[28]E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis*, 4th ed. (Cambridge U. P., Cambridge, England, 1958), p. 105.

[29]The identity of the eigenvalues and eigenfunctions obtained for the right half-crystal in the two cases can easily be proved in perturbation theory. Consider as unperturbed Hamiltonian $\mathcal{H}_0+\mathcal{V}_S+\mathcal{V}_B$. The presence of $\mathcal{V}_B$ has no effect on the solutions for the right half-crystal, which thus represent the eigenstates of $\mathcal{H}_0+\mathcal{V}_S$. Now impose the perturbation $-\mathcal{V}_S$, which converts the Hamiltonian to $\mathcal{H}_0+\mathcal{V}_B$. Represent by γ the typical magnitude of one of the transfer integrals in $\mathcal{V}_S$. Then according to perturbation theory, the lowest-order modifications of energy eigenvalues and wave-function amplitudes are of order $\epsilon\gamma^2$ and $\epsilon\gamma$, respectively. Obviously these go to zero with ϵ. This argument can be made rigorous without much difficulty.

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Extension of a Linear Diatomic-Chain Model for the Calculation of Local-Mode Frequencies in Real Crystals

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Calculations by Mazur, Montroll, and Potts (MMP) have shown that local modes above the optical branch of the host crystal are predicted by a linear diatomic-chain model for all positive values of the mass-defect parameter ϵ. Three-dimensional calculations show that local modes exist only for values of ϵ greater than some critical value. However, these three-dimensional calculations require a knowledge of the eigenvalues and eigenvectors of all the phonon states of the host lattice. We show that the simpler MMP model can be applied to three-dimensional crystals by inclusion of the LO-phonon frequency. In a given system of host crystal and impurity, the determinant parameters are the mass defect of the impurity and the width of the host-crystal reststrahlen band. Calculations on approximately 20 solid solution systems of the form $AB_{1-x}C_x$ have successfully predicted the existence or nonexistence of a local mode when x is large and the mass of B is less than the mass of C. The modified one-dimensional model gives quantitative results for local-mode frequencies which agree with full three-dimensional calculations for local modes in NaI, CdS, and Si.

I. INTRODUCTION

It is well known that small concentrations of substitutional impurities in crystalline lattices can result in local, resonance, or gap vibrational modes.[1] Experimentally these modes are observable by impurity-induced infrared absorption[1] or Raman scattering.[2] Recently, it has been pointed out that certain aspects of the behavior of the long-wavelength optical phonons in pseudobinary mixed crystals could be predicted from the nature of the impurity modes at the low composition limits of the alloy system.[3-6] This paper reports a one-dimensional model calculation for the frequencies of local modes. Our model gives results in good quantitative agreement with the more complicated full three-dimensional calculations, and also reasonably accounts for the experimental observations in many cases where extensive three-dimensional calculations are not available. As developed below, the model is applied to the simpler diatomic crystals. Extension to other systems is straightforward but not considered in detail here.

Calculations of local-mode frequencies[7] (as well as gap- and resonance-mode frequencies) require a knowledge of the eigenfrequencies and eigenvectors of the host-crystal vibrational modes as well as the mass and force-constant changes introduced by the impurity atom. Such calculations were first performed[7] for substitutional impurities in Si, using a mass-defect formalism in which force-constant changes were neglected. The local-mode frequencies were calculated as a function of the mass-defect parameter ϵ_j, where $\epsilon_j=1-M/M_j$. M is the mass of the impurity atom and M_j the mass of the host-crystal atom. These calculations were later extended to include changes in the effective force constant at the impurity site.[8] For the polar diatomic crystals, three-dimensional mass-defect calculations have been performed for a limited number

of crystals including NaI[9] and CdS.[10] Other calculations, using the full lattice dynamics, have been made for specific types of impurities in several host crystals.[11,12]

Mazur, Montroll, and Potts[13] (MMP) have calculated the local- and gap-mode frequencies generated by mass substitutions in a linear diatomic chain and have expressed their results in terms of mass-defect parameters. Bjork[14] extended this model to include force-constant changes as well. In Sec. II of this paper, we discuss the results of the linear chain model impurity mode calculations emphasizing both the similarities and differences between the results of this one-dimensional model and those of the three-dimensional lattice dynamics calculations. We introduce a simple extension[15] to the MMP model and use it to generate values for the local-mode frequencies that are in excellent agreement with those obtained from the more nearly rigorous calculations.[9,10] In Sec. III, the model is applied to local modes in diatomic crystals. In Sec. IV, the model is applied to mixed crystals where we consider the end of the system where local-mode behavior is relevant. For 18 of 21 systems, this model agrees with the behavior observed.

