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MOLECULAR MODEL FOR LOCALISED MODES IN CUBIC CRYSTALS

By T. M. HARIDASAN AND N. KRISHNAMURTHY
(*Department of Physics, Indian Institute of Science, Bangalore-12, India*)

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ABSTRACT

The molecular model of Jaswal[1] has been extended to take into account the second neighbour interactions. The frequencies of the localised modes due to U-centres in alkali halides and substitutional impurities in III-V semiconductors have been computed and discussed in relation to their infrared absorption spectra.

INTRODUCTION

For the study of the local mode vibrations due to point defect in crystals, the molecular model put forward by Jaswal[1] has been found to be of great use in estimating the weakening of the force constant between the defect and its first neighbour by fitting the calculating local mode frequency for the *U*-centre with the experimental infrared absorption frequency. Such a knowledge of the force constants between the *U*-centre and its first neighbour alkali ions in different alkali halides was helpful in explaining the splitting of the degeneracy of the local mode vibration due to *U*-centre in alkali halides when an addition impurity of another alkali ion is introduced in the first coordination sphere of the *U* centre[2]. Since the infrared spectra of alkali halides containing *U*-centres and additive halogen impurity in the second coordination shell have been reported by Mirlin and Reshina[3], it was felt necessary to work out the molecular model to take into account the substitutional impurities in the second neighbour coordination also.

As a first step we have carried out numerical calculations on the localised modes due to *U*-centres in alkali halides and localised modes due to defects in III-V Semiconductors, mainly with the idea of estimating the weakening of the force constants between the defect and its first and second neighbours and the results are presented in this paper.

THEORY AND RESULTS

The theory employed is just an extension of that of Jaswal[1], by taking a bigger molecular unit with the defect at the centre, surrounded by the first neighbours and second neighbours. We assume that in the localised mode, this unit alone takes part in the vibration, with the rest of the lattice at rest.

We treat the interaction potential in the rigid ion approximation and take the electrostatic Coulomb interaction between the different ions and the short range central interaction upto second neighbours. If the number of first neighbours is n_1 and number of second neighbours is n_2, then the potential can be written as

$$\Phi = \left(-\alpha\, e^2/r_1 \right) + n_1\, \Phi_1 \left(r_1 \right) + n_2\, \Phi_2 \left(r_2 \right) \qquad [1]$$

where α is the Madelung constant of the lattice and r_1 represent the distance between an atom and its first neighbour and r_2 the distance between atom and its second neighbour.

Following Jaswal[1], the coupling coefficient due to Coulomb interaction between atom l and atom l' can be written as follows:

1. $l' = l$. By symmetry of the lattices of *NaCl*, *CsCl* and *ZnS*, we find that $D^c_{\alpha\beta}(l-l)$ which represents the interaction on the atom l by the rest of the crystal turns out to be zero.

$$(2)\ l \neq l' \cdot D^c_{\alpha\beta}(l-l') = -\frac{1}{\sqrt{(M_l M_{l'})}} \frac{e(l)\, e(l')}{|r(l-l')|^3} \left[\frac{3\, r_\alpha (l-l')\, r_\beta (l-l')}{|r(l-l')|^2} - \delta_{\alpha\beta} \right] \qquad [2]$$

where $e(l)$ and $e(l')$ are the charges of the ions l and l' and $|r(l-l')|$ represents the equilibrium distance between l and l'.

Following Kellerman[4] the short range potential Φ_1 for nearest neighbours and Φ_2 for next nearest neighbour are defined by

$$\left[\frac{\partial^2 \Phi}{\partial r^2} \right]_{r = r_1^0} = \frac{e^2}{2V} A \qquad [3]$$

$$\left[\frac{1}{r} \frac{\partial \Phi_1}{\partial r} \right]_{r = r_1^0} = \frac{e^2}{2V} B \qquad [4]$$

$$\left[\frac{\partial^2 \Phi_2}{\partial r^2}\right]_{r=r_2^0} = \frac{e^2}{2V} A_1 \qquad [5]$$

$$\left[\frac{1}{r}\,\frac{\partial \Phi_2}{\partial r}\right]_{r=r_2^0} = \frac{e^2}{2V} B_1 \qquad [6]$$

where r_1^0 and r_2^0 represent the equilibrium first neighbour distance and second neighbours distance respectively and V is the volume of the unit cell.

