to generalise the single site CPA to a cellular CPA (CCPA) for a diatomic linear chain. The CCPA applies the general technique to a cell as a whole, instead of a single site, and where, the random effective medium is chosen self-consistently, such that, the average scattering from a single cell (two atoms per unit cell) vanishes. Having constructed such a CCPA, Sen and Hartman have calculated density of states and the electrical susceptibility for a few mixed diatomic systems and compared these with the experimental observations. The agreement is qualitative for different systems, but quantitatively shows some discrepancies. These discrepancies were attributed to the absence of nearest neighbour force constant changes in the theory. Sen and Hartman (1974) have also determined the changes necessary in the force constant which is responsible for this discrepancy. It has been shown by Sen and Hartman that the mixed system  $\text{In}_{1-x}\text{Ga}_x\text{Sb}$  shows a 14% decrease of force constant proceeding from GaSb to InSb. However, attempts have been made to develop a CPA calculation (Kaplan and Mostler 1974; Katayama and Kanamori 1978) which takes care of the force constant change. But in all cases, the introduction of force constant changes is based on some simplified assumptions such as average force constant, where a linear superposition of forces are considered to be a good approximation. With a view to improve the calculation by considering the force constant changes, we generalise the CCPA of Sen and Hartman (1974). Here an impurity atom is substituted at a particular site in one of the sublattice and it couples with two nearest neighbour atoms in the other sublattices. Hence to confine both mass and force constant changes to the cell itself, we have considered the diatomic chain as a tetra-atomic chain with the size of the unit cell twice that of the original size. This is shown in figure 1. The motivation behind this artificial doubling of the cell size, as mentioned above, is to confine the diagonal as well as the off-diagonal perturbation to the cell itself, so that the CCPA technique can be applied to it as well. The quantities thus involved have the form of  $4 \times 4$  matrix instead of a  $2 \times 2$  matrix as in the diatomic case. The doubling of the cell size reduces the Brillouin zone to half the original. In other words, the Brillouin zone, which spreads from  $-\pi/a$  to  $+\pi/a$  in the diatomic case, is limited to  $-\pi/2a$  to  $+\pi/2a$ , and a zone folding appears at the boundary line of the new zone *i.e.* at  $\pm\pi/2a$ . This is depicted in figure 2. Thus, instead of two branches in the dispersion curve, we get four branches, of which, one is acoustic and the other three are optic branches. These have been considered in detail after carefully evaluating the host properties.

The paper is organised as follows. Section 2 deals with the present model and its lattice dynamics. In § 3, we present the theory for mixed tetra-atomic linear chain. In § 4, we briefly review the CPA for a mixed diatomic chain. We then develop the CPA for mixed tetra-atomic chain in § 5. In § 6, we have given the configuration-averaged density of states and the dielectric susceptibility and consider the low

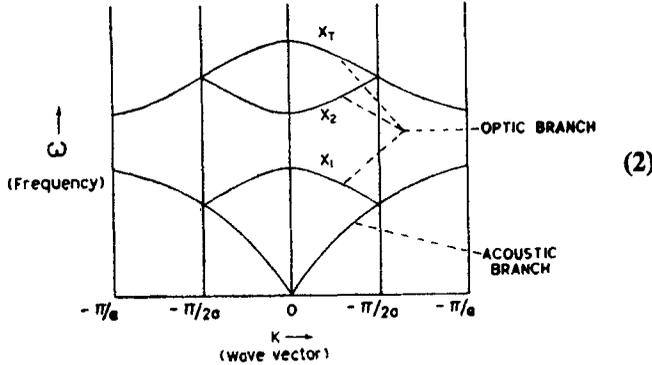
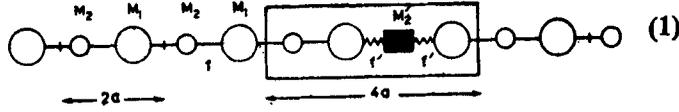


Figure 1. Mixed four-atomic linear chain.

Figure 2. Dispersion curve for four-atomic linear chain showing one-acoustic branch as well as three optic branches in between first Brillouin zone.

concentration limit *i.e.* ATA limit of these quantities. The calculated results and their comparison with experiment are given in § 7. Finally we conclude in § 8.

### 2. Generalised tetra-atomic linear chain model

Here we assume that the impurity atom of mass  $M_2'$ , when substituted in the  $M_2$  sublattice of the diatomic linear chain changes the nearest neighbour force constant from  $f$  to  $f'$ . Due to this change in force constant, this perturbation cannot be confined to the impurity cell of diatomic chain but extends to one of the neighbouring unit cells. Thus to randomize the imperfect unit cells, the diatomic linear chain is considered as a tetra-atomic linear chain. The nearest neighbour atoms being at a separation of distance  $a/2$  with force constant  $f$ .

Let  $U_{la}$  be the displacement from equilibrium of the atom of mass  $M_{la}$  on the sublattice  $a$  in the  $l$ th unit cell, then the equation of motion is given by

$$M_{la} \omega^2 U_{la} = \sum_{l'\beta} A_{ll'a\beta} U_{l'\beta} \tag{1}$$

where  $a, \beta$  takes the values from 1 to 4.  $A_{ll'a\beta}$  is the force constant matrix.

We shall now derive some of the host properties for the tetra-atomic linear chain. The artificial doubling of the cell size from  $a$  to  $2a$ , the Brillouin zone, reduces from the range  $-\pi/a$  to  $+\pi/a$  to the range  $-\pi/2a$  to  $+\pi/2a$ . Thus we have four branches

in the dispersion curve due to the artificial folding of a part of the curve into  $\pm \pi/2a$  to zero from the zone  $(\pi/2a, \pi/a)$  and  $(-\pi/2a, -\pi/a)$ . This is shown in figure 2.

