

Concentration dependence of the mixed crystal modes of vibration

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Abstract. The concentration dependence of the reststrahl absorption in various mixed crystals exhibiting one, two and mixed mode behaviour is investigated using the coherent potential approximation (CPA). The phonon Green's function, the impurity mode frequencies and the strength of absorption are calculated in the Einstein model from the generalized CPA proposed by Tripathi and Behera which takes into account both mass and force constant changes. The introduction of a phenomenological concentration dependence of the force constant change parameter is shown to provide a satisfactory explanation of the concentration dependence of the experimental data for the twenty mixed crystal systems analysed. It is conjectured that the nearest neighbour force constant of an impurity atom substituted at a host site is very much different from that of a perfect crystal consisting of these impurity atoms and that both these play an important role in determining the one, two and mixed mode behaviour of the mixed crystals.

Keywords. Impurity modes; mixed crystals; lattice dynamics; coherent potential approximation.

1. Introduction

The infrared absorption and Raman scattering measurements of mixed crystals reveal that their behaviour can be classified into three distinct categories (Chang and Mitra 1971; Barker and Sievers 1975). The systems showing one mode behaviour have only one absorption peak whose frequency varies from the characteristic reststrahl frequency of one end member to that of the other end member as the concentration (c) goes from 0 to 1, while the strength of absorption remains constant. In the case of systems exhibiting two-mode behaviour there are two absorption peaks at $c=0$, out of which the strength of the one corresponding to the reststrahl absorption is much larger than that of the one corresponding to the 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. Finally there are systems which show two-mode behaviour upto a certain concentration and one-mode behaviour for the rest of the concentration range and such systems are said to exhibit mixed mode behaviour (Behera *et al* 1977).

Many theoretical models have been proposed to explain and predict the behaviour of the mixed crystal systems out of which the random element isodisplacement (REI) model of Chen *et al* (1966) and its modifications (MREI) as proposed by Chang and Mitra (1968) and Genzel *et al* (1974) seem to be widely used. However, in this model

all the atoms of one sublattice are assumed to vibrate with the same amplitude and phase, against all the atoms of the other sublattice. Besides, the model sometimes necessitates the introduction of the next nearest neighbour force constants as parameters which have to take values larger than the nearest neighbour force constants to fit the experimental data. The last mentioned drawback of the theory was removed by Genzel *et al* (1974) who predict four different classes of mixed crystal behaviour instead of three. Lucovsky *et al* (1970) proposed a criterion to predict the mixed crystal behaviour starting from the calculations of a diatomic linear chain model. This criterion as generalized by Behera *et al* (1977) uses for the prediction the existence of local (gap) modes due to impurities at the end members, that is at $C = 0(1)$. If both a local and gap mode at $C = 0(1)$ and $1(0)$ are present the system will exhibit two-mode behaviour. If none of it is present it will be one-mode like and if only one (either local or gap) is present it will exhibit mixed mode behaviour. It has been shown by Behera *et al* (1977) that this criterion successfully predicates the behaviour of almost all the mixed crystal systems examined by them. Probably the best way of calculating the properties of mixed crystal systems theoretically is to use the coherent potential approximation (CPA). A CPA calculation for the diatomic linear chain model within the mass defect approximation was performed by Sen and Hartmann (1974) who successfully demonstrated the existence of one, two and mixed mode behaviour. But theirs being a mass defect, linear chain approximation gave poor quantitative agreement with experimental data. A mass defect CPA calculation for $KCl_c Br_{1-c}$ and $K_{1-c} Rb_c I$ was performed by Taylor (1973) which showed the correct one-mode behaviour for the former and two-mode behaviour for the latter system. However, carrying out CPA calculations including force constant changes become prohibitively difficult. Elliott *et al* (1974) adopted a simple model CPA calculation of Onodera and Toyozawa (1968) to the phonon case to obtain a criterion for the mixed crystal behaviour. In doing so they assume the frequency dependence of the optic modes density of states to be parabolic ($a\omega^2$) and centred at ω_0^2 , thus providing a band width to the optic mode. They relate the band width to the dielectric constant through the longitudinal (LO) and transverse (TO) optic mode frequencies and get the following criterion

$$|1 - \mu/\mu'| > (\epsilon_0 - \epsilon_\infty)/(\epsilon_0 + \epsilon_\infty)$$

for the existence of two peaks. Here μ and μ' are the reduced masses for the host and the defect crystals and ϵ_0 and ϵ_∞ are the static and the high frequency dielectric constants. They show that such a criterion is quite successful in explaining the experimental data. This calculation emphasizes the importance of the optical band width in determining the mixed crystal behaviour. Finally the question of the mixed crystal phonons at the zone boundary and its relationship to the zone centre phonons and the mixed crystal behaviour was considered by Genzel and Bauhofer (1976).

Even though, so many model calculations have been performed to predict the behaviour of the mixed crystals, only MREI model was mostly used to predict the concentration dependence of the mode frequencies and the strengths of absorption (Chang and Mitra 1971; Genzel *et al* 1974). One mass defect CPA calculation was attempted to explain the concentration dependence of the modes of the $Ge_{1-c} Si_c$

mixed crystal by Srivastava and Joshi (1973). But the Raman scattering measurements of Renucci *et al* (1971) show evidence of clustering (Behera and Patnaik 1975) which is not accounted for by this single site CPA calculation. Behera and Tripathi (1974) and Behera (1974a) used the low concentration limit of a generalized CPA calculation by Tripathi and Behera (1974) which includes both mass and nearest neighbour force constant changes to calculate the concentration dependence of $\text{LiH}_{1-c}\text{D}_c$ and $\text{Zn}_c\text{Cd}_{1-c}\text{Te}$ mixed crystals respectively. These investigators analysed the generalized CPA results in the Einstein model assuming that the frequency has a finite width and used the results to calculate the concentration dependence of the mode frequencies and their absorption strengths for small values of concentration from either end ($c = 0$ and 1) and were successful in obtaining agreement with the experimental data. In this calculation the force constant change parameter was fitted to the impurity mode at one end ($C = 0$ or 1) and extrapolated for the other end ($C = 1$, or 0). One of the results of this calculation was that the strength of absorption of the gap mode is always lower by the mass ratio (M/M') where $M' > M$. Later, the same low concentration results were applied to other mixed crystal systems of $\text{GaAs}_{1-c}\text{P}_c$ and $\text{CdSe}_{1-c}\text{S}_c$ (Behera 1974b).

