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APPROXIMATE ANALYTIC FORMS FOR THE FREQUENCIES OF LOCALIZED VIBRATION STATES

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Abstract. — Two models for an approximate derivation of the frequency of localized vibrational modes due to light substitutional impurities are derived. By careful comparison with exact results obtained from a Green's function treatment for a linear diatomic chain and zinc-blende crystals, one of them is shown to give good results for all ranges of mass defects, the other one failing in some cases. Application is done to a calculation of the changes in force constants from the experimental values of the frequencies, showing how rapidly one can obtain the trends in a family of compounds.

Introduction. — Localized vibrational states due to light defects in monoatomic or diatomic crystals have been the subject of many theoretical and experimental studies. The dynamical behavior of the impurities has been described theoretically by Lifschitz [1] who introduced the Green's function technique. This method, although exact, presents the disadvantage of being complicated to handle in the general case, and the solution often requires computational work.

Our purpose here is to derive analytic formulae giving the local vibrational modes with a good accuracy. For this we shall use a method of moments which has already been introduced in the case of electronic states [2]. We treat the problem of a light impurity for which the local mode frequency is greater than the longitudinal optical frequency of the host crystal. Our model allows us to treat not only the pure mass defect but also to introduce local changes in force-constants which we shall be able to evaluate from the experimental value of the local mode frequency.

To derive our expressions for the localized state frequency, we approximate the change in density of states due to the impurity by a few delta functions whose position and amplitude are chosen so that they satisfy the first moments of the exact change in density of states. We had used such a technique previously for a calculation of surface states [3], [4] and also for the U-center [5]. Here we shall be able to show that the approximate value derived in [5] is not always valid and we shall consequently derive a much better analytic form for the localized frequency, the relative error introduced being smaller than two per cent for any position of the localized state.

We believe that such an approximate expression can be useful for experimentalists because its application to any problem is straightforward. It can also be extended without trouble to include changes in force constants and these can be evaluated from the experimental results. Such a procedure can be useful to study the trends in the results in a series of compounds for instance.

In order to check the validity of our models we shall make in the two first parts of this study a careful comparison with exact results which have been derived for pure mass defects in diatomic systems. In section 1 we introduce the method and compare with the exact frequencies in the case of a linear diatomic chain. In section 2 we do this comparison for zinc-blende crystals and also determine some changes in force constants in those systems. Finally, in section 3 we discuss the accuracy of the approximate
expressions and give an application to the U-center in alkali-halides.

Section 1

Définition of the models. Application to the linear diatomic chain. — We shall now present our models and check their accuracy for the linear diatomic chain.

1.1 The method of moments. — The dynamical equations for a perfect crystal in the harmonic approximation can be written in the well-known matrix-form:

\[(D - \omega^2 I) \mathbf{u} = 0\]  \hspace{1cm} (1)

\(D\) is the dynamical matrix, \(\omega\) the normal-mode frequency, \(I\) the unit-matrix and \(\mathbf{u}\) the displacement-vector. If one introduces a defect (here a mass-defect) the matrix \(D\) becomes \(D + V\) where \(V\) represents the perturbation in the dynamical equations. The frequencies for the perturbed system are solutions of the secular equations:

\[\det (D + V - \omega^2 I) = 0.\]  \hspace{1cm} (2)

The density of states of the perfect crystal, \(v(\omega^2)\), is changed into \(v(\omega^2) + \delta v(\omega^2)\), and the moments of the difference can be written [2]:

\[\delta \mu_n = \int \delta v(\omega^2) \omega^{2n} d\omega^2.\]  \hspace{1cm} (3.1)

Or:

\[\delta \mu_n = \text{tr} \left[(D + V)^n - D^n\right]\]  \hspace{1cm} (3.2)

where \(\text{tr}\) means the trace of the matrices. For \(n = 1\) and \(n = 2\) the calculation of the moments [5] is easy, and below we shall use only those moments.

To obtain approximate formulae we can describe the change in density of states \(\delta v(\omega^2)\) inside the band of the perfect crystal by one or two delta-functions whose total weight is \(-1\), and the localized state by a delta function located at \(\omega_{loc}\) with a weight \(+1\).

