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A new criterion for the mixed crystal behaviour in the diatomic linear chain model

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Abstract. Lucovsky, Brodsky, Burstein (LBB) have studied the behaviour of mixed crystals by setting up a criterion for the existence of local mode frequencies in real crystals starting from a diatomic linear chain model. This, while successfully predicting the one and two mode behaviour for some systems fails to predict the mixed mode behaviour. We propose a similar criterion for the existence of gap modes, by demanding that the gap mode predicted by the diatomic linear chain model should lie within the gap of the real three dimensional solid for its existence. It is shown that the gap modes for various systems calculated using this criterion are in reasonable agreement with the experimental values. The infrared behaviour of mixed crystals has to be determined by examining the existence of local as well as gap modes for the two end members of the system. This generalized new criterion successfully predicts the mixed mode behaviour of III–V mixed crystals besides predicting the one and two mode behaviour, observed in infrared absorption of mixed alkali halides and III–V compounds.

Keywords. Impurity modes; mixed crystals; gap modes; defect lattice dynamics.

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 (Barker and Sievers 1975, Chang and Mitra 1971). For some of these (*e.g.* $Rb_{1-x}K_xBr$ $KI_{1-x}Cl_x$) the absorption takes place around the reststrahl frequency of one end member of the system say AC or AB for $x \to 0$ which shifts with increasing x to the reststrahl frequency of the other end member BC or AC for x going to one. Such behaviour is described as the 'one mode' behaviour in contrast to systems showing what is called the 'two mode' behaviour. The latter behaviour is shown by systems like $Rb_{1-x}K_xI$ or $InAs_{1-x}P_x$. Such systems show absorption at two frequencies for x tending to zero corresponding to the reststrahl and local mode, the strength of the former peak decreases and that of the latter increases with increasing x till x becomes one. Yet there exists another set of mixed crystals mostly of III–V compounds like $GaSb_{1-x}As_x$ $InSb_{1-x}As_xIn_{1-x}$ Ga_xAs (Lucovsky *et al*

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(1970)) and $In_{1-x}Ga_xSb$, (Brodsky *et al* 1970) which show two mode behaviour within a range of concentration beyond which these are like one mode systems. Such systems can be said to exhibit the 'mixed mode' behaviour.

Several theoretical models (Barker and Sievers 1975, Chang and Mitra 1971) have been proposed to explain the one and two mode behaviour, such as the diatomic linear chain model of Mazur *et al* (MMP) (1956) and its modification by Lucovsky *et al* (LBB) (1970) the coherent potential approximation (CPA) calculation for the diatomic linear chain by Sen and Hartmann (1974), the modified random element isodisplacement model (MREI) (Chang and Mitra 1971), the three-dimensional mass defect CPA calculation by Taylor (1973), and the one including force constant changes by Behera (1974) and Tripathy and Behera (1974). In the diatomic linear chain model of MMP, a mass defect substituted either in the light or the heavy mass sublattice will produce a local mode, a gap mode or both depending on whether a lighter or heavier impurity is substituted in the light mass sublattice, or a lighter impurity is substituted in the heavy mass sublattice respectively. A heavier impurity in the heavy mass sublattice produces no new modes. This last result is also true for real crystals (Maraduddin 1968). However, the MMP theory predicts that a local mode appears for all light mass impurities in contrast to the real crystal case where the lighter impurity should have a mass below a certain critical mass for the appearance of the local mode. Lucovsky *et al* (1970) improved the MMP model imposing a criterion for the appearance of the local mode by introducing the longitudinal optical mode frequency ω_{LO} of the real crystal. According to the LBB criterion the local mode frequency ω_L must be greater than ω_{LO} in order that it be observable. This criterion is based on the observation that the variation of ω_L with the mass defect parameter ϵ, [$\epsilon = (M' - M)/M$, M' being the impurity and M the host mass] in the MMP calculation closely resembles realistic three-dimensional calculations (Jaswal 1965). They calculated the local modes for various systems using this criterion which showed reasonable agreement with the experimental values. Also they examined some 21 mixed crystal systems and claimed successful prediction of behaviour for eighteen of them. However, a close look at the LBB criterion reveals that this, while predicting correctly the one mode behaviour of systems like $Rb_{1-x}K_xBr$ and the two mode behaviour for systems like $Rb_{1-x}K_xI$ and $ZnSe_{1-x}S_x$ incorrectly predicts systems showing mixed mode behaviour to be two mode type. Recently Sen and Hartmann (1974) have generalized the MMP theory to all concentrations within the CPA. Even though their calculations show partial success for the mixed mode cases, these do not still provide a criterion for predicting the mixed mode behaviour. The failure of the LBB criterion for predicting the mixed mode behaviour can be traced to the lack of examination of the existence of the gap modes in the limit of the concentration going to one. Besides according to the MMP theory as well as the LBB criterion systems like $KBr_{1-x}Cl_x$, $ZnSe_{1-x}S_x$ and $InSb_{1-x}As_x$ should show a three mode behaviour when $x \to 0$ because both a local as well as a gap mode are expected. However, observation of such behaviour is not reported as yet.