(*a*) *Rock Salt Structure*: Let us designate the defect atom (H^- ion) as 1 situated at the origin and we have six first neighbours Na^+ atom labelled from 2 to 7 and situated at $(100)\,r_0$, $(100)\,r_0$, $(010)\,r_0$, $(0\bar{1}0)\,r_0$, $(001)\,r_0$, $(00\bar{1})\,r_0$. The second neighbour cl^- ions are 12 in number and they are labelled from $l = 8$ to 19 and their position vectors in order are given below.

(8) $(1\,1\,1)\,r_0$ (9) $(\bar{1}\bar{1}0)\,r_0$ (10) $(1\,\bar{1}\,0)\,r_0$ (11) $(\bar{1}\,1\,0)\,r_0$
(12) $(0\,1\,1)\,r_0$ (13) $(0\,\bar{1}\,\bar{1})\,r_0$ (14) $(0\,1\,\bar{1})\,r_0$ (15) $(0\,\bar{1}\,1)\,r_0$
(16) $(1\,0\,1)\,r_0$ (17) $(\bar{1}\,0\,\bar{1})\,r_0$ (18) $(\bar{1}\,0\,1)\,r_0$ (19) $(1\,0\,\bar{1})\,r_0$

The main aim is to obtain the dynamical matrix for this molecule with 19 atoms having O_h symmetry and to find out the normal modes.

Using Eq. [2] the Coulomb part of the dynamical matrix can be written. The first neighbour short range interaction is described through the parameter A and B and second neighbour short range interaction through A_1 and B_1 as defined above. The interaction between the defect and its first neighbour is described through similar parameters A' and B' and that between defect and second neighbours through parameters A_1' and B_1'. We assume that there is no relaxation around the defect and that makes $B' = B$ and $B_1' = B_1$. One can however find out the values of B' and B_1' by fitting the infrared data and in order to simplify the problem this has not been done here. Further the second neighbour interactions between the positive ions are neglected. With these parameters the short range coupling coefficients are worked out to be

$$D^R_{\alpha\alpha}(1-1) = (e^2/V)(1/m_1)[A' + 2B + 2A_1' + 4B_1)] \qquad [7]$$

$$\begin{aligned} D^R_{xx}(2-2) &= D^R_{xx}(3-3) = D^R_{yy}(4-4) = D^R_{yy}(5-5) = D^R_{zz}(6-6) \\ &= D^R_{zz}(7-7) = (e^2/V)(1/m_2)[\{(A + A')/2\} + \{A_1' + 7A_1/4\} + 2B + 4B_1] \end{aligned} \qquad [8]$$

$$\begin{aligned} D^R_{yy}(2-2) &= D^R_{zz}(2-2) = D^R_{yy}(3-3) = D^R_{zz}(3-3) = D^R_{xx}(4-4) \\ &= D^R_{zz}(4-4) = D^R_{xx}(5-5) = D^R_{zz}(5-5) = D^R_{xx}(6-6) = D^R_{xx}(7-7) \\ &= D^R_{yy}(7-7) = D^R_{yy}(6-6) = [(A + 2B + 2A_1 + 4B_1)](e^2/V)(1/m_2) \end{aligned} \qquad [9]$$

$$D^R_{\alpha\beta}(l-l) = 0 \text{ for } l = 1,\ 7 \qquad [10]$$

$$\begin{aligned}
D^R_{xx}(8-8) &= D^R_{yy}(8-8) = D^R_{xx}(9-9) = D^R_{yy}(9-9) = D^R_{xx}(10-10) = D^R_{yy}(10-10) \\
&= D^R_{xx}(11-11) = D^R_{yy}(11-11) = D^R_{yy}(12-12) = D^R_{zz}(12-12) = D^R_{yy}(13-13) \\
&= D^R_{zz}(13-13) = D^R_{yy}(14-14) = D^R_{zz}(14-14) = D^R_{yy}(15-15) = D^R_{zz}(15-15) \\
&= D^R_{xx}(16-16) = D^R_{zz}(16-16) = D^R_{xx}(17-17) = D^R_{zz}(17-17) = D^R_{xx}(18-18) \\
&= D^R_{zz}(18-18) = D^R_{xx}(19-19) = D^R_{zz}(19-19) \\
&= (e^2/V)\,(1/m_3)\,[A + 2B + (7A_1 + A_1')/4 - 4B_1] \qquad [11]
\end{aligned}$$