II. MODIFIED DIATOMIC LINEAR CHAIN MODEL FOR LOCAL MODES

The diatomic linear chain model is defined by a unit cell of spacial extent, $2a_0$, containing two atoms of mass M_1 and M_2 with a force constant f_{12} between them. The dispersion curves $\omega(\vec{q})$ for the acoustical- and optical-phonon branches are shown in Fig. 1(a), where ω and $\vec{q}$ are the mode frequency and wave vector, respectively. We have set $M_1 > M_2$. The frequencies of the vibrational modes at the center ($\vec{q}=0$) and edge ($\vec{q}=\pi/2a_0$) of the Brillouin zone are given by

$$\omega_\Gamma^2 = 2f_{12}(1/M_1 + 1/M_2) \qquad \text{at } \vec{q}=0, \tag{1a}$$

$$\omega_1^2 = 2f_{12}/M_1\,, \quad \omega_2^2 = 2f_{12}/M_2 \qquad \text{at } \vec{q}=\pi/2a_0. \tag{1b}$$

MMP[13] studied the impurity modes introduced by the substitution of an impurity atom of mass M for either of the chain atoms. There are four cases to consider, defined by the relative masses involved in the following substitution:

$$\begin{aligned}
&\text{(a) } M \text{ replaces } M_1, \quad M > M_1, \quad \epsilon_1 = 1 - M/M_1 < 0;\\
&\text{(b) } M \text{ replaces } M_1, \quad M < M_1, \quad \epsilon_1 = 1 - M/M_1 > 0;\\
&\text{(c) } M \text{ replaces } M_2, \quad M > M_2, \quad \epsilon_2 = 1 - M/M_2 < 0;\\
&\text{(d) } M \text{ replaces } M_2, \quad M < M_2, \quad \epsilon_2 = 1 - M/M_2 > 0.
\end{aligned} \tag{2}$$

For (a) and (c), the mass-defect parameter ϵ_j is negative and can be arbitrarily large in absolute value, whereas for (b) and (d), $1 > \epsilon_j > 0$. Figure 1(b) illustrates the results of the MMP calculation.

For case (a), substitution for the heavier atom with an even heavier impurity produces no local or gap modes. For case (b), substitution for the heavier atom with a lighter atom produces two impurity modes, a gap mode rising out of the top of the acoustical band and a local mode rising out of the top of the optical band. For case (c), substitution for the lighter atom with a heavier atom yields a gap mode falling out of the bottom of the optical band, whereas, for case (d), substitution for the lighter atom with an even lighter atom produces a local mode rising out of the top of the optical band. Our emphasis here is on the local-mode behavior of cases (b) and (d). The variation of the local-mode frequency $\omega_{1m}(\epsilon_j)$ as a function of the mass-defect parameter is given by

$$\omega_{1m}^2(\epsilon_1) = \frac{2\omega_1^2 + (1-\epsilon_1^2)\,\omega_2^2 + [\,4\epsilon_1^2\,\omega_1^4 + (1-\epsilon_1^2)^2\,\omega_2^4]^{1/2}}{2(1-\epsilon_1^2)} \tag{3}$$

for case (b) and

$$\omega_{1m}^2(\epsilon_2) = \frac{2\omega_2^2 + (1-\epsilon_2^2)\,\omega_1^2 + [4\epsilon_2^2\,\omega_2^4 + (1-\epsilon_2^2)\,\omega_1^4]^{1/2}}{2(1-\epsilon_2^2)} \tag{4}$$

for case (d) where ω_1^2 and ω_2^2 are defined by Eq. (1b). Bjork[14] has generalized this model to include force-constant changes as well. However, our primary concern here is a comparison of the results of the linear chain calculation and those of the full three-dimensional lattice dynamics mass-defect calculation. A comparison of the results of a mass-defect calculation for NaI by Jaswal,[9] who used a deformation dipole model for the lattice dynamics, and the results of the MMP calculation shows that the number and type of impurity modes are the same