In this paper we aim at improving the LBB criterion by imposing a suitable restriction on the appearance of the gap mode, in order to get rid of the failures mentioned above. In section 2 we examine the gap modes within the MMP theory and develop a criterion for its existences following the same line of argu-

ment as that of LBB. In section 3 we apply this criterion to the calculation of gap modes and compare the predicted values with the existing experimental data. Section 4 is devoted to developing criteria and predicting the behaviour of mixed crystal systems; and demonstrate the success of the theory. Finally we conclude in section 5, by pointing out the merits and demerits of this simple calculation.

2. Extension of LBB criterion to gap modes

The gap mode frequency for the case of a single mass defect in a diatomic linear chain can be calculated in a straightforward manner from the MMP theory. Recently the MMP theory has been generalized to the case of a pair of impurities by Behera and Patnaik (1975, 1976), which reproduces the single impurity result when one of the mass defect parameters is equated to zero. Following their notation the impurity mode (gap and local) frequency is given by

$$Z_{\binom{G}{L}} = \{(1 + b^{-1} - a^{-1}\epsilon_2^2) \mp [(1 + b^{-1} - a^{-1}\epsilon_2^2)^2 - 4b^{-1}(1 - \epsilon_2^2)]^{\frac{1}{2}}\}/2(1 - \epsilon_2^2) \tag{1}$$

where

$$Z = (\omega^2/\omega_m^2); \quad a = 1 + (M_1/M_2); \quad b = 1 + (M_2/M_1) \tag{2a}$$

$$\epsilon_2 = (M'_2 - M_2)/M_2; \quad \omega_m^2 = 2\gamma\left(\frac{1}{M_1} + \frac{1}{M_2}\right). \tag{2b}$$

γ is the nearest neighbour force constant and M_2' is the impurity mass substituted into the defect sublattice of mass M_2. It can be easily seen that Z_L given by eq. (1) is identical to that given by LBB as calculated from the MMP theory.

In order that this simple diatomic linear chain model calculation can be applied to real solids LBB introduced the criterion that the local mode frequency given by eq. (1) be greater than the ω_{LO} of the real crystal, *i.e.*,

$$Z_L(\epsilon_2) \geqslant (\omega_{LO}/\omega_m)^2 \tag{3}$$

where the maximum frequency ω_m is related to the transverse optic (ω_{TO}) and longitudinal optic (ω_{LO}) mode frequencies through the sum rule (Lucovsky *et al* 1970)

$$3\omega_m^2 = 3(\omega_1^2 + \omega_2^2) = 2\omega_{TO}^2 + \omega_{LO}^2 \tag{4}$$

where

$$\omega_1^2 = 2\gamma/M_1; \quad \omega_2^2 = 2\gamma/M_2; \quad \omega_1^2/\omega_2^2 = M_2/M_1$$

and ω_1 and ω_2 being the zone boundary frequencies for the acoustic and optical bands. Equation (3) defines a critical mass defect parameter for the appearance of the local mode.