The dispersion relation obtained from (1) is given by

$$x_j(K) = \frac{1}{2} X_T \pm \frac{1}{2} [X_T^2 - 2X_1 X_2 (1 \mp \cos Ka)]^{1/2}, \quad (2)$$

where,  $x_j(K) = \omega_j^2(K)$ ,

$$\text{and } X_1 = \frac{2f}{M_1}, X_2 = \frac{2f}{M_2}, X_T = X_1 + X_2. \quad (3)$$

From (2) it is evident that out of 4 branches only one branch goes to zero at  $K=0$ . Thus we have only one acoustic branch and three optic branches and are given by

$$x_A(K) = (X_T/2) - B_1, \quad (4a)$$

$$x_0^{(1)}(K) = (X_T/2) - B_2, \quad (4b)$$

$$x_0^{(2)}(K) = (X_T/2) + B_1, \quad (4c)$$

$$x_0^{(3)}(K) = (X_T/2) + B_2, \quad (4d)$$

$$\text{where, } B_1 = \frac{1}{2} [X_T^2 - 2X_1 X_2 (1 - \cos Ka)]^{1/2}, \quad (5a)$$

$$\text{and } B_2 = \frac{1}{2} [X_T^2 - 2X_1 X_2 (1 + \cos Ka)]^{1/2}. \quad (5b)$$

Writing the displacement in terms of eigen vectors for normal modes of vibration, we get

$$M_a^{1/2} U_{ia} = \sum_{jK} \sigma_a^j(K) \exp(i\mathbf{k} \cdot \mathbf{R}_i), \quad (6)$$

where  $a$  takes values from 1 to 4,  $R_i$  is the position of the  $i$ th unit cell and  $\sigma_a^j(K)$ 's are given by the following,

$$\sigma_1^j(K) = \left[ \frac{X_2 - x_j(K)}{2 [X_T - 2x_j(K)]} \right]^{1/2}, \quad (7a)$$

$$\sigma_2^j(K) = \frac{(X_1 X_2)^{1/2}}{2 [X_2 - x_j(K)]} (1 + e^{iKa}) \sigma_1^j(K), \quad (7b)$$

$$\sigma_3^j(K) = e^{iKa} \sigma_1^j(K), \quad (7c)$$

$$\text{and } \sigma_4^j(K) = \frac{e^{iKa} (1 + e^{iKa})}{2 [X_2 - x_j(K)]} (X_1 X_2)^{1/2} \sigma_1^j(K) \quad (7d)$$

The definition for the Fourier transform of the retarded Green function (Zubarev (1960) defined as  $P$  is given by

$$P_{\alpha\beta ll}^{(x)} = \lim_{\phi \rightarrow 0} (M_\alpha M_\beta)^{-1/2} \frac{1}{N} \sum_{K_j} \frac{\sigma_\alpha^{j*}(K) \sigma_\beta^j(K)}{x - x_j(K) + i\phi} \exp[-iK(\mathbf{R}_l - \mathbf{R}_{l'})]. \quad (8)$$

Using (1), (2) and (8) we can find out all the elements of  $P_{\alpha\beta ll}$ . Out of the sixteen elements thus obtained for  $P_{\alpha\beta ll}$ , only six elements are independent and the remaining are given by

$$P_{\alpha\beta ll} = P_{\beta\alpha ll}^* \quad (9)$$

The six independent  $P_{\alpha\beta ll}$  are given by

$$\begin{aligned} P_{22}(x) &= \frac{1}{N} \sum_K P_{22}(K, x) \\ &= \frac{(x - X_1)}{2M_2} \frac{1}{N} \sum_K \left[ \frac{1}{[x - x_A(k)][x - x_0^{(3)}(K)]} + \frac{1}{[x - x_0^{(1)}(k)][x - x_0^{(2)}(K)]} \right], \end{aligned} \quad (10a)$$

$$P_{11}(x) = \frac{x - X_2}{x - X_1} \frac{M_2}{M_1} \frac{1}{N} \sum_K P_{22}(K, x), \quad (10b)$$

$$P_{12}(x) = \frac{-X_1}{2} \frac{1}{N} \sum_K (1 + e^{iKa}) P_{22}(K, x), \quad (10c)$$

$$P_{13}(x) = \frac{x - X_2}{x - X_1} \frac{M_2}{M_1} \frac{1}{N} \sum_K e^{iKa} P_{22}(K, x) \quad (10d)$$

$$P_{14}(x) = \frac{-X_1}{2} \frac{1}{N} \sum_K e^{iKa} (1 + e^{iKa}) P_{22}(K, x), \quad (10e)$$

and 
$$P_{24}(x) = \frac{1}{N} \sum_K e^{iKa} P_{22}(K, x). \quad (10f)$$

In the above, the subscript ll has been dropped. While deriving these quantities, we assume that the masses  $M_1$  and  $M_2$  are at the first, third and second fourth sites respectively. It is also assumed that  $M_1 > M_2$ .

### 3. Theory for mixed tetra-atomic linear chain

In this mixed tetra-atomic linear chain the defects atom is substituted at any one of the four sublattice sites that constitute the cell. Since, we consider the nearest neighbour force constant change, the defect atom is placed either at the second or third sites, so that when it couples to the nearest neighbours it is confined to the cell itself. Here we choose the second sublattice site as one with the defective atom.