Encouraged by the success of the above approach, we shall generalize the Behera-Tripathi (1974) calculation to all concentrations in this paper. It will be shown that an exact solution for the generalized CPA Green's function can be obtained in the Einstein model and as discussed above the strength of absorption of the gap mode $M' > M$ is lowered by the mass ratio (M/M') for all concentrations. However, unlike the low concentration result in this case, the mixed crystal mode frequencies become independent of concentration. Various ways of phenomenologically introducing a concentration dependence will be discussed. Finally the concentration dependence will be introduced in the impurity mode frequency through the force constant change parameter. It will be shown that on prescribing a certain well defined procedure for fixing these parameters for the one, two and mixed mode systems reasonably good agreement with the experimental data can be obtained.

The plan of the rest of the paper is as follows. § 2 gives the model theory and the phenomenology of the concentration dependence. In § 3, the results of the calculation are compared with the experimental data for the various one, two and mixed mode systems. Finally in the concluding § 4, the successes and failures of the theory are discussed and the reasons for its shortcoming are pointed out.

2. Theory

A generalization of the coherent potential approximation, which takes into account changes in the nearest neighbour force constants approximately has been proposed by Tripathi and Behera (1974) (we follow their notation), where the self-consistent phonon self-energy is a 2×2 matrix and is given by

$$\hat{M}(\omega) = C\hat{\Lambda} [\hat{1} - \hat{D}(\omega) (\hat{\Lambda} - \hat{M}(\omega))]^{-1}, \quad (1)$$

where

$$\hat{\Lambda} = \begin{pmatrix} \tau & 0 \\ 0 & \lambda \end{pmatrix}, \quad (2)$$

$$\hat{D}(\omega) = \sum_k U(k) \hat{D}_k(\omega) U(-k), \quad (3)$$

and

$$\hat{D}_k(\omega) = [\hat{D}_k^{0-1}(\omega) - U(k) U(-k) \hat{M}(\omega)]^{-1}, \quad (4)$$

with

$$U(k) = \frac{1}{(4N)^{1/2}} e_a(k) (\omega_k)^{1/2} \exp(i\mathbf{k} \cdot \mathbf{R}_i^{(0)}), \quad (5a)$$

$$\hat{D}_k^0(\omega) = \frac{1}{\pi(\omega^2 - \omega_k^2)} \begin{pmatrix} \omega_k & -\omega \\ \omega & -\omega_k \end{pmatrix}, \quad (5b)$$

where $\tau = (\Phi - \Phi^{(0)})/\Phi^{(0)}$ is the force constant change parameter and $\lambda = (M' - M)/M'$ is the mass change parameter associated with the impurity atoms and C is their concentration. Equations (1)–(5) form a set of self-consistent equations and the phonon self-energy $\hat{M}(\omega)$ as given by (1) is similar in form to the mass defect result (Elliott *et al* 1974). In the Einstein model (which is equivalent to taking the atomic limit in the case of CPA for electron state, see Elliott *et al* 1974) the self-consistent equations (1) to (5) can be solved exactly to give

$$\hat{M}(\omega) = C \hat{\Lambda} [\hat{\Lambda} - (1 - C) \hat{D}^0(\omega, \omega_0) \hat{\Lambda}]^{-1}, \quad (6)$$

where

$$\hat{D}^0(\omega, \omega_0) = \frac{\omega_0}{\pi(\omega^2 - \omega_0^2)} \begin{pmatrix} \omega_0 & -\omega \\ \omega & -\omega_0 \end{pmatrix}, \quad (7)$$

where ω_0 is the Einstein frequency of the phonon to be identified later with the transverse optic phonon (ω_{TO}) of the host.

At this stage it is worth pointing out that the exact result of (6) is identical with the average t -matrix approximation (ATA) result. The ATA result can be obtained from (1) for low concentrations, replacing $\hat{M}(\omega)$ by $C\hat{\Lambda}$ and $\hat{D}(\omega)$ by $\hat{D}^{(0)}(\omega)$ on the right side of (1). On taking this limit it becomes obvious that (1) reduces to (6). The displacement-displacement Green's function (which is the (1, 1) element of the matrix Green's function (4)) can be calculated by substituting (6) in (4), which turns out to be

$$D^{aa}(\omega, \omega_0) = \frac{\omega_0 [(\omega^2 - \omega_0^2)(1 - c\lambda) + (1 - c)\omega_0^2(\lambda - \tau + \lambda\tau)]}{\pi(\omega^2 - \omega_0^2)[\omega^2 - \omega_0^2(1 - \lambda)(1 + \tau)]}. \quad (8)$$