In order to obtain a similar criterion for the existence of the gap mode it is first necessary to compare how the predicted variation of the gap mode frequency with ϵ_2 for the diatomic linear chain case compares with the realistic three dimensional model calculations. Of course one can positively say that the gap mode will not exist (i) if the host crystal does not have a gap and (ii) if $\epsilon_2 > 0$ for

$M_2 > M_1$, *i.e.*, if a heavy mass impurity is substituted in the heavy mass sublattice. The variation of ω_G with ϵ_2 for the NaI host as calculated from the diatomic linear chain model as well as a realistic calculation carried on by Jaswal (1965) is shown in figure 1. As can be seen from the figure the two curves are pretty close to each other for the case of a heavy impurity substituted into the light mass sublattice (*i.e.*, $\epsilon_2 > 0$ and $M_2 < M_1$) and hence for this case the predicted gap mode frequency is expected to agree well with that of the three dimensional calculations and with experiment. On the other hand, for a light mass impurity substituted into the heavy mass sublattice (*i.e.*, $\epsilon_2 < 0$ and $M_2 > M_1$) the agreement between the two curves is rather poor, thus indicating that the diatomic linear chain model will give poor results for these cases. Note that the two curves have to be compared within the real gap of the crystal; and that the diatomic linear chain ω_G values are calculated using the sum rule given by eq. (4). The partial agreement with the realistic calculation also indicates the criterion to be set up for the existence of the gap mode, namely the calculated gap mode frequency must be within the real gap of the host crystal. Hence one can set up the criterion that the gap mode will exist only if ω_G given by eq. (1) will lie between the experimentally observed zone boundary values of longitudinal acoustic mode frequency (ω_{LA}^{max}) and the minimum value of the transverse optic mode fre-