If we have  $M_1 > M_2$ , then the definition of the above quantities, such as  $X_1, X_2$ , does not change and the defect atom is said to be in the light sublattice. If we have  $M_1 < M_2$  then the definition of  $X_1, X_2$  is just interchanged and the defect atom is said to be in the heavy sublattice.

If we have impurity atoms of mass  $M'_2$  substituted at the second site, then for a small concentration of this defect atom, the Green function for the defective chain is given by

$$\mathbf{G}(x) = \mathbf{P}(x) + \mathbf{P}(x) \sum^\circ(x) \mathbf{G}(x), \quad (11)$$

where,  $\Sigma^\circ(x)$  is the perturbation matrix having both diagonal and off-diagonal terms and is of  $4 \times 4$  matrix form which is given by

$$\sum^\circ(x) = \begin{pmatrix} -f\tau & f\tau & 0 & 0 \\ f\tau & M_2 \epsilon_{22} x - 2f\tau & 0 & 0 \\ 0 & f\tau & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \quad (12)$$

$$\text{where } \tau = (f - f')/f \text{ and } \epsilon_{22} = (M_2 - M'_2)/M_2. \quad (13)$$

Before considering the theory for arbitrary concentration  $C$ , let us first study the case for a single defect. Then the defect Green function is given by

$$\mathbf{G} = \mathbf{P} + \mathbf{P} t \mathbf{P}, \quad (14)$$

where, the  $t$ -matrix is

$$t = \sum^\circ (1 - \mathbf{P} \sum^\circ)^{-1}. \quad (15)$$

Equation (15), which determines the impurity mode is obtained when the real part of the denominator of this  $t$ -matrix becomes zero. This is equivalent to stating that the real part of the determinant  $(1 - \mathbf{P} \Sigma^\circ)$  vanishes *i.e.*

$$\text{Re det} \left[ 1 - \mathbf{P} \sum^\circ \right] = 0. \quad (16)$$

Thus, when the latter equation is solved, we get

$$\begin{aligned} \text{Re} \{ [1 - M_2 \epsilon_{22} x P_{22} + f\tau (P_{11} + P_{13} + 2P_{22} - 4P_{12}) - f\tau M_2 \epsilon_{22} \\ x \{ P_{22} (P_{11} + P_{13}) - 2P_{12}^2 \}] [1 - f\tau (P_{13} - P_{11})] \} = 0. \end{aligned} \quad (17)$$

When we put  $\tau = 0$ , the above equation reduces to

$$\operatorname{Re} [1 - M_2 \epsilon_{22} \times P_{22}] = 0, \quad (18)$$

which is a well-known theory (Maradudin *et al* 1971) for single defect, assuming mass change only. On solving (10), it can be shown that the host Green functions  $P_{ij}$  for  $i = j$  are completely imaginary inside the bands. Therefore (18) does not give any solution for the occurrence of resonant modes. On the contrary, (17) gives solutions to resonant modes. Thus the theory for a single defect is exact. But for an arbitrary concentration of defects no exact solution to (14) is possible. An approximate solution following the CPA is discussed below.

#### 4. Coherent potential approximation

The CPA and the expression for the self-energy can be obtained by following altogether different approaches. We give below a brief calculation of an expression for the self-energy, where one sees the impurities as embedded in an effective medium whose propagator  $G_0$  has a self-energy adjusted so that  $t$ -matrix for the scattering off a single impurity in this medium is zero.

For a disordered chain the single particle Green function satisfies the Dyson equation

$$G = P + P \sum^{\circ} G, \quad (19a)$$

$$= P + PtP. \quad (19b)$$

In the CPA one assumes an effective medium Green function  $G_0$ , which obeys the equation

$$G_0 = P + P \sum G_0, \quad (20a)$$

$$= (1 - P \sum)^{-1} P, \quad (20b)$$

where,  $\Sigma$  is the unknown self-energy of the effective medium which has to be determined self-consistently as given below. Solving (20a) for  $P$  and substituting into (19a), eliminates  $P$  and gives the modified Dyson equation as

$$G = G_0 + G_0 (\sum^{\circ} - \sum) G, \quad (21a)$$

$$= G_0 + G_0 t G_0, \quad (21b)$$

$$\text{where, } t = (\sum^{\circ} - \sum) [1 - G_0 (\sum^{\circ} - \sum)]^{-1}. \quad (22)$$

In CPA one demands that the configurationally-averaged total Green function

$\langle G \rangle$  be equal to the effective medium Green function  $G_0$ , which is equivalent to demanding that

$$\langle t \rangle = 0, \quad (23)$$

or 
$$\langle (\Sigma^0 - \Sigma) [1 - \langle G \rangle (\Sigma^0 - \Sigma)]^{-1} \rangle = 0. \quad (24)$$

In the single site approximation the average in (24) can be performed by noting that the potential at the  $C$  impurity sites is  $(\Sigma^0 - \Sigma)$  and at the  $(1 - C)$  host sites is  $(-\Sigma)$ ,  $C$  being the concentration of impurity atoms. This ultimately brings (24) to

$$C (\Sigma^0 - \Sigma) [1 - \langle G \rangle (\Sigma^0 - \Sigma)]^{-1} + (1 - C) (-\Sigma) [1 + \langle G \rangle \Sigma]^{-1} = 0, \quad (25)$$

which, when solved gives the expression for the self-energy to be of the form

$$\Sigma = C \Sigma^0 [1 - \langle G \rangle (\Sigma^0 - \Sigma)]^{-1}. \quad (26)$$

Equation (26) is the self-consistent equation for the CPA self-energy and it has to be solved together with (20a) which defines  $G_0$ .