The frequencies of the modes of vibration are given by the poles of (8) *i.e.*

$$(i) \quad \omega^2 = \omega_0^2, \quad (9a)$$

$$(ii) \quad \omega^2 = \omega_0^2(1 - \lambda)(1 + \tau), \quad (9b)$$

Note that both the frequencies are independent of concentration. If we identify ω_0 to be the transverse optic mode frequency, $\omega_{\text{TO}}^{\text{A(B)}}$ of one end member $C = 0(1)$ then the other frequency (equation 9b) corresponds to the impurity mode. If there is no change in the force constants then this impurity mode is the same as the transverse optic mode frequency $\omega_{\text{TO}}^{\text{B(A)}}$ of the other end member $C = 1(0)$ of the mixed crystal $A_{1-c} B_c C$. The density of the states for zero wave vector which will reflect the infrared absorption spectrum will be proportional to the imaginary part of (8) and becomes

$$\begin{aligned} \rho(\omega) &= -\frac{1}{\pi} \text{Im } D^{aa}(\omega + i\eta, \omega_0) \\ &= (1 - c) \omega_0 \delta(\omega^2 - \omega_0^2) + c(1 - \lambda) \omega_0 \delta[\omega^2 - \omega_0^2(1 - \lambda) \\ &\quad (1 + \tau)]. \end{aligned} \quad (10)$$

Thus there are two δ -function absorption peaks (i) at $\omega = \omega_0$ whose strength is equal to $(1 - c)$ and (ii) at $\omega = \omega_0(1 - \lambda)^{1/2}(1 + \tau)^{1/2}$ whose strength is equal to $C(1 - \lambda)$. Clearly the strength of absorption of the first peak decreases and that of the second peak increases with increasing concentration, thus agreeing with the two-mode like behaviour. But the strength of the second peak for a given concentration gets enhanced by the factor $(1 - \lambda) = (M/M')$ for local modes ($M' < M$) and gets suppressed for gap modes ($M' > M$). This is in agreement with the result obtained earlier by Behera and Tripathi (1974). However, because of the concentration independence of the mode frequencies (equations (9)) this calculation as it is cannot explain the one- and the mixed-mode behaviour of mixed crystals.

2.1 Introduction of concentration dependence

According to (9) the absorption frequencies are independent of concentration. But Behera and Tripathi (1974) have obtained a concentration dependence by attributing a finite width to the transverse optic frequencies (ω_{TO}). This automatically provides a width to the optic band whose importance has been emphasized by Elliott *et al* (1974). However it becomes impossible to obtain an analytic solution of (1) when ω_0 is replaced by $(\omega_0 + i\eta)$. Hence we shall not pursue that approach here. Instead we shall attribute a phenomenological concentration dependence to the frequencies and show that it accounts for the one, two and mixed mode behaviour of a mixed crystal. For a mixed crystal $A_{1-c} B_c C$ the quantities ω_0 , λ and τ can take two sets of values corresponding to the end members, namely at $C = 0$ these have values $\omega_{\text{TO}}^{\text{A}}, \lambda_{\text{A}}, \tau_{\text{A}}$ and at $C = 1$ the values are $\omega_{\text{TO}}^{\text{B}}, \lambda_{\text{B}}$ and τ_{B} . As the concentration varies from 0 to 1, these quantities should smoothly extrapolate from one set of values to the other, and this can be achieved by attributing a virtual crystal like concentration dependence to these quantities, *i.e.*

$$Z = (1 - C)Z_{\text{A}} + CZ_{\text{B}}, \quad (11)$$

where $Z = (\omega_0, \lambda, \tau)$. Let us consider the effect of this on (9) when one or more of these parameters obey (11). Thus various possibilities arise. (i) If ω_0 satisfies (11) then

(9a) extrapolates between $\omega_{\text{TO}}^{\text{A}}$ and $\omega_{\text{TO}}^{\text{B}}$, thus providing a one- mode like behaviour. However the other root given by (9b) will give either only a local mode or only a gap made at either end of the concentration. But this is physically not possible because if at one end the impurity mass $M' < M$ giving rise to a local mode; at the other end the mass M becomes the impurity replacing the host M' , which will result in a gap mode. (ii) Next let us consider the possibility that λ obeys (11) extrapolating between $\lambda_{\text{A}} (= (M' - M)/M')$ and $\lambda_{\text{B}} (= (M - M')/M)$. Then while the root corresponding to ω_0 will remain flat, the other root will vary from a local (gap) mode at one end to a gap (local) mode at the other end. This while explaining the end member impurity, the modes will not explain both the end member reststrahl absorptions. If we attribute the concentration dependence (equation (11)) to both ω_0 and λ it will result in a band crossing which is unphysical. (iii) The third possibility is to attribute a concentration dependence to the force constant change parameter τ as per (11) while keeping ω_0 and λ concentration independent. The latter quantities have to be kept independent of concentration to avoid the unphysical feature of band crossing. However, now there are two parameters τ_{A} and τ'_{A} corresponding to the force constant changes at the two end members. These have to be fitted to the experimental values of the local (gap) and transverse optic frequencies as per the prescriptions to be followed depending on whether one is dealing with a one, two or a mixed mode system. To state the prescription let us first write (9) together with (11) for τ for the case when B is an impurity in AC replacing an A atom so that (9) become

$$\omega = \omega_{\text{TO}}^{\text{A}}, \quad (12a)$$

$$\omega = \omega_{\text{TO}}^{\text{A}} (1 - \lambda_{\text{A}})^{1/2} [1 + (1 - c) \tau_{\text{A}} + c \tau'_{\text{A}}]^{1/2}, \quad (12b)$$

where

$$\lambda_{\text{A}} = (M_{\text{B}} - M_{\text{A}})/M_{\text{B}}, \quad (13a)$$

$$\tau_{\text{A}} = (\Phi_{\text{BC}} - \Phi_{\text{AC}}^{(0)})/\Phi_{\text{AC}}^{(0)}, \quad (13b)$$

$$\tau'_{\text{A}} = (\Phi_{\text{BC}}^{(0)} - \Phi_{\text{AC}}^{(0)})/\Phi_{\text{AC}}^{(0)}. \quad (13c)$$