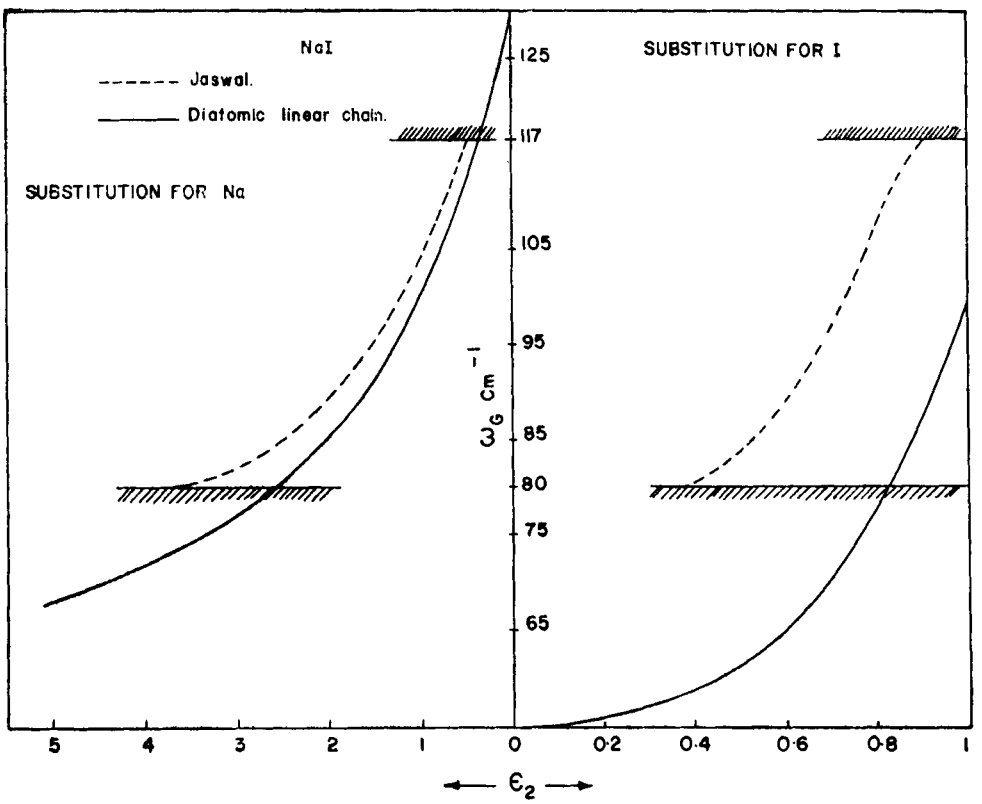

Figure 1. Variation of the gap mode frequency with the mass defect parameter ϵ_2 from the diatomic linear chain calculation and the realistic three-dimensional calculation of Jaswal for NaI. The real gap of the crystal is also indicated.

quency (ω_{TO}^{min}). The zone boundary values are chosen as the limiting values because these will correspond to the maxima in the density of states. Thus even if there exist frequencies ω_{qj} such that $\omega_{TO}^{min} > \omega_{qj} > \omega_{LA}^{max}$ which will amount to reducing the gap, one need not take these values of ω_{qj} as the limiting values because at such frequencies the density of states will be low and as a result the gap mode which falls in these ranges will be observable. Thus the criterion for the existence of the gap mode becomes

$$[(\omega_{TO}^{min})^2/\omega_m^2] \geqslant Z_G \geqslant [(\omega_{LA}^{max})^2/\omega_m^2] \tag{5}$$

where ω_m is given by eq. (4) and ω_{LA}^{max} and ω_{TO}^{min} are determined from the experimental phonon dispersion curves. It is worth pointing out at this stage that the existence criterion for the gap modes as given by eq. (5) has been used earlier (Behera and Patnaik 1975) for calculating the gap modes due to impuirity pairs in some alkali halide crystals and the results showed good qualitative agreement with the experimental values. In what follows we shall apply these results to calculate the gap mode frequencies and predict the infrared behaviour of mixed crystals.

3. Calculation of gap modes

The gap modes are calculated from eq. (1) using the existence criterion given by eq. (5) for sixteen mixed crystal systems, out of which seven are mixed ionic crystals and the rest nine are mixed semiconducting compounds. Table 1 gives the mass defect parameters, the experimental values of ω_{TO} and ω_{LO} as well as the values of ω_m calculated using the sum rule given by eq. (4) in the limits of x going to zero and one, corresponding to the end member systems. Table 2 gives the range of the gap frequencies determined from the experimental phonon dispersion curves wherever available for both the end member host crystals and also the calculated gap mode frequencies for $x \to 0$ and $x \to 1$. If the calculated value of ω_G falls within the range of the gap, then it is a true gap mode otherwise not. The existing experimental values of ω_G are also tabulated. For the sake of completeness the last column of table 2 gives the calculated local mode frequencies as given by LBB, which will be needed in determining the infrared behaviour of the mixed crystal systems. The theory predicts the existence of gap modes for seven systems, out of which it is observed for five systems namely KBr : Cl^-, KI: Cs^+, KI: Ag^+, KI: Rb^+ and GaP: As. For these systems the predicted and experimental values of ω_G show qualitative agreement. For many other systems the predicted gap modes could not be confirmed because of the non-availability of experimental data on the range of the gap. However, gap modes are observed for another three systems namely CdS: Se, KI: Br^- and KI: Cl^-. The experimentally observed frequencies for the first system is 188 cm^{-1} and the theory predicts gap mode at 168·56 cm^{-1} which cannot be confirmed as the gap ranges for this system is not known. In the case of CdS, the realistic three-dimensional calculation of Pfeuty *et al* (1968) shows a region of low density of states between 150 cm^{-1} and 200 cm^{-1}, but no real gap. Hence one can conclude that the gap mode predicted at 168·56 cm^{-1} can be observed and this is in good agreement

Table 1. Values of the mass defect parameters ϵ_2, the experimental values of the transverse optic (ω_{TO}) and longitudinal optic (ω_{LO}) mode frequencies and the values of ω_m calculated from eq. (4) for the two end member host crystals corresponding to $x = 0$ and $x = 1$.