$$\begin{aligned}
D^R_{zz}(8-8) &= D^R_{zz}(9-9) = D^R_{zz}(10-10) = D^R_{zz}(11-11) = D^R_{xx}(12-12) \\
&= D^R_{xx}(13-13) = D^R_{xx}(14-14) = D^R_{xx}(15-15) = D^R_{yy}(16-16) = D^R_{yy}(17-17) \\
&= D^R_{yy}(18-18) = D^R_{yy}(19-19) = (e^2/v)\cdot(1/m_3)\,(A + 2B + 2A_1 + 4B_1) \qquad [12]
\end{aligned}$$

$$\begin{aligned}
D^R_{xy}(8-8) &= D^R_{xy}(9-9) = D^R_{yz}(12-12) = D^R_{yz}(13-13) = D^R_{zx}(16-16) \\
&= D^R_{zx}(17-17) = (e^2/V)\cdot(1/m_3)\,(A_1' - A_1)/4 \qquad [13]
\end{aligned}$$

$$\begin{aligned}
D^R_{xy}(10-10) &= D^R_{xy}(11-11) = D^R_{yz}(14-14) = D^R_{yz}(15-15) = D^R_{zx}(18-18) \\
&= D^R_{zx}(19-19) = (e^2/V)\cdot(1/m_3)\,(A_1 - A_1')/4 \qquad [14]
\end{aligned}$$

$$D^R_{\alpha\beta}(1-l) = -\frac{e^2}{2V}\,\frac{1}{\sqrt{(m_1 m_2)}}\left[\frac{(A' - B)\, r_{0\alpha}(1-l)\, r_{0\beta}(1-l)}{r_0^2(1-l)} + B\,\delta_{\alpha\beta}\right] \qquad [15]$$

for l running from 2 to 7

$$D^R_{\alpha\beta}(1-l) = -\frac{e^2}{2V}\,\frac{1}{\sqrt{(m_1 m_3)}}\left[\frac{(A_1' - B_1)\, r_{0\alpha}(1-l)\, r_{0\beta}(1-l)}{r_0^2(1-l)} + B_1\,\delta_{\alpha\beta}\right] \qquad [16]$$

where l runs from 8 to 19

For first neighbours interaction with $l \neq 1$ and $l' \neq 1$, we have

$$D^R_{\alpha\beta}(l-l') = -\frac{e^2}{2V}\,\frac{1}{\sqrt{(m_l m_{l'})}}\left[\frac{(A - B)\, r_{0\alpha}(l-l')\, r_{0\beta}(l-l')}{r_0^2(l-l')} + B\,\delta^{\alpha\beta}\right] \qquad [17]$$

For second neighbour halogen-halogen interaction with $l \neq 1$ and $l' \neq 1$, one can obtain

$$D^R_{\alpha\beta}(l-l') = -\frac{e^2}{2V}\,\frac{1}{\sqrt{(m_l m_{l'})}}\left[\frac{(A_1 - B_1)\, r_{0\alpha}(l-l')\, r_{\alpha\beta}(l-l')}{r_0^2(l-l')} + B_1\,\delta_{\alpha\beta}\right] \qquad [18]$$

The ions are assumed to carry unit charges. The parameters A, B, A_1, B_1 are related to the elastic constants and the infrared frequency as given by Cowley[5]

$$c_{11} = \frac{e^2}{V r_0}\left[\frac{A + A_1 + B_1}{2} - 2.55604\, z^2\right] \qquad [19]$$

$$c_{12} = \frac{e^2}{V r_0}\left[\frac{A_1 - 2\,B + 3\,B_1}{4} + 0.11298\, z^2\right] \qquad [20]$$

$$c_{44} = \frac{e^2}{V r_0}\left[\frac{(A_1 - B_1)}{4} + 0.69550\, z^2\right] \qquad [21]$$

$$\omega_{T0}^2 = \frac{e^2}{V \mu}\left[A + 2\,B - \frac{4\,\pi\, z^2}{3}\right] \qquad [22]$$

The equilibrium condition is

$$B + 2\,B_1 = -\,2/3\,\alpha_M z^2 \qquad [23]$$

When α_M is the Madelung constant. From these equations using the avilable experimental data of C_{11}, C_{12}, $\omega_{T.0}$ etc. the short range parameters are calculated for the sodium, potassium and rubidium halides. We assume a weakening of the short range interaction by 50% for U centres and hence A' is taken as $A/2$ and A_1'' is taken as $A\,1/2$.