Φ_{BC} is the force constant when a B atom is substituted at the A site of an AC crystal and $\Phi_{\text{BC}(\text{AC})}^{(0)}$ is the force constant of a perfect BC (AC) crystal. Note that $\Phi_{\text{BC}(\text{AC})}$ and $\Phi_{\text{BC}(\text{AC})}^{(0)}$ are quite different from each other. τ'_{A} as a new force constant change parameter, so chosen that (12b) goes to $\omega_{\text{TO}}^{\text{B}}$ at $C = 1$. Correspondingly there is a set of two other equations, if one starts with BC as host and A as impurity

$$\omega = \omega_{\text{TO}}^{\text{B}}, \quad (14a)$$

$$\omega = \omega_{\text{TO}}^{\text{B}} (1 - \lambda_{\text{B}})^{1/2} [1 + (1 - c) \tau_{\text{B}} + c \tau'_{\text{B}}]^{1/2}, \quad (14b)$$

$$\text{where } \lambda_{\text{B}} = (M_{\text{A}} - M_{\text{B}})/M_{\text{A}}, \quad (15a)$$

$$\tau_B = (\Phi_{AC} - \Phi_{BC}^{(0)})/\Phi_{BC}^{(0)} \approx \frac{-\tau_A}{1 + \tau_A}, \quad (15b)$$

$$\text{and} \quad \tau'_B = (\Phi_{AC}^{(0)} - \Phi_{BC}^{(0)})/\Phi_{BC}^{(0)} = \frac{-\tau'_A}{1 + \tau'_A}. \quad (15c)$$

In (14b) C is measured from the end member BC, thus describing the mode at $C = 0$. Again τ'_B will force (14b) to go to ω_{TO}^A at $C = 1$. It is worth noticing that (15c) is an exact relation whereas (15b) is only an approximation. This will be reflected upon while comparing the predictions of the theory with experiment. Thus, out of the four only two force constant change parameters should be fitted to end member data, and the other two can be calculated as shown by (15). Now the prescriptions for fitting the two parameters to the experimental data for various systems are the following. (a) For a two mode system τ_A and τ'_A should be fitted to the observed local (gap) mode at $C = 0$ and to ω_{TO}^B at $C = 1$ respectively. Then τ_B and τ'_B should be calculated from (15). The concentration dependence is obtained by plotting (12b) and (14b). The other two roots (12a) and (14a) need to be plotted because (12b) ends up at (14a) and (14b) ends up at (12a). (b) On the other hand for a one mode system for which impurity modes do not appear, τ_A should be so chosen that the impurity mode given by (12b) is forced to coincide with ω_{TO}^A at $C = 0$ and τ'_A chosen to reduce (12b) to ω_{TO}^B at $C = 1$. On calculating τ_B and τ'_B and plotting the concentration dependent (14b) the curve is expected to coincide with the curve of (12b) thus giving a one mode behaviour. (c) For mixed mode systems the parameters are chosen following the procedure similar to that of the two mode systems (*i.e.* prescription (a)). As will be shown while discussing the experimental data, the mixed mode behaviour arises in most cases because of the reduction of the strength of absorption beyond a critical concentration, rather than the overlapping of the two modes.

3. Results and discussion

Here we shall compare the results of our calculation with the experimental concentration dependence of the observed modes. The emphasis of the calculation is to explain the concentration dependence, with the prior knowledge of the experimental mixed crystal behaviour (tabulated by Elliott and Leath 1975) of the systems. Once, we know that the system shows one (I) two (II) or mixed (I-II) mode behaviour, we can apply the prescription of § 2 to determine the various force constant change parameters τ_A , τ'_A , τ_B and τ'_B and then determine the concentration dependence from (12b) and (14b). These calculations are carried out for twenty mixed crystal systems. The fitted and calculated values of the force constant change parameters are given in table 1. In table 1, we have also given the calculated values (from (14b)) of one of the transverse optic mode frequencies (ω_{TO}) and one of the impurity modes (local or gap) which depend on τ'_B and τ_B respectively. The latter quantities are calculated from a knowledge of τ'_A and τ_A respectively using (15c) and (15b). It can be seen from the table that the calculated values of ω_{TO} coincide exactly with the experimental values. This is expected because τ'_B as calculated from τ'_A when substituted in (14b) for the appropriate value of the concentration (0 or 1) gives the exact value of ω_{TO} for that end. On the other hand the calculated value of the impurity mode (local or gap)

Table 1. The experimental transverse optic mode (ω_{TO}) frequencies, the impurity local (L) and gap (G) modes the fitted and calculated force constant change parameters, together with the calculated ω_{TO} and $\omega_{G(L)}$ is given for the end members $c = 0$ and $c = 1$. The experimentally observed mode behaviours and the references are also tabulated. Wherever the impurity mode frequencies are taken from references other than the references from which the data for the concentration dependence are taken are also indicated.