System	$\epsilon_2 = (M_2' - M_2)/M_2$		ω_{TO} in cm^{-1}*		ω_{LO} in cm^{-1}*		ω_m in cm^{-1} from eq. (4)	
	$x = 1$	$x = 0$	$x = 1$	$x = 0$	$x = 1$	$x = 0$	$x = 1$	$x = 0$
$KBr_{1-x}Cl_x$	1·2507	−0·557	142	113	214	165	169·434	132·618
$Rb_{1-x}K_xBr$	1·1867	−0·5427	113	88	165	127	132·618	102·659
$Rb_{1-x}K_xI$	1·1867	−0·5426	101	75	139	103	115·069	85·360
$KI_{1-x}Br_x$	0·5882	−0·3704	113	101	165	139	132·618	115·069
$KI_{1-x}Cl_x$	2·5746	−0·7202	142	101	214	139	169·434	115·069
$Cs_{1-x}K_xI$	2·3989	−0·7458	101	62	139	85	115·069	70·5
$Ag_{1-x}K_xI$	1·7591	−0·638	101	108	139	..	115·069	..
$ZnSe_{1-x}S_x$	1·461	−0·5937	271	209	352	250	300·046	223·504
$CdSe_{1-x}S_x$	1·461	−0·5937	228	166	305	211	256·250	182·239
$In_{1-x}Ga_xAs$	0·647	−0·3929	269	219	292	243	276·879	227·282
$GaSb_{1-x}As_x$	0·6262	−0·3851	269	225	292	236	276·879	228·725
$In_{1-x}Ga_xSb$	0·647	−0·3929	225	174	236	183	228·725	177·051
$InSb_{1-x}As_x$	0·6261	−0·3851	219	174	243	183	227·282	177·051
$In_{1-x}Ga_xP$	0·647	−0·3929	366	307	402	351	378·380	322·335
$GaAs_{1-x}P_x$	1·4161	−0·5861	366	269	402	292	378·380	276·879
$InAs_{1-x}P_x$	1·4161	−0·5861	307	219	351	243	322·334	227·282

* See Barker and Sievers (1975).

with the experimental value of 188 cm^{-1}. On the other hand, for the last two systems mentioned above, namely KI: Br^- and KI: Cl^-, gap modes are observed at 88·94 cm^{-1} and 77·1 cm^{-1} whereas the theory predicts no gap mode for the first system and a mode at 68·235 cm^{-1} for the second system which lies just below the gap minimum of 69 cm^{-1}. The failure of the theory in these two cases can be attributed to the fact that both these systems belong to light mass impurities in heavy mass sublattice category for which the diatomic linear chain theory is expected to be bad as pointed out in section 2. Finally the theory predicts gap modes for the systems InP: Ga and InP : As at 147·38 cm^{-1} and 213·12 cm^{-1} respectively for which no experimental data exists. We suggest that these modes may be looked for experimentally. It is also noteworthy that out of all the systems studied not a single one exhibit the expected three mode behaviour due to the appearance of both a local mode and a gap mode when a light mass impurity is substituted into the heavy mass sublattice.