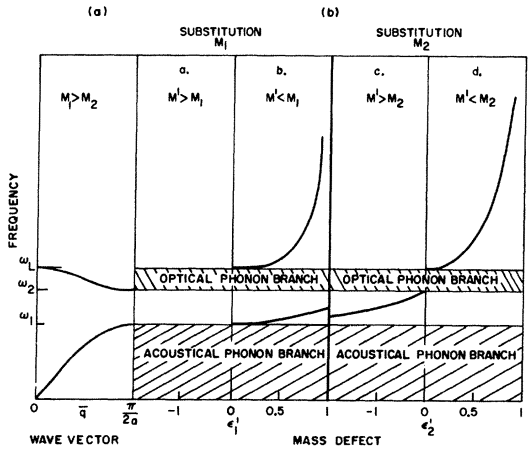

FIG. 1. (a) Optical- (upper curve) and acoustical- (lower curve) phonon branches of the dispersion relation for a diatomic linear lattice. (b) Frequencies of the local- and gap-mode frequencies in a diatomic linear lattice as functions of the mass-defect parameter characterizing the isotropic substitution M'. $M_1 > M_2$, so that the four situations shown correspond to cases (a)–(d) of the text [Eq. (2)].

in both cases for equivalent types of substitutions with one restriction. For the linear chain calculation, where impurity modes are generated, cases (b)–(d), they are produced for all physically allowable values of ϵ_j, whereas in the full lattice dynamics calculation they are defined only for restricted values of ϵ_j.

We propose a simple addition to the MMP formulation which defines a minimum value of ϵ_j required for local-mode formation. A similar procedure for treating the gap-mode cases is not apparent. We first set $\omega_\Gamma = \omega_{TO}(M_1, M_2)$, the transverse-optical phonon frequency of the host crystal that is represented by the linear diatomic chain. We introduce the longitudinal-optical phonon frequency $\omega_{LO}(M_1, M_2)$ of the host and define a range of frequencies $\omega_{LO} > \omega > \omega_{TO}$, where local-mode formation is not allowed. We apply the sum rule[16] at the center and edge of the zone ($\vec{q} = 0$ and $\vec{q} = [\pi/2a_0]$) by setting

$$3\omega_1^2 + 3\omega_2^2 = 2\omega_{TO}^2 + 1\omega_{LO}^2 \ . \tag{5}$$

As used here ω_1 and ω_2 are representative of the weighted averages of the three-dimensional acoustical and optical mode frequencies at the zone edges. We maintain the ratio of ω_1 to ω_2 as it occurs in the linear chain dispersion curve, i.e.,

$$\omega_1^2/\omega_2^2 = M_2/M_1 \ . \tag{6}$$

The values of ω_1^2 and ω_2^2 as determined by Eqs. (5) and (6) are then used in Eqs. (3) and (4) to calculate the local-mode frequencies as functions of ϵ_1 and ϵ_2. Minimum values of ϵ_j for local-mode formation are found by setting

$$\omega_{lm}(\epsilon_j) \geq \omega_{LO}(M_1, M_2) \ . \tag{7}$$

Different minimum values of ϵ_j are found for the two types of substitutions; for $M_1 > M_2$, $(\epsilon_1)_{min} > (\epsilon_2)_{min}$. For values of $\epsilon_j < (\epsilon_j)_{min}$, the impurity modes are visualized as in-band modes and are degenerate with optical-phonon modes of the host lattice. In contrast to the local modes which are always observable at sufficient impurity densities ($\sim 10^{18}/cm^3$),[7] in-band modes are usually only observable at low temperatures where damping by other modes is significantly reduced. The damping also depends on the density of states so that in-band modes may be most readily observed for those crystals where the LO-TO phonon frequency separation is largest and where the in-band mode lies close to ω_{LO}.

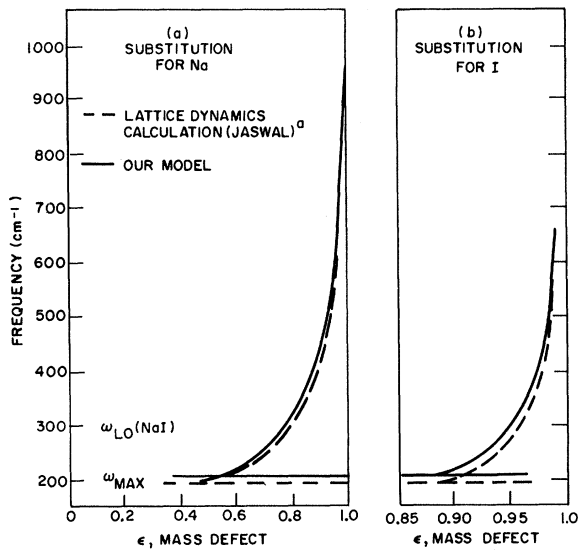

FIG. 2. Local-mode frequencies versus mass-defect parameter for NaI for (a) substitutions for Na^+ by a lighter impurity, and (b) substitution for I^- by a lighter impurity using the modified linear chain model and the full lattice dynamics calculation (Ref. 9).