### 5. CPA for mixed tetra-atomic chain

Now if we translate these expressions to our tetra-atomic linear chain the corresponding expression for  $t$ -matrix and effective medium Green function  $\bar{G}$  is given by

$$\langle t_i \rangle = \langle V_{ii} [1 - \bar{G}_{ii} V_{ii}]^{-1} \rangle, \quad (27)$$

and 
$$\bar{G}(K, x) = P(K, x) + P(K, x) \Sigma \bar{G}(K, x). \quad (28)$$

Here  $P$ ,  $G$ ,  $\Sigma$  are all in the form of  $4 \times 4$  matrix and the expression for  $V_{ii}$  is given by

$$V_{ii} = \begin{cases} (\Sigma^0 - \Sigma) & \text{for } C \text{ defect cells} \\ -\Sigma & \text{for } (1 - C) \text{ host cells,} \end{cases} \quad (29)$$

where  $\Sigma^0$  as given by (12),  $C$  being the concentration.

On evaluating the average of (27) using (29) one gets the matrix self energy  $\Sigma$  as

$$\Sigma = C \Sigma^0 [1 - \bar{G} (\Sigma^0 - \Sigma)]^{-1}. \quad (30)$$

Both (30) and (28) constitute the self-consistent equation and is solved for the self-consistent self energy  $\Sigma$ .

It is worthwhile to note that if the low concentration limit *i.e.*  $C \rightarrow 0$  is taken, then  $\Sigma$  is replaced by  $C \Sigma^0$  and  $\bar{G}$  is replaced by the host Green function  $P$ . Putting these quantities on the right side of (30) we get

$$\Sigma = C \Sigma^0 [1 - (1 - C) P \Sigma^0]^{-1}. \quad (31)$$

Equation (31) is just the expression for the self-energy in ATA. This shows the equivalence of the CPA and ATA at the low concentration limit. Equation (31) constitutes the starting value of  $\Sigma$ , which is required for the calculation of the self-consistent values of the Green function  $G$ , as well as the self energy  $\Sigma$ . The latter is ultimately required for the evaluation of the physical properties such as density of states and dielectric susceptibility (Nayak and Behera 1981). This will be discussed later.

Equation (31) when solved gives only nine equations out of sixteen and the remaining seven are redundant. This is evident from the nature of the perturbation matrix  $\Sigma^\circ$  (equation (12)). Again from symmetry considerations (equation (9)) we finally get only four independent equations. These are given by

$$\begin{aligned} \Sigma_{11} = & -Cf\tau [1 - (1-C)M_2 \epsilon_{22} f x P_{22} - (1-C)f\tau (2P_{12} - P_{22} - P_{11}) \\ & + (1-C)^2 M_2 \epsilon_{22} x f \tau (P_{12}^2 - P_{11} P_{22})] / D_2, \end{aligned} \quad (32a)$$

$$\Sigma_{12} = Cf\tau [1 - (1-C)M_2 \epsilon_{22} x P_{12}] / D_1, \quad (32b)$$

$$\begin{aligned} \Sigma_{13} = & Cf\tau [(1-c)f\tau (2P_{12} - P_{13} - P_{22}) + (1-C)^2 M_2 \epsilon_{22} x f \tau \\ & \otimes (P_{13} P_{22} - P_{12}^2)] / D_2, \end{aligned} \quad (32c)$$

$$\begin{aligned} \text{and} \quad \Sigma_{22} = & [CM_2 \epsilon_{22} x \{1 - (1-C)f\tau (2P_{12} - P_{11} - P_{13})\} \\ & - 2Cf\tau \{1 - (1-C)M_2 \epsilon_{22} x P_{12}\}] / D_1, \end{aligned} \quad (32d)$$

$$\begin{aligned} \text{where} \quad D_1 = & [1 - (1-C)M_2 \epsilon_{22} x P_{22} + (1-C)f\tau (P_{11} + P_{13} + 2P_{22} - 4P_{12}) \\ & + (1-C)^2 M_2 \epsilon_{22} x f \tau (2P_{12}^2 - P_{11} P_{22} - P_{13} P_{22})], \end{aligned} \quad (33a)$$

$$\text{and} \quad D_2 = D_1 [1 - (1-C)f\tau (P_{13} - P_{11})]. \quad (33b)$$

We now discuss the procedure of evaluation of the self-consistent values of  $\Sigma$  and  $G$ . Substituting the values of  $P_{ij}$ 's (equation (10)) with the known values of  $M_2, \epsilon_{22}$  for a particular value of  $x$  (where  $x = \omega^2$ ) in (31) and (32), we determine the first set of  $\Sigma$ 's. Now these values of  $\Sigma$ 's are substituted into (28) for  $\bar{G}(K, x)$  and the first set of  $G_{ij}(K, x)$  is calculated. The quantities are integrated over the whole Brillouin zone to get the corresponding values in  $x$  i.e.  $G_{ij}(x)$ . Now replacing  $P_{ij}(x)$  by these  $G_{ij}(x)$  and substituting in (31) and (32) the second set of  $\Sigma$ 's are calculated. These  $\Sigma$  values are again substituted in (28) as before to get the second set of quantities of  $G_{ij}(x)$ . This procedure is repeated till  $\Sigma$  and  $G(x)$  values become self-consistent.

When the force constant change parameter  $\tau$  becomes zero we get back the exact equations of Sen and Hartman (1974). For  $\tau = 0$ , only one  $\Sigma$  value is left and is given by

$$\Sigma_{22} = \frac{CM_2 \epsilon_{22} x}{1 - (1-C)M_2 \epsilon_{22} x P_{22}}. \quad (34)$$

It is also seen that the inclusion of force constant changes does not reduce the solutions to a single scalar equation as in mass change. Therefore the evaluation of the self-consistent quantities  $\Sigma$  and  $G$  is more difficult compared to the mass change (Sen and Hartman 1974). In the next section we discuss the method of calculation of some of the physical properties such as density of states and dielectric susceptibility both for low and total concentration. However for comparing our calculation with experimental results, we evaluate the quantities numerically for low concentration only.