System (1)	C (2)	Experimental values		Fitted τ_A (5)	Calculated τ_B (6)	Calculated values		Mode behaviour (9)	Reference (10)
		ω_{TO} in cm^{-1} (3)	$\omega_{G(L)}$ in cm^{-1} (4)			ω_{TO} in cm^{-1} (7)	$\omega_{G(L)}$ in cm^{-1} (8)		
KBr _{1-c} Cl _c	0	113	95(G) ^b	-0.5557	1.2507	113		I	a,b
	1	142		-0.29838	0.4253			I	
Rb _{1-c} K _c I	0	75		0.6637	-0.39893		86.08(L)	I	c,d
	1	101	88(G) ^c	0.20845	-0.1725	101		I	
K _{1-c} Rb _c Cl	0	142		1.186748	-0.5427	142		I	a
	1	122		0.61414	-0.38047			I	
K _{1-c} Na _c Cl	0	142		-0.41176	0.69998	172		I	e
	1	172		-0.2042	0.2566			I	
CdSe _{1-c} S _c	0	170	276(L)	0.05712	-0.054	170		II	a
	1	240	188(G)	-0.2348	0.30699		147.82(G)	II	
Ga _{1-c} Al _c Sb	0	225	312(L) ^{f,g}	-0.2557	0.34353	225		II	a,f,g
	1	318	205(G)	-0.22679	0.29331		229(G)	II	
Ga _{1-c} Al _c P	0	366	438(L)	-0.4456	0.80387	366		II	h
	1	439	350(G)	-0.4431	0.79566		366(G)	II	
Ga _{1-c} Al _c As	0	268	360(L)	-0.30153	0.431714	268		II	i
	1	364	252(G)	-0.285928	0.40042		270(G)	II	
ZnSe _{1-c} S _c	0	205	285(L)	-0.2161	0.27567	205		II	a
	1	260	216(G)	-0.3476	0.5328		187(G)	II	
Ga _{1-c} In _c Sb	0	225		-0.2296	0.298		199(G)	I	d,j
	1	174	200(L) ^j	0.01525	-0.01502	174		II	
In _{1-c} Ga _c As	0	219	240(L) ^{k,l}	-0.27081	0.371385	219		II	d,k,l
	1	269		-0.08394	0.0916		245.4(G)	I	
In As _{1-c} P _c	0	213	303(L)	-0.16246	0.19397	213		II	m
	1	310	223(G)	-0.123314	0.14066		218(G)	II	

GaAs _{1-c} P _c	0	266	340(L) ^m 270(G)	-0.3388 -0.225412	0.5124 0.29101	266	291(G)	II II	k,n d
Ga _{1-c} In _c P	0	366		0.6469 0.1587	-0.3928 -0.137	366		I I	d
Zn _{1-c} Cd _c S	0	271		0.7186 0.30339	-0.41815 -0.23277	271		I I	d
Ni _{1-c} Co _c O	0	401		0.0034065 -0.23995	-0.003395 0.31571	401		I I	d
GaAs _{1-c} Sb _c	0	272	238(L)	-0.33578 -0.13245	0.50553 0.15267	229	261(G)	I II	k,o
In As _{1-c} Sb _c	0	219		-0.18686 -0.025	0.2298 0.025676	174	190(G)	I II	d,k
Hg _{1-c} Cd _c Te	0	116	200(L) 138(L)	-0.2008 -0.17358	0.251258 0.210045	116	118(G)	II II	p
K _{1-c} Tl _c Cl	0	142		4.2274 1.29067	-0.8087 -0.56345	142		I I	e

(a) Chang and Mitra 1968, (b) Nolt *et al* 1967, (c) Genzel 1971, (d) Barker and Sievers 1975, (e) Chang and Mitra 1971, (f) Lucovsky *et al* 1975, (g) Ipatova *et al* 1976, (h) Lucovsky *et al* 1976, (i) Illegems and Pearson 1970, (j) Brodsky *et al* 1970, (k) Lucovsky and Chen 1970, (l) Brodsky and Lucovsky 1968, (m) Kekelidze *et al* 1973, (n) Hayes *et al* 1970, (o) Pottor and Stierwalt 1964, (p) Mooradian and Harman 1971.

frequency shows only qualitative agreement because of the approximate nature of the relation between τ_B and τ_A as given by (15b). This emphasizes the point that the nearest neighbour force constant Φ_{AC} of an impurity atom A substituted at the B site of the host BC is considerably different from that of the perfect AC crystal, namely $\Phi_{AC}^{(0)}$. Further this difference plays a crucial role in determining the concentration dependence of the frequencies of the mixed crystal systems. Table 1 also gives the experimental values of the ω_{TO} 's and impurity mode frequencies (if observed) of the end members of the mixed crystal. The references to original measurements as well as the experimental behaviour are also tabulated. The results of the calculation for these twenty mixed crystal systems are compared with the experimental data in figures 1-5. In these figures the behaviour of the mixed crystal systems as determined from experiments, is denoted by I, II and I-II. The experimental points are given by open circle (and circles with a cross, where the data is taken from two different measurements). The end member transverse optic mode frequencies (ω_{TO}) are marked by closed circles and the impurity modes (local or gap) by crosses, the values of which are taken from experiments other than mixed crystal measurements in some cases. The results of the calculation are presented as full lines. Out of all the twenty cases considered, the experimental concentration dependence plot for one of the systems, In $As_{1-c}Sb_c$ is not given so the frequencies are taken to be the peak positions of the reflectivity measurements.

Figures 1 (a, b, c, d) and 5(d) give the comparison of the theory with experiment for ionic mixed crystals out of which the systems $KBr_{1-c}Cl_c$, $K_{1-c}Rb_cCl$, $K_{1-c}Na_cCl$ and $K_{1-c}Tl_cCl$ show one mode behaviour and the system $Rb_{1-c}K_cI$ shows two mode behaviour. It can be seen from these figures that the agreement between theory and