Figure 2 compares the results of our calculation for local-mode frequencies with the results of the full lattice dynamics calculations for NaI,[9] and Fig. 3 compares the same results for CdS.[10] For CdS (wurtzite structure) we here consider only the Γ_3 branch in this comparison. The quantitative agreement is very good; and in the case of NaI, the almost exact agreement is probably fortuitous. The comparison does serve to identify the physical origin of the lower limit on ϵ_j for local-mode formation. First, the variation of local-mode frequency with ϵ_j is very well approximated by the MMP calculation, and the inclusion of the sum rule, Eq. (5), brings the curves into excellent quantitative agreement with each other. We feel that this is a manifestation of the fact that the local-mode frequency is determined by a weighted average of the phonon frequencies of the host lattice for all directions and that the diatomic-chain dispersion characteristics, subjected to the sum rule, approximate this weighted average. Second, the inclusion of the LO-phonon frequency and its role in determining the minimum value of ϵ_j for local-mode formation is apparently validated. The larger values of $(\epsilon_j)_{min}$ for NaI as compared to those for CdS bear this out. Another example of the importance of the LO frequency will become apparent in our discussion below of pseudobinary mixed crystal systems where we examine the impurity modes of Ga in InP, InAs, and InSb.

III. LOCAL MODES IN DIATOMIC CRYSTALS

Experimental studies of local modes have been made for a large number of systems. Early studies emphasized very light impurities, for example, B[8] and C[17] in Si, and H and D in the alkali halides.[18] More recently, the list of systems has grown to include the study of impurities in the II-VI[7,19]

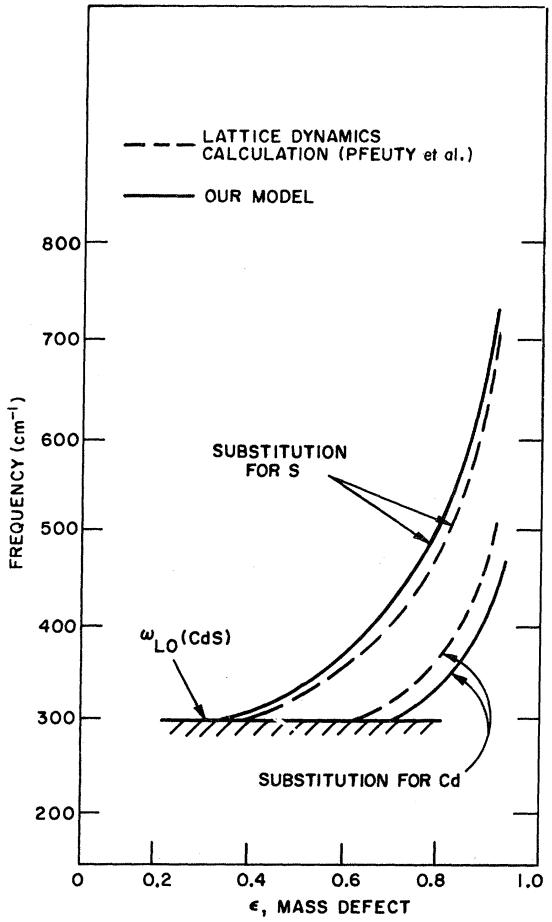

FIG. 3. Local-mode frequencies in CdS versus mass-defect parameter as calculated using the modified linear chain model and the full lattice dynamics calculation (Γ_3 branches of Ref. 10).