## 6. Physical properties

For the vibrational state of any system the density of states  $\rho(x)$  is given by

$$\begin{aligned}\rho(x) &= -\frac{1}{\pi N} I_m T_\gamma \langle MG \rangle_{av} \\ &= -\frac{1}{\pi N} I_m \sum_a \langle M_{0a} G_{00aa} \rangle_{av},\end{aligned}\quad (35)$$

Here we use the conditional configuration-averaged Green function  $\bar{G}_{00aa}^d$  and  $\bar{G}_{00aa}^h$ . The configuration with defects in the cell  $l = 0$  is included in the averaging for  $\bar{G}_{00aa}^d$  while with host atoms in the cell,  $l = 0$ , the Green function  $\bar{G}_{00aa}^h$  is included. Using these conditional-averaged Green functions we have the following expressions respectively for (i) the density of states for mass change and (ii) mass and nearest neighbour force constant change

$$\rho(x) = \frac{-1}{\pi} \text{Im} \left[ M_1 (\bar{G}_{11} + \bar{G}_{33}) + M_2 \bar{G}_{44} + M_2 \left( 1 - \frac{\Sigma_{22}}{M_2 x} \right) \bar{G}_{22} \right], \quad (36)$$

$$\begin{aligned}\rho(x) &= -\frac{1}{\pi} \text{Im} \left[ M_1 (\bar{G}_{11} + \bar{G}_{33}) + M_2 (\bar{G}_{22} + \bar{G}_{44}) \right. \\ &\quad \left. - \frac{1}{x} (\Sigma_{11} + \Sigma_{12} + \Sigma_{13}) (\bar{G}_{12} + \bar{G}_{32}) + (2\Sigma_{12} + \Sigma_{22}) \bar{G}_{22} \right].\end{aligned}\quad (37)$$

Here we have used the relation

$$\bar{G}_{00aa}^h = \bar{G}_{00aa} - \bar{G}_{00aa}^d. \quad (38)$$

The density of states can also be evaluated in the Einstein model. This is possible when the atom vibrates with a single frequency which is usually,  $\omega_{T0}$ . This is equivalent to the case of  $M_2 \rightarrow \infty$  or  $M_1 \rightarrow \infty$ . Thus, the density of states in this limit becomes

$$\begin{aligned}\rho(x) &= -\frac{1}{\pi} \text{Im } G(\omega + i\phi) \\ &= (1 - C) \delta(\omega^2 - \omega_{T0}^2) - \frac{C}{(1 - \epsilon)} \delta\left[\omega^2 - \omega_{T0}^2 \left(\frac{1 - \tau}{1 - \epsilon}\right)\right],\end{aligned}\quad (39)$$

where  $\phi$  is a small imaginary part.

The dielectric susceptibility  $\chi$  is given by

$$\chi(x) = \sum_{\alpha, \beta} Q_\alpha Q_\beta \bar{G}_{\alpha\beta}(k=0), \quad (40)$$

where  $\alpha$  and  $\beta$  take values from 1 to 4. If we assume the situation of point charge ions and charge neutrality

$$Q_1 = Q_3 = -Q_2 = -Q_4, \quad (41)$$

we find that the expression for the dielectric susceptibility for mass change as well as mass and force constant changes respectively

$$\chi(x) = \frac{\frac{4 Q_1^2}{M_2} [A_1 - \frac{1}{2} \beta A_2 \sigma_{22}] A_2}{A_4 [2A_3 - (x - X_1) A_2 \sigma_{22}]} \quad (42)$$

and

$$\chi(x) = \frac{\frac{4 Q_1^2}{M_2} [A_1 - \frac{1}{2} \beta A_2 (\sigma_{22} - 2\sigma_{11} + 4\sigma_{13})] A_2}{[2A_3 A_4 - 2(\frac{1}{2}(x - X_1)\sigma_{22} + \beta(x - X_2)\sigma_{11} - 2X_1\sigma_{12}) A_2 A_4 + \beta A_2^2 (\sigma_{11}' \sigma_{22} - 2\sigma_{12}^2)]}, \quad (43)$$

where  $A_1 = x(x - X_1)(x - X_2)(1 + \beta)$ ,

$$A_2 = (x - X_1)(x - X_2) + x(x - X_T),$$

$$A_3 = x(x - X_1)(x - X_2)(x - X_T),$$

$$A_4 = (x - X_1)(x - X_2)$$

and  $\sigma_{ij} = \Sigma_{ij}/M_2$  and  $\sigma'_{11} = \sigma_{11} + \sigma_{13}$ .

It is known that for real systems, the peaks in the reflectivity spectrum are associated with the peaks in  $\text{Im } \chi$  (Sen and Hartman 1974). Therefore we have calculated the values of  $\text{Im } \chi$  using the  $\Sigma$  value from (31) and these are compared with experimental observations. All the calculations here are done assuming the host force constant  $f$  to be 1.