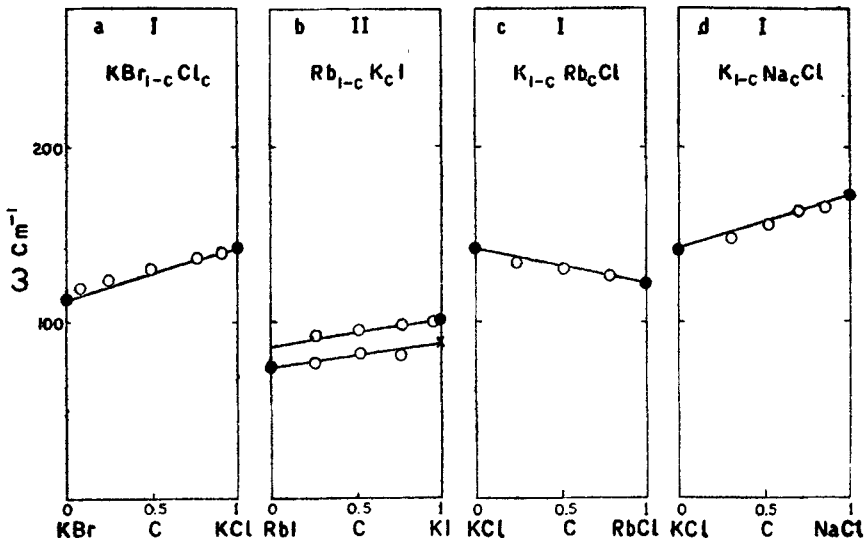


Figure 1. a.b.c.d show the concentration dependence of the frequencies for $KBr_{1-c}Cl_c$, $Rb_{1-c}K_cI$, $K_{1-c}Rb_cCl$ and $K_{1-c}Na_cCl$ mixed crystal systems. I, II and I - II at the top of the figure denote the observed mode behaviour.

⊗, ○: experimental data points; ●: transverse optic mode frequencies of the end member host crystals, X: experimentally observed impurity (local or gap) mode and the solid line gives the result of the present calculation. Legend as in figure 1.

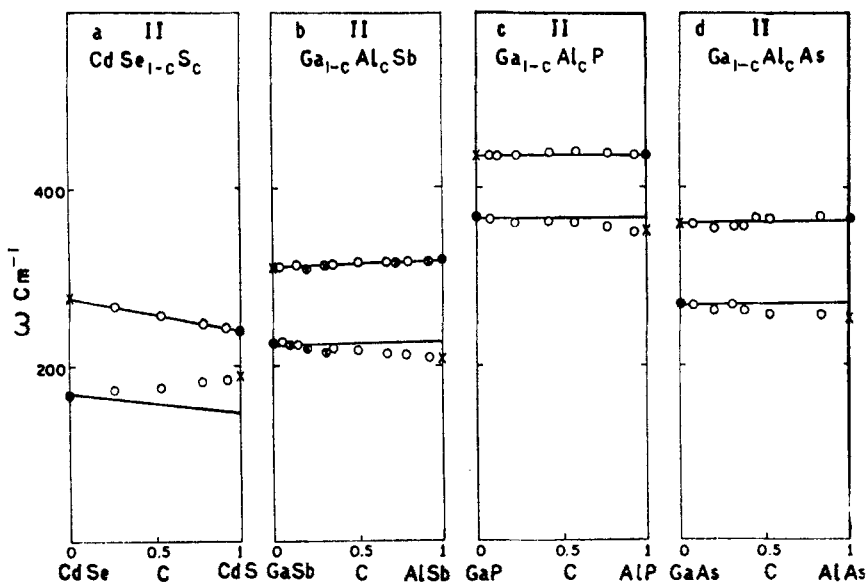


Figure 2. a, b, c, d show the concentration dependence of the frequencies for CdSe_{1-c}S_c, Ga_{1-c}Al_cSb, Ga_{1-c}Al_cP and Ga_{1-c}Al_cAs mixed crystals respectively. Legend as in figure 1.

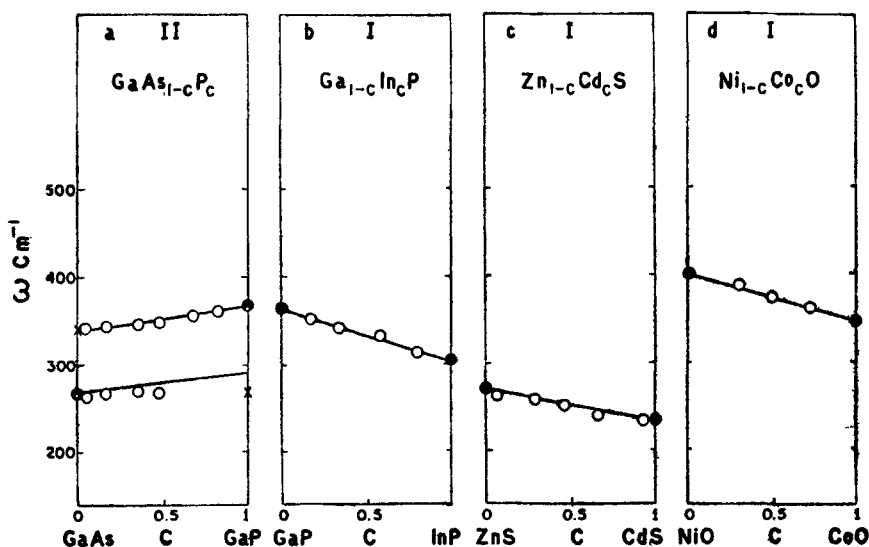


Figure 3. a, b, c, d show the concentration dependence of the frequencies for GaAs_{1-c}P_c, Ga_{1-c}In_cP, Zn_{1-c}Cd_cS and Ni_{1-c}Co_cO mixed crystals respectively. Legend as in figure 1.

experiment is quite good, which indicates that the values of the force constant change parameters provide a good representation of the actual systems for the ionic mixed crystals. A general trend that persists in all the figures 1 to 5 is that (12b) and (14b) when plotted for the one mode systems almost coincide (the difference is usually in the second decimal place, hence it cannot be resolved in these figures) for all one mode systems whether they represent ionic mixed crystals or the III-V (Ga_{1-c}In_cP) or II-VI (Zn_{1-c}Cd_cS) compounds. In the case of the two mode systems the agree-