and III-V[6,20] semiconductors. Table I contains a representative list of the systems so far examined. Included are the reported local-mode frequencies and the local-mode frequencies calculated for the model proposed in this paper. We also include the local-mode frequencies as obtained from a lattice dynamics calculation for the isotopes of C and B in Si[8] and H and D in NaCl[11] and KCl.[11] For C and B in Si, the agreement between the reported and calculated frequencies [Eq. (3) with $\omega_1^2=\omega_2^2$, $\omega_{TO}=\omega_{LO}=\omega_L=523\ \mathrm{cm}^{-1}$] is fair, the differences being of the order of 6%. More important, we observe that local-mode frequencies as calculated by our technique and by the full lattice dynamics calculation differ by at most 1%. The differences between calculated and measured frequencies can be explained by noting that both model calculations are based on mass-defect formulations in which the force constants at the impurity site are assumed to be the same as those of the host lattice. Because there are differences in size and polarizability between the host and impurity atoms, the neglect of force-constant changes represents an approximation. Using a one-dimensional approximation for monatomic lattice, force-constant differences of approximately 10% have been calculated for B^{10} and B^{11} in Si.[8] For the III-V and II-VI materials, the agreement between reported and calculated frequencies is somewhat better, except for Li^6 and Li^7 in GaAs. The impurity mode frequencies of Li in most crystals deviate from those estimated from mass-defect theories,[19,20] presumably because of the complicated nature of the Li defect centers, for example, the tendency of Li to form complexes with other impurities. Our calculation and the reported impurity mode frequency of Se in CdTe[19] suggest that the mode is an in-band mode rather than a local mode. It is observable owing to the fact that it lies very close to $\omega_{LO}(\mathrm{CdTe})=173\ \mathrm{cm}^{-1}$, where the density of the host-crystal optical-phonon mode is low. For both H and D in the alkali halides, our calculated values differ from the reported frequencies by about 50% on the average. However, our calculated frequencies are very similar to those arrived at from a lattice dynamics calculation based on the deformation dipole model[11] and using a mass-defect approach. We assume again that the disagreement between theory and experiment is due to neglect of effective force-constant changes associated with the large differences in size and polarizability of the impurity and host-crystal atoms involved in these substitutions.

IV. APPLICATION TO MIXED CRYSTALS

We here consider pseudobinary systems of the form $AB_{1-x}C_x$ where $M_C > M_B$. Examples of the pseudobinary systems include $Na_{1-x}K_xCl$, $GaP_{1-x}As_x$, and $CdS_{1-x}Se_x$. We also consider the true binary system $Si_{1-x}Ge_x$; since both Si and Ge have two atoms per unit cell, a diatomic linear chain model is relevant. Experiments have demonstrated that the behavior of the long-wavelength optical phonons of mixed crystals can be predicted from the properties of the impurity modes at the low composition limits of the system, $x\sim 1$ and $x\sim 0$.[3-6] We now consider the impurity mode formation which is necessary for two-mode behavior near $x=1$. Table II summarizes the results of our calculation applied to local-mode formation in 21 alloy systems. In 18 cases, the correct type of mode is observed, or the correct number of modes is predicted. The absence of an observed impurity mode in a one-mode system is taken to imply that the impurity mode is degenerate with optical phonons of the host crystal and sufficiently damped to prevent its observation as a distinct and separate mode. All of

TABLE I. Local-mode frequencies in diatomic crystals.

System	Substitution	Mass defect	Reported local-mode frequency (cm^{-1})	Calculated frequency linear chain model (cm^{-1})	Calculated frequency full lattice dynamics (cm^{-1})
B : Si	B^{10} for Si	0.64	644[a]	683	686[a]
	B^{11} for Si	0.61	620[a]	661	660[a]
	C^{12} for Si	0.57	611[b]	635	640[a,b]
C : Si	C^{13} for Si	0.52	590[b]	613	618[a,b]
	C^{14} for Si	0.50	573[b]	605	612[a,b]
Al : GaSb	Al for Ga	0.61	316.7[c]	318	
P : GaSb	P for Sb	0.75	324[c]	319	
Al : InSb	Al for In	0.76	295[c]	295	
Li : GaAs	Li^{7} for Ga	0.90	422[c]	656	
	Li^{6} for Ga	0.91	451[c]	680	
Si : GaAs	Si for Ga	0.60	384[c]	355	
	Si for As	0.62	399[c]	357	
Se : CdTe	Se for Te	0.38	170[d]	164[d]	
H : NaF	H for F	0.948	858.9[e]	1012	
H : NaCl	H for Cl	0.972	563[e]	771	800[f]
H : NaBr	H for Br	0.988	498[e]	721	
H : NaI	H for I	0.992	426.8[e]	810	
H : KCl	H for Cl	0.972	502[e]	740	716[f]
D : KCl	D for Cl	0.943	357[e]	520	500[f]
H : RbCl	H for Cl	0.972	476[e]	695	

[a]See Ref. 8.
[b]See Ref. 17.
[c]See Ref. 20.
[d]See Ref. 19, ω_{LO} for CdTe = 173 cm^{-1}, so that the observed and calculated mode frequencies both represent in-band modes.
[e]See Ref. 18.
[f]Deformation dipole model of Ref. 11.

the results quoted are from room-temperature experiments, except for $K_{1-x}Rb_xI$ [21] where they were taken at 80 °K, and for $Cd_{1-x}Hg_xTe$ [22] where Raman measurements were made at 1.7 °K.