With these short range and long range coupling coefficient the dynamical matrix of order (57×57) for the set of determinental equations can be written and this was diagonalised to get the eigenvalues and eigenvectors. The 57 eigen frequencies fall under the following irreducible representations for the 0_h point group

$$\Gamma_{57} = 2\;A_{1g} + A_{2g} + 3\;E_g + 3\;F_{1g} + 3\;F_{2g} + \;A_{2u} + E_u + 6\;F_{1u} + 3\;F_{2u}$$

The U centre local mode falls under F_{1u} representation and corresponds to the highest three degenerate eigenfrequencies. The other perturbed normal modes are less than the longitudinal optical frequency for zero wavevector of the perfect lattice. They can be classified into the various irreducible representations by comparing the eigenvectors obtained with those given in the tables of Ludwig.[6]

Just to see the nature of U centre frequency for no change in force constants namely $A' = A$ $A_1' = A_1$, a simple calculation was done for U centre in $NaCl$. The U centre frequency was found to be 15.83×10^{13} sec^{-1} as against the value of 15.90×10^{18} sec^{-1} obtained by Jaswal[1] for his first neighbour model for $A' = A$.

In fact, A' was given values ranging from A to $A/4$ and similarly A_1' from A_1 to $A_1/4$ and all possible combinations of the values of A' and A_1' were tried in a sample calculation for the U centre frequency in *NaCl*. It is found that the best fit could be made with the combination $A' = A/2$ and $A_1' = A1/2$ and accordingly in subsequent calculations of U centres of other alkali halides, only this combination of A' and A_1' is taken.

Table I gives the results of our computation for U centre frequencies of various alkali halides. Experimental results of Fritz *et al*[7] are also given for comparison. We have also made computations for the gap mode frequencies in *KI* due to both anion and cation impurities. Table II gives our computed results and experimental results of Sievers[8].

TABLE 1

U Centre frequencies from Alkali halides

Crystal	Local mode frequency in units of 10^{13} sec^{-1}	
	Calculated	Experimental
NaCl	9.88	10.65
NaBr	9.26	7.71
NaI	8.57	8.12
KCl	8.91	9.45
KBr	8.51	8.48
KI	7.68	7.19
RbCl	8.63	8.96
RbBr	7.94	8.06
RbI	7.31	6 81

TABLE 2

Gap mode frequencies in KI (in units of 10^{13} *sec*$^{-1}$*)*

Impurity	Localised mode frequency in units of 10^{13} sec^{-1}	
	Calculated	Experimental
F^-	2.86	2.4
Cl^-	1.59	1.45
Br^-	1.18	1.90
Na	2.81	1.22
Ca	0.98	1.57

From the results it is evident that the weakening of the force constant for U centre is around 50% for halkali halides and a second neighbour model does not improve the calculated value of U centre frequency from that of a first neighbour model as can be seen from the present results of U centre in $NaCl$ and that of Jaswal. This is further reflected in our computed results of U Centre in $NaCl$, where we found that one A' is fixed at $A/2$, different values of A'_1 did not yield very different values for local mode frequencies showing thereby that the condition of the variation of A'_1 was less stringent for the fit. This shows that the U centres give rise to ideal cases of localised modes where the amplitudes of vibration die down very fast as one goes from the site of the defect. There is no agreement between the computed and experimental results for the gap modes in KI, mainly because most of them lie in the continuum of the frequency distribution except that for the Cl^- replacement and hence are not of localised nature in the strict sense.

(b) *Caesium Chloride Type Lattice*: Eventhough extensive calculations have not been done as in the case of $NaCl$ we have extended the model to $CsCl$ and Z_nS type lattices as well. Sample calculation in the $CsCl$ type lattice has been done for the U centres in $CsBr$.