## 7. Results and discussions

We have calculated the density of states as well as the susceptibility for a few systems. Though our model provides a theory for substitutionally-disordered chain for all concentrations having both diagonal as well off-diagonal randomness, we have reported numerical calculations, in the low concentration limit *i.e.* in the ATA limit only. The calculated values when compared with experimental and numerical plots of Painter (1973) show good agreement. However, the detailed structure obtained in numerical calculations cannot be reproduced as our results are in ATA limit only and our theory does not include clusters such as pairs and triplets, etc. We are looking for peak positions only in the impurity mode in these calculations. In figure 3 we plot the density of states for an arbitrary system where  $M_1 = 4$ ,  $M_2 = 2$  and

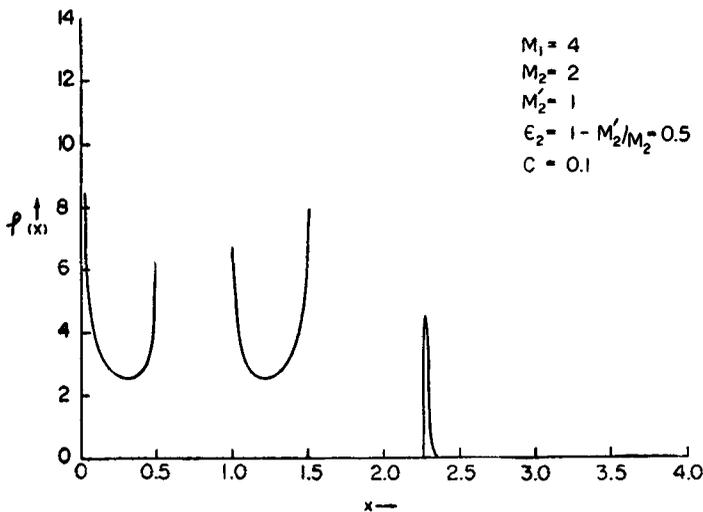


Figure 3. Phonon density of states in the ATA limit for  $M_1 = 4$ ,  $M_2 = 2$ ,  $\epsilon_2 = 0.5$  and  $C = 0.1$ .

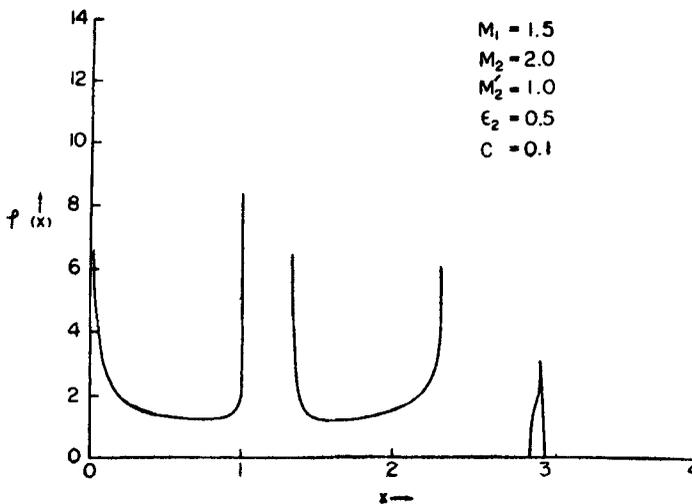
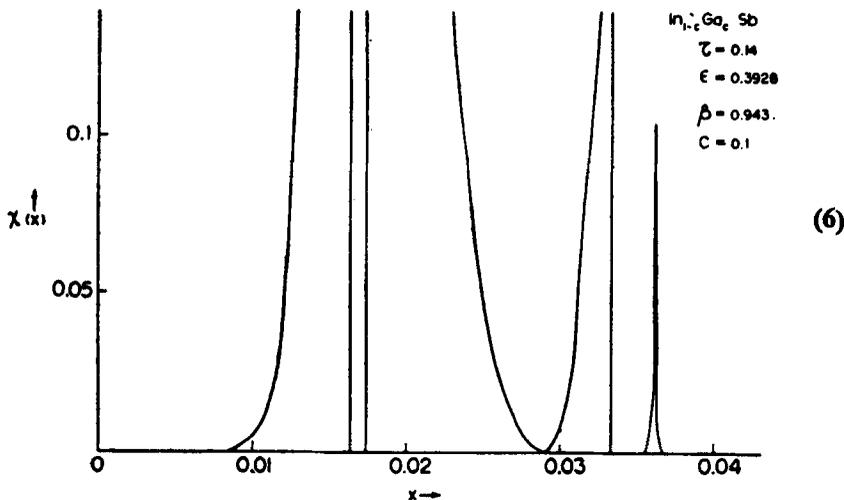
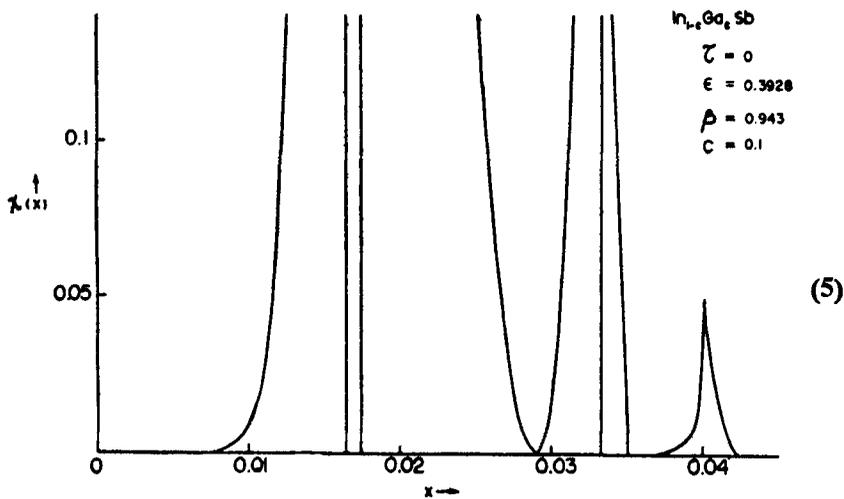