For two of the three systems for which the predictions of this model differ from the reported behavior, the degree of the failure of the model is modest. For $Ga_{1-x}In_xAs$, the model predicts an in-band mode at 237 cm^{-1}, 1 cm^{-1} below the LO-phonon frequency, whereas a local-mode frequency at 240 cm^{-1} is estimated by extrapolation.[5] For $K_{1-x}Rb_xI$, the failure of the model is in the reverse sense; whereas a local mode is predicted to occur at 106 cm^{-1}, an in-band mode is observed at 101 cm^{-1}, or 2 cm^{-1} below the LO-phonon frequency. For $Cd_{1-x}Hg_xTe$, Mooradian and Harmon[22] have not been able to resolve the frequencies of the TO modes of the high-frequency branch and the LO mode of the low-frequency branch; however, Carter *et al.*,[23] find the high-frequency TO mode at 154 cm^{-1} for a composition with $x = 0.8$. In any case, it would appear as though the impurity mode frequency of Cd in HgTe lies above the LO-phonon frequency of HgTe, in disagreement with our model. The failure here may lie in the unsuitability of a short-range force model for the HgTe semimetallic host lattice. For those cases where local modes are predicted and observed, the calculated frequencies are in general lower than those observed. In all cases a force-constant correction brings the observed and calculated values into better agreement and also shifts the impurity mode of Ga in InAs to a local mode. Where the complete three-dimensional lattice dynamics calculations have been made and applied to local-mode frequencies, B [8] and C [17] in Si, for example, it was found necessary to postulate force-constant corrections to account for the observed differences.[8]

An interesting illustration of the role of ω_{LO} as the demarcation criterion for local-mode behavior is obtained by comparing the three systems $Ga_{1-x}In_xSb$,[6] $Ga_{1-x}In_xAs$,[5] and $Ga_{1-x}In_xP$[24]: The mass defect for the Ga : In substitution is the same for all three systems; however, the width of the reststrahlen region ($\omega_{LO} - \omega_{TO}$) increases from 12 cm^{-1} in InSb, to 23 cm^{-1} in InAs, and to 44 cm^{-1} in InP. For the Ga substitution, the model predicts a local mode in InSb 9 cm^{-1} above ω_{LO}(InSb), an in-band mode in InAs 1 cm^{-1} below ω_{LO}(InAs), and an in-band mode in InP 21 cm^{-1} below ω_{LO}(InP). These three predictions of a distinct local mode, a marginally observable mode, and a distinct in-band

TABLE II. Local modes in mixed crystals at 300 °K.

System	Substitution	Mass defect	Host-crystal optical-phonon frequencies (cm^{-1})		Impurity mode frequency (cm^{-1}) and type	Reported impurity mode behavior, frequency type (cm^{-1})	Mixed crystal behavior $x>0.50$
			ω_{TO}	ω_{LO}			
$NA_{1-x}K_xCl$	Na for K	0.41	142	214	185, in band	a	1 mode[b]
$KCl_{1-x}Br_x$	Cl for Br	0.55	113	165	147, in band	a	1 mode[c]
$K_{1-x}Rb_xCl$	K for Rb	0.54	116	173	150, in band	a	1 mode[d]
$K_{1-x}Rb_xBr$	K for Rb	0.54	88	127	122, in band	a	1 mode[c]
$K_{1-x}Rb_xI$	K for Rb	0.54	80	103	106, local	101, in band[c]	2 mode[c]
$RbCl_{1-x}Br_x$	Cl for Br	0.55	88	127	122, in band	a	1 mode[c]
$ZnS_{1-x}Se_x$	S for Se	0.59	210	250	272, local	297, local[e]	2 mode[e]
$CdS_{1-x}Se_x$	S for Se	0.59	170	215	242, local	265, local[f]	2 mode[f]
$ZnSe_{1-x}Te_x$	Se for Te	0.38	179	206	197, in band	a	1 mode[g]
$Zn_{1-x}Cd_xS$	Zn for Cd	0.42	239	300	268, in band	a	1 mode[h]
$Cd_{1-x}Hg_xTe$	Cd for Hg	0.43	116	139	133, in band	a	2 mode[i]
$Ni_{1-x}Co_xO$	Ni for Co	0.003	348	545	413, in band	a	1 mode[j]
$Al_{1-x}Ga_xAs$	Al for Ga	0.61	268	291	342, local	353, local[k]	2 mode[k]
$Ga_{1-x}In_xP$	Ga for In	0.39	307	351	330, in band	a	1 mode[l]
$Ga_{1-x}In_xAs$	Ga for In	0.39	215	238	237, in band	240 local[m]	2 mode[m]
$Ga_{1-x}In_xSb$	Ga for In	0.39	179	191	200, local	196, local[n]	2 mode[n]
$GaP_{1-x}As_x$	P for As	0.59	268	291	340, local	351, local[o]	2 mode[p]
$GaAs_{1-x}Sb_x$	As for Sb	0.38	227	237	241, local	240, local[q]	2 mode[q]
$InP_{1-x}As_x$	P for As	0.59	215	238	192, local	195, local[r]	2 mode[r]
$InAs_{1-x}Sb_x$	As for Sb	0.38	179	191	197, local	200, local[q]	2 mode[q]
$Si_{1-x}Ge_x$	Si for Ge	0.61	300	300	378, local	389, local[s]	2 mode[s]