Here surrounding the H^- ion at the origion which we label as 1, we have 8 Cs^+ ions labelled from 2 to 9, situated at the following sites in order $(111)r_0$, $(\bar{1}\bar{1}\bar{1})r_0$, $(\bar{1}11)r_0$, $(1\bar{1}\bar{1})r_0$. $(1\bar{1}1)r_0$, $(\bar{1}1\bar{1})r_0$, $(11\bar{1})r_0$, $(\bar{1}\bar{1}1)r_0$. Also we have 8 second neighbour halogen ions labelled from 10 to 15 situated respectively at $(200)r_0$, $(200)r_0$, $(020)r_0$, $(0\bar{2}0)r_0$, $(002)r_0$, $(00\bar{2})r_0$. The electrostatic coupling coefficients can be written using equation [2].

For the short range part, following the procedure of Krishnamurthy,[9] we define for the first neighbour

$$[(\partial^2 \Phi_1)/(\partial r^2)]_{r=\sqrt{3}r_0} = (e^2/V)\,A \qquad [24]$$

$$[(1/r)(\partial \Phi_1/\partial r_1]_{r=\sqrt{3}r_0} = (e^2/V)\,B \qquad [25]$$

the case of perfect lattice and corresponding dashed parameters for the interaction of defect with its first neighbours. We also put $B = B'$.

Similarly for second neighbours of perfect lattice we define

$$[(\partial^2 \Phi_2)/(\partial r^2)]_{r=2r_0} = (e^2/V)\,A_1 \qquad [26]$$

$$[(1/r)(\partial \Phi_2/\partial r)]_{r=2r_0} = (e^2/V)\,B_1 \qquad [27]$$

We have A'_1 and B'_1 for the defect Again we assume $B'_1 = B_1$ and also that the $(Cs\ Cs)$ and $(Br\text{-}Br)$ interactions are the same. to make the situation simpler. Then the non-vanishing elements of short range matrix can be written as follows:

$$D^R_{\alpha\alpha}(1-1) = (e^2/V)(1/m_1)\,[(8A' + 16B)/3 + 2A'_1 + 4B_1] \qquad [28]$$

$$D^{R}_{\alpha\alpha}(l-l) = (e^2/V)(1/m_2)\left[(A' + 7A + 16B)/3 + 2A_1 + 4B_1\right] \quad [29]$$

with l running from 2 to 9.

$$D^{R}_{\alpha\alpha}(l-l) = (e^2/V)(1/m_3)\left[(8A + 16B)/3 + A_1 + A_1' + 4B_1\right] \quad [30]$$

with l running from 10 to 15.

$$D^{R}_{\alpha\beta}(1-l) = -\frac{e^2}{V}\frac{1}{\sqrt{m_1 m_2}}\left[(A' - B)\frac{r_{0\alpha}(1-l)\, r_{0\beta}(1-l)}{r_0^2(1-l)} + \beta\,\delta_{\alpha\beta}\right] \quad [31]$$

with l running from 2 to 9

$$D^{R}_{\alpha\beta}(1-l) = -\frac{e^2}{V}\frac{1}{\sqrt{m_1 m_3}}\left[(A_1' - B_1)\frac{r_{0\alpha}(1-l)\, r_{0\beta}(1-l)}{r_0^2(1-l)} + B_1\,\delta_{\alpha\beta}\right] \quad [32]$$

for l running from 10 to 15.

For $l \neq 1$, $l' \neq 1$ the first neighbours interaction gives

$$D^{R}_{\alpha\beta}(l-l') = -\frac{e^2}{V}\frac{1}{\sqrt{m_l m_{l'}}}\left[(A - B)\frac{r_{0\alpha}(l-l')\, r_{0\beta}(l-l')}{r_0^2(l-l')} + B\,\delta_{\alpha\beta}\right] \quad [33]$$