Table 2. The observed range of the host crystals, the calculated and observed gap mode frequencies (ω_G) for $x = 1$ and $x = 0$ for various mixed crystal systems*

System	Gap range in cm^{-1}		ω_G in cm^{-1}		Gap mode (Expt) in cm^{-1}		ω_L in cm^{-1} (LBB)
	$x = 1$	$x = 0$	$x = 1$	$x = 0$	$x = 1$	$x = 0$	$x = 0$
$KBr_{1-x}Cl_x$	no gap	94–102[a]	119·129 no mode	101·956 gap mode	..	95[g]	147 inband
$Rb_{1-x}K_xBr$	94–102	..	91·692 no mode	71·902	..	..	222 inband
$Rb_{1-x}K_xI$	69– 98[a]	..	78·891 gap mode	no mode	88[h]	..	106 local
$KI_{1-x}Br_x$	94–102	69–98	no mode	58·651 no mode	..	88·94[i]	no local
$KI_{1-x}Cl_x$	no gap	69–98	117·706 no mode	68·235 no mode	..	77·1[j]	no local
$Cs_{1-x}K_xI$	69–98	..	69·064 gap mode	49·65	83·5[k]	..	one local
$Ag_{1-x}K_xI$	69–98	..	73·276 gap mode	..	86·2[l]	..	one local
$ZnSe_{1-x}S_x$	204·2– –274[p]	193·4– 203·3[b]	201·841	154·151 no mode	220[m]	..	272 local
$CdSe_{1-x}S_x$	..		168·561	no mode	188[n]	..	242 local
$In_{1-x}Ga_xAs$	232·7– 245·3[c]		197·304 no mode	146·529	..	..	237 inband
$GaSb_{1-x}As_x$	232·7– 245·3	175·85– 225	no mode	142·335 no mode	..	..	241 local
$In_{1-x}Ga_xSb$	175·85– 225	144–158[e]	168·568 no mode	no mode	..	..	200 local
$InSb_{1-x}As_x$	..	144–158	166·802	123·794 no mode	..	..	197 local
$In_{1-x}Ga_xP$	245·3– 366[e]	125–246[f]	no mode	147·371 gap mode	..	..	330 inband
$GaAs_{1-x}P_x$	245·3– 366	232·7– 245·3	254·498 gap mode	194·009 no mode	270[o]	..	340 local
$InAs_{1-x}P_x$	125–246	..	213·128 gap mode	no mode	..	..	one local

* The local mode (ω_L) frequency for $x = 0$ as calculated by LBB is given in the last column. The existence of the calculated and observed gap modes is also indicated. The systems for which the MMP theory does not predict a gap mode is indicated by writing 'no mode'. Wherever calculated gap mode frequencies are given without a remark about its existence, it means no conclusion is drawn because of the lack of experimental data on the gap range.

[a]Bauerles 1973; [b]Kunc *et al* 1971; [c]Dolling and Waugh 1965; [d]Marvin K. Farr *et al* 1975; [e]Yarnell *et al* 1968; [f]Alfrey *et al* 1972; [g]Nolt *et al* 1967; [h]Genzel 1971; [i]Waro and Clayman 1974; [j]Sievers *et al* 1965; [k]Sievers 1965; [l]Kirby 1971; [m]Brafman *et al* 1968; [n]Parish *et al* 1967; [o]Hayes *et al* 1970; [p]Feldkamp *et al* 1971;