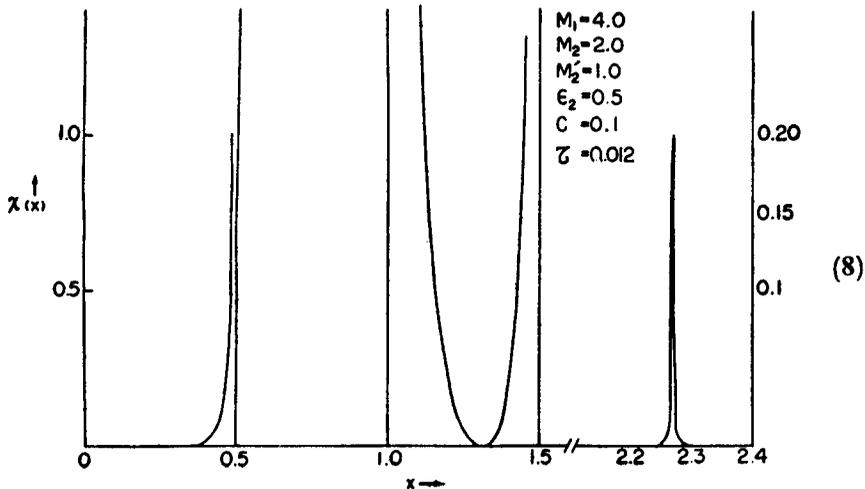
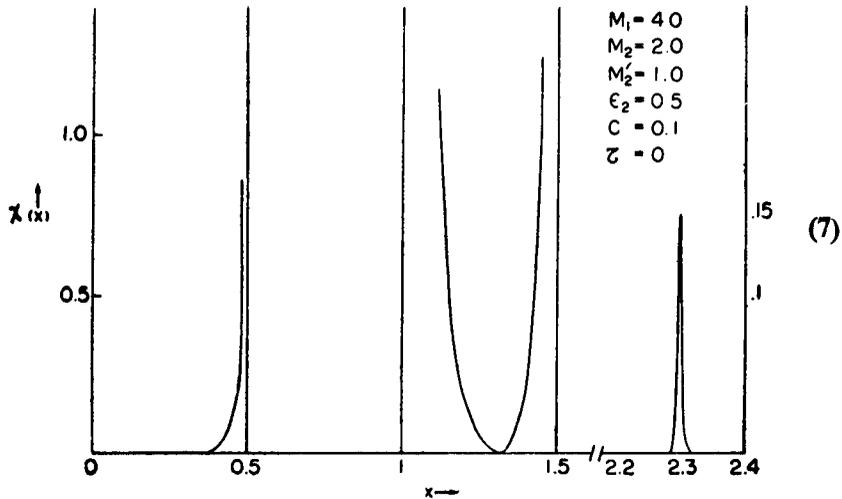
Figure 4. Phonon density of states in the ATA limit for  $M_1 = 1.5$ ,  $M_2 = 2$ ,  $\epsilon_2 = 0.5$  and  $C = 0.1$ .

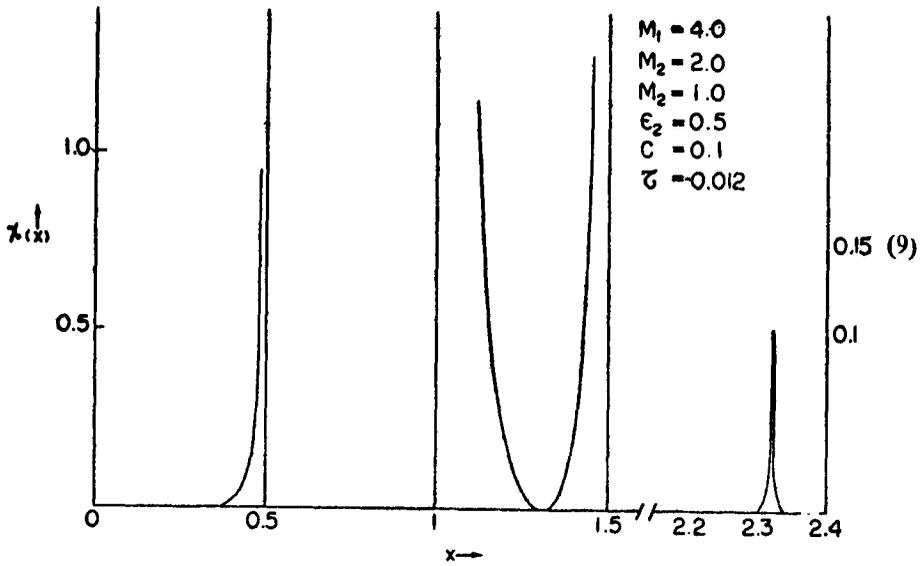
$\epsilon_2 = 0.5$  and the concentration  $C$  is 0.1 and find a peak in the impurity mode at  $x = 2.28$ . This is found to be same when compared with the numerical calculation of Painter (1973). Figure 4 shows a similar plot for masses  $M_1 = 1.5$ ,  $M_2 = 2$  and  $\epsilon_2 = 0.5$  and  $C = 0.1$ . Here the impurity peak appears at  $x = 2.88$  and is similar to that of Painter 1973. The susceptibility values for a mixed system  $\text{In}_{1-c}\text{Ga}_c\text{Sb}$  have been plotted in figures 5 and 6. Figure 5 is a plot for a zero force constant change *i.e.*  $\tau = 0$  while figure 6 is for  $\tau = 0.14$ , suggested by Sen and Hartman (1974). Peaks are found in the susceptibility at  $x = 0.04$  for  $\tau = 0$  and at  $x = 0.036$  for  $\tau = 0.14$ . In addition, strong peaks are observed at  $x = X_1$ ,  $x = X_2$  and  $x = X_T$ . On comparison, it is found that the peaks at  $x = X_1$  and  $x = X_2$  are absent in the observed spectra. These peaks which appear at  $x = X_1$  and  $x = X_2$  in our calculation are considered to be spurious and arise due to the artificial folding at the zone