For second neighbours

$$D^{R}_{\alpha\beta}(l-l') = -\frac{e^2}{V}\frac{1}{\sqrt{m_l m_{l'}}}\left[(A_1 - B_1)\frac{r_{0\alpha}(l-l')\, r_{0\beta}(l-l')}{r_0^2(l-l')} + B_1\,\delta_{\alpha\beta}\right] \quad [34]$$

$$\begin{aligned} D^{R}_{\alpha\beta}(2-2) &= D^{R}_{\alpha\beta}(3-3) = D^{R}_{yz}(4-4) = D^{R}_{yz}(5-5) = D^{R}_{zx}(6-6) \\ &= D^{R}_{zx}(7-7) = D^{R}_{xy}(8-8) = D^{R}_{xy}(9-9) = (e^2/V)(1/m_2)(A' - A)/3 \quad [35] \end{aligned}$$

$$\begin{aligned} D^{R}_{xy}(4-4) &= D^{R}_{zx}(4-4) = D^{R}_{xy}(5-5) = D^{R}_{zx}(5-5) = D^{R}_{xy}(6-6) \\ &= D^{R}_{yz}(6-6) = D^{R}_{xy}(7-7) = D^{R}_{yz}(7-7) = D^{R}_{yz}(8-8) = D^{R}_{zx}(8-8) \\ &= D^{R}_{yz}(9-9) = D^{R}_{zx}(9-9) = (e^2/V)(1/m_2)(A - A')/3 \quad [36] \end{aligned}$$

The elements of the resulting matrix of order (45 × 45) can be easily written down. The charges on the ions, z are assumed to be unity. We are left with only four independent parameters A, B, A_1 and B_1. They are related to the elastic constants and $\omega_{T.O}$ by the relations[5]

$$c_{11} = (e^2/Vr_0)\left[\tfrac{1}{6}(A + 2B) + \tfrac{1}{2}A_1 + 1\cdot40179\,z^2\right] \quad [37]$$

$$c_{12} = (e^2/Vr_0)\left[\tfrac{1}{6}(A - 4B) - \tfrac{1}{2}B_1 - 1\cdot37935\,z^2\right] \quad [38]$$

$$c_{44} = (e^2/Vr_0)\left[\tfrac{1}{6}(A + 2B) + \tfrac{1}{2}B_1 - 0\cdot70089\,z^2\right] \quad [39]$$

$$\omega^2_{T.O} = (e^2/V\mu)\left[\tfrac{4}{3}(A + 2B) - (4\pi/3)\,z^2\right] \quad [40]$$

The equilibrium condition is

$$B + B_1 = -\tfrac{1}{3}\alpha_M z^2. \qquad [41]$$

From these equations using known values of elastic constants and $\omega_{T.0}$ the parameters A, B, A_1, B_1 are evaluated. Computations have been done for two cases first with $A' = A$ and $A_1' = A_1$ and then with $A' = A/2$ and $A_1' = A_1/2$.

For $A' = A$, etc., the value obtained for U centre frequency is 13.6×10^{13} sec. $^{-1}$ and for $A' = A/2$ etc. the value is 8.7×10^{13} sec. $^{-1}$. The experimentally observed values by Mitra *et al*[10] is $6\ 83 \times 10^{13}$ sec. $^{-1}$ This shows that the force constant changes are definitely more than 50% unlike in other alkali halides.

(c) *Z_nS Type Lattice*: We had extended the first neighbour molecular model to Z_nS structure earlier[11] and here we have also included the interaction of second neighbours. A sample calculation has been done for the case of *Al* in *I_nSB*.

We have *Al* atom labelled as 1 at the origin with four nearest neighbours of *Sb* atoms labelled from 2 to 5 situated respectively at $(111)r_0/2$, $(1\bar{1}\bar{1})r_0$ $(\bar{1}1\bar{1})r_0$ $(\bar{1}\bar{1}1)r_0$

There are 12 second neighbours of *In* atom labelled from 6 to 17 whose positions in order are defined as follows:

(6) $(110)r_0$ (7) $(\bar{1}\bar{1}0)r_0$ (9) $(1\bar{1}0)r_0$ (9) $(\bar{1}10)r_0$
(10) $(011)r_0$ (11) $0\bar{1}\bar{1})r_0$ (12) $(01\bar{1})r_0$ (13) $(0\bar{1}1)r_0$
(14) $(101)r_0$ (15) $(\bar{1}0\bar{1})r_0$ (16) $(\bar{1}01)r_0$ (17) $(10\bar{1})r_0$