4. Mixed crystal behaviour

The experimental investigation (Barker and Sievers 1975, Chang and Mitra 1971) of the infrared and Raman scattering of a large number of mixed alkali halide and III-V semiconducting compound systems has indicated that according to the pattern of their behaviour these can be essentially grouped into three categories namely the one mode, the two mode and the mixed mode systems as discussed in the introduction. The behaviour of a mixed crystal can be predicted by examining the existence of the impurity modes in the extreme limit of the concentration $x \simeq 0$ and $x \approx 1$. LBB examined the appearance of only a local mode and as a result their theory failed to predict the existence of mixed mode systems such as $GaSb_{1-x}As_x$, $In_{1-x}Ga_xAs$, $InSb_{1-x}As_x$ (Lucovsky and Chen 1970) and $In_{1-x}Ga_xSb$ (Brodsky *et al* 1970). Hence, to predict this behaviour, one has to look for the existence of both the local mode and the gap mode in the limits $x \approx 0$ and $x \approx 1$ respectively. If neither the local nor the gap mode exist, the system is characterized as one mode, if both the local and gap modes exist, the system will be two mode and if either the local or the gap mode exist, the system will show a mixed mode behaviour. In analysing various systems we apply the LBB criterion for the existence of the local mode and the criterion given by eq. (5) for the existence of the gap mode, when the mode frequencies are calculated from the MMP theory. The local and gap mode frequencies thus determined are given in table 2. We have analysed sixteen mixed crystal systems, out of which the prediction for thirteen systems agrees with experimental results. The results are analysed in table 3. Out of these in three cases namely $CdSe_{1-x}S_x$, $In_{1-x}Ga_xAs$ and $InSb_{1-x}As_x$ the theoretical prediction could not be decisive because of the unavailability of data on the range of the gaps of CdS and InAs. However noting the fact that for the first system a gap mode has been observed for $x \approx 1$, one can argue that the corresponding predicted gap modes will exist and thus conclude that this system is two mode like which agrees with the experiments. In case of $ZnSe_{1-x}S_x$, the theory predicts a gap mode at 201·841 cm^{-1} for $x \approx 1$, which lies marginally below the gap (204·2 to 274 cm^{-1}). However a gap mode is observed for this system. Because of the marginal nature of this gap mode, we can conclude that the system is two mode like. Similarly for $In_{1-x}Ga_xAs$ in the limit $x \approx 0$, there exists a local mode at 240 cm^{-1}, but the predicted local mode at 237 cm^{-1} is 1 cm^{-1} below ω_{LO} and hence LBB argue that this mode will be observable which again makes the system a mixed mode type. Thus the theoretical prediction is really indecisive for the only remaining system of $InSb_{1-x}As_x$. For two systems that is $Cs_{1-x}K_xI$ and $Ag_{1-x}K_xI$, the theory predicts two mode behaviour, but because of the lack of the experimental measurements, this prediction could not be confirmed. Finally we come to the only system $KBr_{1-x}Cl_x$ for which theoretical prediction disagrees with the experimental result in the sense that the theory predicts this to be a mixed mode type whereas experimentally it is found to be one mode. However, the experimental result is rather surprising because of the fact that a gap mode has been observed for KBr: Cl^- at 95 cm^{-1}, which agrees with the prediction of a gap mode almost at the top of the gap at 101·95 cm^{-1}. In mixed crystals, the observation of this gap mode could be hindered if the width of the reststrahl absorption peak for KBr is large so as to superpose the gap mode peak. The three-dimensional CPA calculation

Table 3. The mixed crystal behaviour predicted by the present calculation is compared with the experimental data as well as the predictions by the theories due to Sen and Hartman (1974), Taylor (1973), the MREI (1971) model and Lucovsky *et al.* (1970).

System	LBB	MREI	Taylor (CPA calculation) -3-dimensional	Sen and Hartmann (CPA calculation) diatomic linear chain	Present theory	Expt.
$KBr_{1-x}Cl_x$	one mode	one mode	one mode	one mode	mixed mode	one mode[a]
$Rb_{1-x}K_xBr$	two mode	two mode	..	..	one mode	one mode[b]
$Rb_{1-x}K_xI$	two mode	two mode	two mode	two mode	two mode	two mode[a]
$KI_{1-x}Br_x$	one mode	one mode	..	..	one mode	Not conclusive[c]
$KI_{1-x}Cl_x$	one mode	one mode	..	..	one mode	one mode[c]
$Cs_{1-x}K_xI$	two mode	two mode	..	..	two mode	
$Ag_{1-x}K_xI$	two mode	two mode	..	..	two mode	
$ZnSe_{1-x}S_x$	two mode	two mode	..	two mode	two mode	two mode[d]
$CdSe_{1-x}S_x$	two mode	two mode	..	two mode	two mode	two mode[e]
$In_{1-x}Ga_xAs$	one mode	one mode	..		mixed mode	mixedmode[f]
$GaSb_{1-x}As_x$	two mode	one mode	..	mixed mode	mixed mode	mixed mode[f]
$In_{1-x}Ga_xSb$	two mode	one mode	..	mixed mode	mixed mode	mixed mode[g]
$InSb_{1-x}As_x$	two mode	one mode	..	mixed mode	mixed or two mode	mixed mode[g]
$In_{1-x}Ga_xP$	one mode	one mode	..		mixed mode	mixed mode[f]
$GaAs_{1-x}P_x$	two mode	two mode	..	two mode	two mode	one mode[h] + structure
$InAs_{1-x}P_x$	two mode	two mode	..	two mode	two mode	two mode[i]