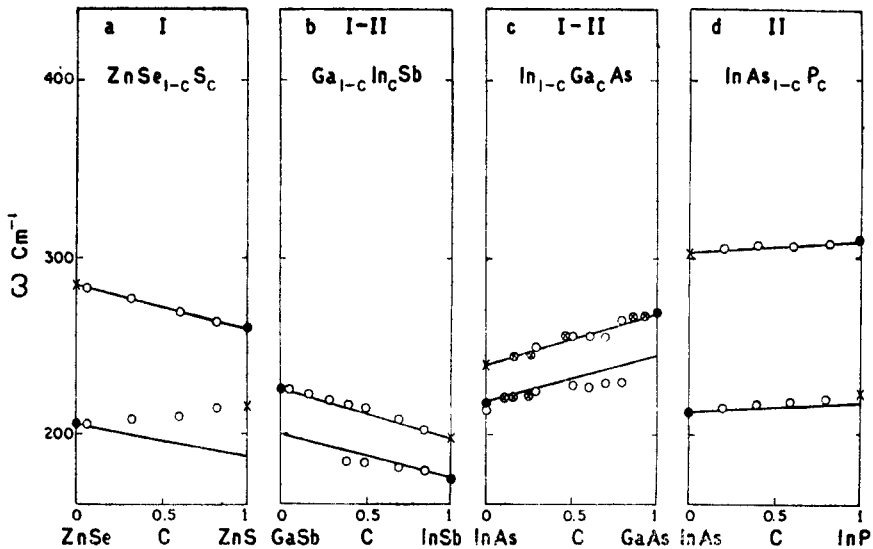


Figure 4. a, b, c, d show the concentration dependence of the frequencies for $\text{ZnSe}_{1-c}\text{S}_c$, $\text{Ga}_{1-c}\text{In}_c\text{Sb}$, $\text{In}_{1-c}\text{Ga}_c\text{As}$ and $\text{InAs}_{1-c}\text{P}_c$ mixed crystal systems respectively. Legend as in figure 1.

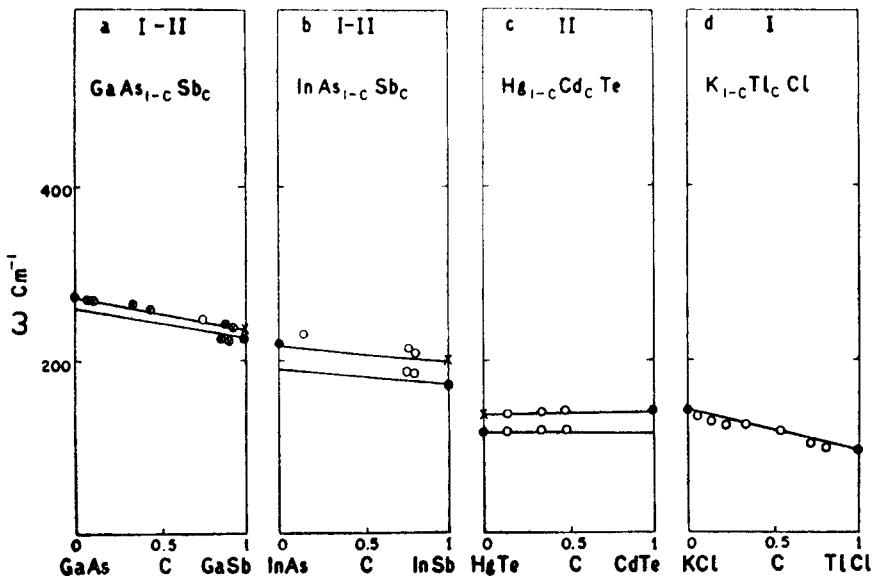


Figure 5. a, b, c, d show the concentration dependence of the frequencies for $\text{GaAs}_{1-c}\text{Sb}_c$, $\text{InAs}_{1-c}\text{Sb}_c$, $\text{Hg}_{1-c}\text{Cd}_c\text{Te}$ and $\text{K}_{1-c}\text{Tl}_c\text{Cl}$ mixed crystal systems respectively. Legend as in figure 1.

ment between theory and experiment is reasonable for some systems like $\text{Rb}_{1-c}\text{K}_c\text{I}$ (figure 1b), $\text{InAs}_{1-c}\text{P}_c$ (figure 4d) $\text{GaAs}_{1-c}\text{P}_c$ (figure 3a) and $\text{Hg}_{1-c}\text{Cd}_c\text{Te}$ (figure 5c). It should be noted that in the last mentioned case a gap mode for $C = 1$ could not be determined experimentally. But there are large discrepancies between theory and experiment in the other two mode systems *i.e.* $\text{CdSe}_{1-c}\text{S}_c$ (figure 2a), $\text{Ga}_{1-c}\text{Al}_c\text{Sb}$ (P, As) (figure 2 b, c, d, and $\text{ZnSe}_{1-c}\text{S}_c$ (figure 4a). One dominant feature in the discrepancy is that the fitted curve equation (12b) shows good agreement with the experi-