The Coulomb coupling coefficients are written using Equation [2]. We define parameters A, B, A_1, B_1, A', A_1' etc. as in the case of *NaCl* type lattice for short range interaction, with the further assumption that (*In-In*) interaction and (*Sb-Sb*) interaction are the same. Then the short range matrix elements) can be written as follows:

$$D^{\mathrm{R}}_{\alpha\alpha}(1-1) = (e^2/V)(1/m_1)\left[(2A' + 4B)/3 + 2A_1' + 4B_1\right] \qquad [42]$$

$$D^{\mathrm{R}}_{\alpha\alpha}(l-l) = (e^2/V)(1/m_2)\left[(A' + 3A + 8B)/6 + 2A_1 + 4B_1\right] \qquad [43]$$

for l 2 to 5

$$\begin{aligned}
D^{\mathrm{R}}_{xx}(6-6) &= D^{\mathrm{R}}_{yy}(6-6) = D^{\mathrm{R}}_{xx}(7-7) = D^{R}_{yy}(7-7) = D^{\mathrm{R}}_{xx}(8-8)\\
&= D^{\mathrm{R}}_{yy}(8-8) = D^{\mathrm{R}}_{xx}(9-9) = D^{\mathrm{R}}_{yy}(9-9) = D^{\mathrm{R}}_{yy}(10-10) = D^{\mathrm{R}}_{zz}(10-10)\\
&= D^{\mathrm{R}}_{yy}(11-11) = D^{\mathrm{R}}_{zz}(11-11) = D^{\mathrm{R}}_{yy}(12-12) = D^{\mathrm{R}}_{zz}(12-12)\\
&= D^{\mathrm{R}}_{yy}(13-13) = D^{\mathrm{R}}_{zz}(13-13) = D^{\mathrm{R}}_{zz}(14-14) = D^{\mathrm{R}}_{xx}(14-14)\\
&= D^{\mathrm{R}}_{xx}(15-15) = D^{\mathrm{R}}_{zz}(15-15) = D^{\mathrm{R}}_{xx}(16-16) = D^{\mathrm{R}}_{zz}(16-16)\\
&= D^{\mathrm{R}}_{xx}(17-17) = D^{\mathrm{R}}_{zz}(17-17) = (e^2/V)(1/m_3)\left[(2A + 4B)/3\right.\\
&\quad \left. + (7A_1 + A_1')/4 + 4B_1\right]
\end{aligned} \qquad [44]$$

$$\begin{aligned} D^{\mathrm{R}}_{zz}(6-6) &= D^{\mathrm{R}}_{zz}(7-7) = D^{\mathrm{R}}_{zz}(8-8) = D^{\mathrm{R}}_{zz}(9-9) = D^{\mathrm{R}}_{xx}(10-10) \\ &= D^{\mathrm{R}}_{xx}(11-11) = D^{\mathrm{R}}_{xx}(12-12) = D^{\mathrm{R}}_{xx}(13-13) = D^{\mathrm{R}}_{yy}(14-14) \\ &= D^{\mathrm{R}}_{yy}(15-15) = {}^{\mathrm{R}}_{yy}(16-16) = D^{\mathrm{R}}_{yy}(17-17) \\ &= (e^2/V)\,(1/m_3)\,[(2A+4B)/3+2A_1+4B_1] \end{aligned} \qquad [45]$$

$$D^{\mathrm{R}}_{\alpha\beta}(1-l) = -\frac{e^2}{2V}\,\frac{1}{\sqrt{m_1 m_2}}\left[(A'-B)\frac{r_{0\alpha}(1-l)\,r_{0\beta}(1-l)}{r_0^2(1-l)} + B\,\delta_{\alpha\beta}\right]$$

far $l = 2$ to 5 [46]

$$D^{\mathrm{R}}_{\alpha\beta}(1-l) = -\frac{e^2}{2V}\,\frac{1}{\sqrt{m_1 m_3}}\left[(A_1'-B_1)\frac{r_{0\alpha}(1-l)\,r_{0\beta}(1-l)}{r_0^2(1-l)} + B_1\,\delta_{\alpha\beta}\right]$$

for $l = 6$ to 17 [47]

For first neighbour interaction with l and l' not equal to 1

$$D^{\mathrm{R}}_{\alpha\beta}(l-l') = -\frac{e^2}{2V}\,\frac{1}{\sqrt{m_l m_{l'}}}\left[(A-B)\frac{r_{0\alpha}(l-l')\,r_{0\beta}(l-l')}{r_0^2(l-l')} + B\,\delta_{\alpha\beta}\right] \qquad [48]$$