[a]Fertel and Perry 1969; [b]Buyers and Cowley 1969; [c]Nair and Walker 1973; [d]Brafman *et al* 1968; [e]Verleur and Barker 1966; [f]Lucovsky and Chen 1970; [g]Brodsky *et al* 1970; [h]Lucovky *et al* 1971; [i]Kekelidze *et al* 1973;

of reflectivity by Taylor (1973) shows such a two peak structure within the optical band in confirmation with our conjecture. Table 3 also gives the predictions of the other theories such as the diatomic linear chain CPA calculation by Sen and Hartmann (1974), the three-dimensional CPA calculation by Taylor (1973), the results of the MREI theory (Chang and Mitra 1971) and the LBB predictions. It can be seen that besides the predictions of the present theory, the detailed calculations of Sen and Hartmann also predict correct behaviour for most of the systems. However, the criterion they propose is the same as that due to LBB. The results of these two theories are much better than that of MREI and LBB models.

In order to demonstrate the utility of the criterion given by eq. (5) to determine the gap modes, we consider below two sets of similar situations. First consider the systems GaAs: In, GaSb: In and GaP: In, for all of which the mass difference due to the impurity is the same, but the widths of the gaps are $12{\cdot}6\,cm^{-1}$, $49{\cdot}15\,cm^{-1}$ and $127{\cdot}3\,cm^{-1}$ respectively. As per the predictions of the present calculation no mode exists for GaP: In, the gap mode for GaSb: In falls $7{\cdot}3\,cm^{-1}$ below and that for GaAs: In falls $35{\cdot}4\,cm^{-1}$ below the bottom of the gap, thus forbidding the appearance of gap modes; which agrees with the experimental result. Next we consider the systems KCl: Rb^+, KBr: Rb^+ and KI: Rb^+, for which again the mass difference due to the impurity is the same, but the widths of the gaps are $0\,cm^{-1}$, $8\,cm^{-1}$ and $29\,cm^{-1}$ respectively. For these three systems the theory predicts no gap mode for KCl: Rb^+, a gap mode which lies $2{\cdot}3\,cm^{-1}$ below the bottom of the gap for KBr: Rb^+ and a gap mode at $78{\cdot}89\ cm^{-1}$ for KI: Rb^+. This again agrees with the experimental result that a gap mode is observed at $88\,cm^{-1}$ only for KI: Rb^+ and no gap modes exist for the other two systems. These results could never be reproduced by the simple MMP theory.

5. Conclusion

In concluding we remark that we have generalized the LBB theory, by proposing a criterion for the existence of gap modes in addition to that for local modes. This generalization when taken into account predicts the behaviour of almost all the mixed crystal system correctly. The validity of the theory can be tested by experimentally looking for the predicted gap modes for the systems InP: Ga and InP: As. By setting up the criteria for the existence of local and gap modes the applicability of the diatomic linear chain model, to study real crystal system is greatly improved. The quantitative disagreement between calculated and observed impurity mode frequencies, however, should not be considered as a setback of the present theory keeping in mind the simplicity of the model and the fact that changes in force constants (Behera 1974, Patnaik and Behera 1976) around the impurity are neglected. The latter is presently under investigation and will be reported elsewhere.

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