[a]Not reported as yet.

[b]F. Kruger, O. Reinkober, and E. Koch-Holm, Ann. Physik 85, 110 (1928).

[c]See Ref. 21; the results for $K_{1-x}Rb_xI$ are at 80 °K.

[d]A. Mitsuishi, in Proceedings of the U. S.-Japan Cooperative Seminar on Far-Infrared Spectroscopy, Columbus, Ohio, 1965 (unpublished).

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[f]H. W. Verleur and A. S. Barker, Jr., Phys. Rev. 155, 750 (1967); J. Parrish, C. H. Perry, O. Frafman, I. F. Chang, and S. S. Mitra, *II-VI Semiconducting Compounds*, 1967 *International Conference*, edited by D. G. Thomas (Benjamin, New York, 1967), p. 1164; M. Balkanski, R. Besserman, and J. M. Besson, Solid State Commun. 4, 201 (1966).

[g]O. Brafman, I. F. Chang, and S. S. Mitra (unpublished).

[h]See Ref. 4.

[i]See Ref. 22, the results for $Cd_{1-x}Hg_xTe$ are at 1.7 °K.

[j]P. J. Gielisse, J. N. Plendl, L. C. Mansur, R. Marshall, S. S. Mitra, R. Mykolajewycz, and A. Smakula, J. Appl. Phys. 36, 2446 (1965).

[k]G. L. Pearson and M. Ilegems, Phys. Rev. (to be published).

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[m]See Ref. 5.

[n]See Ref. 6.

[o]W. Spitzer, J. Phys. Chem. Solids 28, 33 (1967).

[p]H. W. Verleur and A. S. Barker, Jr., Phys. Rev. 149, 715 (1966); Y. S. Chen, W. Shockley, and G. L. Pearson, *ibid.* 151, 648 (1967).

[q]See Ref. 26.

[r]F. Oswald, Z. Naturforsch. 14a, 347 (1959).

[s]D. W. Feldman, M. Ashkin, and J. H. Parker, Phys. Rev. Letters 17, 1209 (1966).

mode agree with the experimental data and could not have been predicted by the simple MMP model, i.e., by a model that does include the LO phonon.

Table III lists the minimum mass-defect parameters necessary for local-mode formation as calculated from the criterion of Eq. (7) as applied to several well-known diatomic insulators and semiconductors.

It would be tempting to try to extend our model to gap-mode frequencies and predict alloy system behavior near $x=0$. However, the correspondence between the shape of the gap-mode curves as a function of the mass-defect parameter as calculated from the diatomic linear chain model and the full

TABLE III. Minimum mass-defect parameters for local-mode formation according to the criterion of Eq.(7).