For second neighbour interaction with l and l' not equal to 1

$$D^{\mathrm{R}}_{\alpha\beta}(l-l') = -\frac{e^2}{2V}\,\frac{1}{\sqrt{m_l m_{l'}}}\left[(A_1-B_1)\frac{r_{0\alpha}(l-l')\,r_{0\beta}(l-l')}{r_0^2(l-l')} + B_1\,\delta_{\alpha\beta}\right] \qquad [49]$$

$$\begin{aligned} D^{\mathrm{R}}_{\alpha\beta}(2-2) &= D^{\mathrm{R}}_{yz}(3-3) = D^{\mathrm{R}}_{zx}(4-4) = D^{\mathrm{R}}_{xy}(5-5) \\ &= (e^2/V)\,(1/m_2)\,(A-A')/6 \end{aligned} \qquad [50]$$

$$\begin{aligned} D^{\mathrm{R}}_{xy}(3-3) &= D^{\mathrm{R}}_{zx}(3-3) = D^{\mathrm{R}}_{xy}(4-4) = D^{\mathrm{R}}_{yz}(4-4) = D^{\mathrm{R}}_{yz}(5-5) \\ &= D^{\mathrm{R}}_{zx}(5-5) = (e^2/V)\,(1/m_2)\,(A'-A)/6 \end{aligned} \qquad [51]$$

$$\begin{aligned} D^{\mathrm{R}}_{xy}(8-8) &= D^{\mathrm{R}}_{xy}(9-9) = D^{\mathrm{R}}_{yz}(12-12) = D^{\mathrm{R}}_{yz}(13-13) = D^{\mathrm{R}}_{zx}(16-16) \\ & D^{\mathrm{R}}_{zx}(17-17) = (e^2/V)\,(1/m_3)\,(A_1-A_1')/4 \end{aligned} \qquad [52]$$

$$\begin{aligned} D^{\mathrm{R}}_{yz}(10-10) &= D^{\mathrm{R}}_{yz}(11-11) = D^{\mathrm{R}}_{zx}(14-14) = D^{\mathrm{R}}_{zx}(15-15) = D^{\mathrm{R}}_{xy}(16-16) \\ &= D^{\mathrm{R}}_{xy}(17-17) = (e^2/V)\,(1/m_3)\,(A_1'-A_1)/4 \end{aligned} \qquad [53]$$

Following Rajagopal and Srinivasan[12] expressions were derived for the elastic constants C_{11}, C_{12} and C_{44} in terms of A, B, A_1, B_1 and Z^2.

$$C_{11} = (e^2/Vr_0)\,[(A+2B)/12 + A_1 + B_1 + 0\cdot12381\,z^2] \qquad [54]$$

$$C_{12} = (e^2/Vr_0)\,[(A-4B)/12 + A_1 - 5B_1/2 - 1\cdot32296\,z^2] \qquad [55]$$

$$C_{44} = (e^2/Vr_0\,[(A+2B)/12 + (A_1+3B_1)/2 - (A-B)^2/12(A+2B) - 0\cdot0619\,z^2] \qquad [56]$$

The equilibrium condition is

$$B + 8B_1 = -2\cdot52193\,z^2 \qquad [57]$$

Using these relations and $\omega_{T.0}$ the values of A, B, A_1, B_1 and Z^2 are determined for *InSb* and *AlSb* We found that values of B and B_1 are roughly the same for both *InSb* and *AlSb* respectively.

The resulting (51×51) matrix when diagonalised yields eigenfrequencies which fall under the irreducible representations of the T_d point group. The localised mode falls under F_2 representations and gave a frequency of 5.3×10^{13} sec.$^{-1}$ which is lower than the experimental value of $5\ 83 \times 10^{13}$ sec.$^{-1}$ whereas a first neighbour model itself gave the local mode frequency as 5.77×10^{-13} sec.$^{-1}$ for $A' = A$.

CONCLUSIONS

Thus one may conclude that the model with second neighbour interaction is not really needed to explain the localised modes in *InSb*, Whereas the localised modes due to defects in III-V compound can be explained even in the mass defect approximation we find that for U centres a weakening of the force constants by about 50% has to be invoked to fit the computed result with those of the experimental observation.

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