mental data whereas the calculated curve equation (14b) shows deviation from the experimental data towards the impurity mode end. One of the reasons for this disagreement is again the approximate calculation of τ_B the force constant change parameter at the impurity end from that of τ_A . The three two-mode systems $\text{Ga}_{1-c}\text{Al}_c\text{Sb}$ (P, As) (shown in figures 2 b, c, d) show some general trends. It can be seen from table 1 that the magnitude of the force constant change parameters have the largest value for the system $\text{Ga}_{1-c}\text{Al}_c\text{P}$, but decrease gradually as one goes to $\text{Ga}_{1-c}\text{Al}_c\text{As}$ and then the $\text{Ga}_{1-c}\text{Al}_c\text{Sb}$. The predicted gap models in all the three cases have values higher than the observed values, again the agreement worsens as one goes from $\text{Ga}_{1-c}\text{Al}_c\text{P}$ to $\text{Ga}_{1-c}\text{Al}_c\text{Sb}$. Lucovsky *et al* (1976) have made an analysis of the experimental data of these three systems using the MREI model, with varying force constant change parameters. Even the six parameter MREI model calculation does not reproduce the exact concentration dependence. Their fitted nearest neighbour force constants have nearly equal values for both the end member components which they argue is consistent with the almost equal lattice parameters of the end member systems. However, they found large variations in the next nearest neighbour force constants of the end members which is difficult to understand. The large values of force constant change parameters obtained by us (table 1), however, indicate that the nearest neighbour force constants of the end members have quite dissimilar values. Finally, we remark that the spectrum of some of the one and two mode systems like $\text{Ga}_{1-c}\text{In}_c\text{P}$ and $\text{GaAs}_{1-c}\text{P}_c$ respectively show considerable structure, but the present theory which neglects effects of clustering is not adequate to account for this structure.

Let us now turn to the more complicated mixed (I-II) mode systems. We have analysed four such systems *i.e.* $\text{Ga}_{1-c}\text{In}_c\text{Sb}$, $\text{In}_{1-c}\text{Ga}_c\text{As}$ (figure 4b and c), $\text{GaAs}_{1-c}\text{Sb}_c$ and $\text{InAs}_{1-c}\text{Sb}_c$ (figures 5a and b). As mentioned in § 2.1, the prescription for the theoretical calculation of the mixed mode system is the same as that of the two mode systems. Hence our calculations show two-mode like behaviour of all the above mentioned systems. The following general features of these four mixed mode systems is worth noting: (i) one of the modes abruptly vanishes beyond a critical concentration. The concentration dependence of the frequencies does not show any indication that the two modes merge beyond this critical concentration. From this one could conclude that the vanishing of the mode is due to the reduction and ultimate vanishing of the strength of absorption of this mode. (ii) In all the systems the vanishing of the mode takes place towards the end member where a gap mode is expected. These observations are in qualitative agreement with the predictions of the present theory. As can be seen from (10) and the discussion following it, the strength of absorption of the impurity mode is equal to the concentration times a factor of $(1 - \lambda) = M/M'$. For a gap mode, $M' > M$ and hence the strength of absorption is lowered. In particular the strength of absorption of the gap mode for values $C \rightarrow 0$ will be lowered so much that it cannot be observed if $M' \gg M$, thus giving rise to the mixed mode behaviour. This is also borne out in two mode systems like $\text{Ga}_{1-c}\text{Al}_c\text{P}$ (Lucovsky *et al* 1976) an examination of the reflection spectra of which reveals that for $C = 0.08$ the Al local mode is quite prominent as compared to the Ga gap mode at the corresponding concentration of $C = 0.92$. It can be further seen from figures 4(c) and 5(a) that for the mixed mode systems $\text{In}_{1-c}\text{Ga}_c\text{As}$ and $\text{GaAs}_{1-c}\text{Sb}_c$ the calculated curves for the impurity modes (gap) tend to merge into the optical band and as a result these will not be observable. In the former case the calculated gap mode frequency at

$C = 1$ is 245.4 cm^{-1} (table 1), which just merges into the optical band of GaAs having a gap between 232.7 cm^{-1} and 245.3 cm^{-1} (Dolling and Waugh 1965). But in the latter case the calculated gap mode curve for Sb in Ga As falls right inside the optic band of Ga As being at 261 cm^{-1} . Thus the calculated curve merges into the optical band for $C \lesssim 0.5$ and hence cannot be observed experimentally for this range of the concentration. In fact experimentally the mode was not observed for $C \lesssim 0.85$. Thus we suggest that the merger of the mode into the optical band together with the reduction of the strength of the gap mode at low concentrations is the cause for the existence of the mixed mode behaviour. In fact, to be more accurate one has to take into account the concentration dependence of the optical band width of the mixed crystals which we have not considered here.

4. Conclusion

To conclude we would like to summarize the main results of the present calculation. We have tried to explain the concentration dependence of the observed frequencies of mixed crystal systems starting from the Einstein model analysis of the generalized CPA result of Tripathi and Behera (1974). In doing so we introduced the concentration dependence through the force constant change parameter τ , by demanding that it follows a virtual crystal like behaviour. Emphasis should be given to the behaviour of the end members for fitting and calculating the force constant change parameters. An important realization which emerges from the analysis is that the nearest neighbour force constant of an impurity atom substituted into a host site is very much different from that of a perfect crystal constituting of the impurity atoms themselves. Prescriptions for determining these force constant change parameters and hence the concentration dependence of the frequencies for one, two and mixed mode systems are provided. Comparison of the results of the calculation with the experimental data for some twenty systems show qualitative agreement. So far all the concentration dependence calculations have taken recourse to the MREI model and its variations which is an even cruder model than the present one and uses the same virtual crystal like concentration dependence for the force constants. However one of the major drawbacks of the model is the neglect of the width of the reststrahlen band whose importance was pointed out by Elliott *et al* (1974). Besides it was shown by Behera and Tripathi (1974) and Behera (1974) that attributing a width (γ_0) to the transverse optic frequency ω_{TO} automatically results in a concentration dependence of the frequencies of mixed crystal systems. However their calculations were confined to the low concentration or the ATA regime. The generalization of this to a CPA calculation is presently under investigation.

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