Crystal	Masses		Mass ratio	Minimum mass defect for local mode	
	M_1	M_2	M_1/M_2	ϵ_1	ϵ_2
LiF	19.0	6.9	2.76	0.84	0.62
LiCl	35.5	6.9	5.55	0.89	0.58
LiBr	79.9	6.9	11.6	>0.90	0.53
NaF	23.0	19.0	1.21	0.69	0.65
NaCl	35.5	23.0	1.54	0.70	0.58
NaBr	79.9	23.0	3.47	0.80	0.49
NaI	126.9	23.0	5.52	0.88	0.52
KF	39.1	19.0	2.06	0.76	0.58
KCl	39.1	35.5	1.10	0.62	0.60
KBr	79.9	39.1	2.04	0.70	0.50
KI	126.9	39.1	3.24	0.75	0.42
RbF	85.5	19.0	4.50	0.87	0.54
RbCl	85.5	35.5	2.41	0.74	0.50
RbBr	85.5	79.9	1.07	0.60	0.58
RbI	126.9	85.5	1.49	0.62	0.50
CsCl	132.9	35.5	3.76	0.83	0.52
CsBr	132.9	79.9	1.68	0.69	0.55
CsI	132.9	126.9	1.05	0.56	0.55
TlCl	204.4	35.5	5.77	0.91	0.62
TlBr	204.4	79.9	2.56	0.84	0.65
CuCl	63.5	35.5	1.79	0.57	0.40
CuBr	79.9	63.5	1.24	0.53	0.47
CuI	129.9	63.5	2.00	0.46	0.27
AgCl	107.9	35.5	3.05	0.83	0.58
AgBr	107.9	79.9	1.35	0.71	0.64
AgI	126.9	107.9	1.19	0.40	0.35
ZnS	65.4	32.1	2.04	0.62	0.42
ZnSe	79.0	65.4	1.21	0.47	0.42
ZnTe	127.6	65.4	1.95	0.51	0.32
CdS	112.4	32.1	3.51	0.70	0.35
CdSe	112.4	79.0	1.42	0.56	0.45
CdTe	127.6	112.4	1.13	0.50	0.45
BN	14.0	10.8	1.30	0.53	0.46
BP	31.0	10.8	2.87	0.25	0.10
AlAs	74.9	27.0	2.77	0.52	0.23
AlSb	121.8	27.0	4.52	0.57	0.18
GaP	69.7	31.0	2.25	0.46	0.24
GaAs	74.9	69.7	1.08	0.33	0.31
GaSb	121.8	69.7	1.75	0.30	0.19
InP	114.8	31.0	3.71	0.62	0.25
InAs	114.8	74.9	1.53	0.43	0.30
InSb	121.8	114.8	1.06	0.29	0.26
SiC	28.1	12.0	2.34	0.61	0.36
PbS	207.2	32.1	6.45	0.92	0.64
PbSe	207.2	79.0	2.62	0.86	0.69
PbTe	207.2	127.6	1.62	0.83	0.74

lattice dynamics calculation is poor. Further, there is no simple procedure with a reasonable physical basis for defining the range of ϵ_j for which gap-mode formation would be allowed. Where applied,[1] even the full lattice dynamics calculations have not given agreement with experiment. The only definitive statements that can be made are the following: (1) Gap modes cannot occur if there is no gap (or at least no low density of states) in the host crystal, and (2) gap modes are not allowed if $M_B > M_A$. The last result is predicted by both the linear diatomic-chain model[13] and the full lattice dynamics mass-defect calculation.[1]

Chang and Mitra[25] have defined criteria for one- or two-mode behavior of mixed crystal systems in terms of another model, the modified random element isodisplacement model (MREI). The predictions of their model are also based on local- and gap-mode behavior; however, their criterion for local-mode behavior, or a modification of it as proposed by Fertel and Perry,[21] is not equivalent to the one described in this paper. For example, when applied to $Ga_{1-x}In_xSb$, $GaAs_{1-x}Sb_x$, and $InAs_{1-x}Sb_x$, the MREI model and the Fertel-Perry modification of the MREI predict one-mode behavior, or equivalently no local mode at $x=1$. Our model predicts two-mode behavior for each of these systems, in accord with the experimental results.[26]

V. CONCLUSIONS

We have introduced a simple addition to the MMP model for calculating local-mode frequencies introduced by light-atom substitutions in a linear diatomic chain. The local-mode frequencies, as well as the minimum value of the mass-defect parameter required to produce a local mode as obtained from this model, are in excellent agreement with the results obtained from the full three-dimensional lattice dynamics calculations. For light-atom substitutions in Si and the III-V and II-VI semiconductors, the predictions of the model are in good agreement with the reported values. Applied to some 21 alloy systems, the model predicts the correct behavior at the appropriate end of the composition range for 18 of the systems. The model emphasizes the importance of the width of the host crystal reststrahlen band in determining the minimum value of the mass-defect parameter, or equivalently the largest lighter mass, that will generate a local mode. Extension of the model to other than diatomic crystals can be accomplished readily by first generating the appropriate chain – for example, an $(ABA)_m$[13] chain approximates the alkaline earth fluorides – and then applying the modified MMP approach to calculate the impurity mode frequencies.

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