Figures 5 and 6. Plot of imaginary part of dielectric susceptibility for  $\text{In}_{1-c}\text{Ga}_c\text{Sb}$  in ATA for force constant change parameter  $\tau = 0$  and 0.14 respectively.

boundary. Therefore, at  $k = 0$  instead of a single peak at  $x = X_T$ , we get peaks at  $x = X_1$  and  $x = X_2$  as well, which are not observed in the diatomic case. On comparison with the two impurity peak positions mentioned above it is found that the position of the peak corresponding to  $\tau = 0.14$  shifts towards  $\omega_{T0}$  (the optic mode frequency), where there is a softening of force constant. Figures 7, 8 and 9 depict the susceptibility plots for an arbitrary system with different force constant changes, where  $M_1 = 4$ ,  $M_2 = 2$ ,  $\epsilon_2 = 0.5$ ,  $C = 0.1$  and for the force constant change  $\tau = 0$ ,  $0.012$  and  $-0.012$  respectively. In figure 7, which is for  $\tau = 0$ , we find the same spurious peaks at  $x = X_1$  and  $x = X_2$  while the impurity peak is at  $x = 2.29$ . Figures 8 and 9 are the cases of softening and tightening respectively and again we find the spurious and impurity peaks appearing at  $x = 2.27$  and  $2.32$  respectively. The trend of the peak positions is in right direction. Finally we plot the concentration dependence of peak positions for an arbitrary system with a very small impurity mass parameter. We know that in the ATA limit the strength of the impurity mode is





Figures 7, 8 and 9. Plot of imaginary part of dielectric susceptibility for  $M_1 = 4$ ,  $M_2 = 2$  and  $\epsilon_2 = 0.5$ ,  $C = 0.1$  and for  $\tau = 0, 0.012$  and  $-0.012$ .

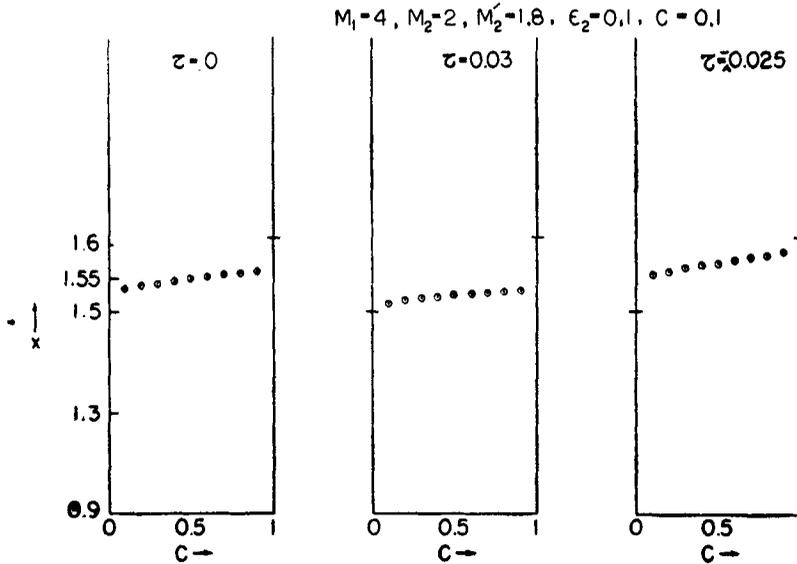


Figure 10. Plot of peak positions of the dielectric susceptibility for the whole concentration range for an arbitrary system with  $M_1 = 4$ ,  $M_2 = 2$  and  $M_2' = 1.8$  (impurity mass very close to host mass) and  $\tau = 0, 0.03, -0.025$ .

proportional to the product of concentration  $C$  and the impurity mass parameter, *i.e.* to  $C \epsilon_{22}$ , which is a small quantity. If one takes the impurity mass parameter to be very small, even when the concentration increases from 0 to 1, the product  $C \epsilon_{22}$  still remains a small quantity. In this situation ATA will work for the whole range of concentrations. So for the sake of completeness we have taken this drastic approximation and considered an arbitrary system with very small impurity mass parameter. This occurs when the difference between host and impurity mass is very small. Figure 10 gives such a plot of  $M_1 = 4$ ,  $M_2 = 2$ ,  $M_2' = 1.8$  with three dif-

rent values of force constant changes *i.e.*  $\tau = 0, 0.3$  and  $-0.025$ . This has been done for the whole concentration range varying from 0 to 1. In all these three cases it is found that the peak positions in the susceptibility spectra shift smoothly with the concentration. This behaviour shows that the systems are of one-mode type. Since the approximation is crude, we cannot get an exact concentration dependence.

## 8. Conclusion

The numerical calculations are carried out in the ATA limit for some systems with mass as well as force constant changes and the trend is seen to give a satisfactory explanation to the experimental data. In order to get the values of these quantities within the CPA one has to take these ATA limit values as the starting input and iterate till one gets the self-consistent values of both the Green function  $G$  and the self energy  $\Sigma$ . But such a programme will involve a time-consuming computation and could not be carried out presently. However these calculations are in progress and will be reported after completion.

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