Let us consider two simple models. The simplest model which was derived previously [3], [5] and applied to the U-center contains only one delta-function at \(\omega_{loc}\) to approximate roughly the variation \(\delta v(\omega^2)\) (Fig. 1). We have then two delta-functions to consider and require that they satisfy the two first moments of \(\delta v(\omega^2)\). This leads to the equations:

\[\delta \mu_1 = \omega_1^2 - \omega_0^2\]
\[\delta \mu_2 = \omega_1^4 - \omega_0^4\]  \hspace{1cm} (4)

where \(\omega_1\) is the localized frequency in this first model. The result turns out to be

\[\omega_1^2 = \frac{1}{2} \left(\delta \mu_1 + \frac{\delta \mu_2}{\delta \mu_1}\right).\]  \hspace{1cm} (5)

Such an expression evidently gives good values for highly localized states. However one can show (Appendix A) that \(\omega_1\) is always smaller than the exact value, with a maximum error when \(\omega_{loc}\) is close to \(\omega_l\) the longitudinal optical frequency. The reason for this is that one neglects the width of \(\delta v(\omega^2)\) inside the band.

This fact has led us to consider another extreme model where \(\delta v(\omega^2)\) inside the band is approximated by two delta-functions weighted by \(A_1\) and \(A_2\) \((A_1 + A_2 = -1)\) and placed at the two limits of the band 0 and \(\omega_l\) (Fig. 2).

We have now three unknowns: \(A_1\), \(A_2\) and the localized frequency which we call \(\omega_2\) in this model. If one requires that they satisfy the three first moments of \(\delta v(\omega^2)\) one obtains:

\[A_1 + A_2 + 1 = 0\]
\[A_2 \omega_L^2 + \omega_2^2 = \delta \mu_1\]
\[A_2 \omega_L^4 + \omega_2^4 = \delta \mu_2]\]  \hspace{1cm} (6)

The solution of this system is:

\[\omega_2^2 = \frac{1}{2} \left[ \omega_L^2 + [\omega_L^2 + 4(\delta \mu_1 - \omega_L^2 \delta \mu_1)]^{1/2} \right].\]  \hspace{1cm} (7)

We shall see later that this second value \(\omega_2\) is good not only away from the band limit \(\omega_L\) but also with a good precision when we are near the band.

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**Fig. 1.** — First model for \(\delta v(\omega^2)\).

**Fig. 2.** — Second model for \(\delta v(\omega^2)\).
1.2 LINEAR DIATOMIC CHAIN. GREEN’S FUNCTION TREATMENT. — To test our formulae we shall first compare them to the exact values for the linear diatomic chain. These can be derived from a Green’s function treatment which we now recall.

Let us denote 0, 1, 2, ..., −1, −2, ... the atoms, alternatively with the masses \( M_0 \) and \( M_1 \) and an interatomic distance \( a \). Let us call \( x, \beta, \gamma \) the force constants between nearest-neighbours, next-nearest-neighbours of \( M_0 \)-type, next-nearest-neighbours of \( M_1 \)-type, respectively.

Let us introduce the following parameters:

\[
\eta = \frac{M_0}{M_1}, \quad \lambda = \frac{\beta}{x}, \quad \lambda' = \frac{\gamma}{x}.
\]

Now, when we replace the mass \( M_0 \) at the central site by a mass \( M' \) we create a perturbation \( V \) and it is well known [6] that the localized modes obey the equation:

\[
det (I - VG) = 0
\]

where \( G \) is the Green function.

If we put \( \varepsilon \) for the « mass-defect » we get:

\[
\varepsilon = 1 - M' M_0
\quad V = \varepsilon \omega^2.
\]

We shall consider two cases:

1.2.1 First case. — Nearest-neighbours only: in this case the Green function can be evaluated analytically. One finds, putting

\[
\omega_L^2 = z_0 + z_1,
\]

\[
\left( \frac{\omega_G}{\omega_L} \right)^2 = \frac{2 z_0 + (1 - \varepsilon^2) z_1 + [4 \varepsilon^2 z_0^2 + (1 - \varepsilon^2)^2 z_1^2]^{1/2}}{2(1 - \varepsilon^2)}
\]

if we denote by \( \omega_G \) the value of the localized mode frequency. Let us observe that in the extreme case when \( M_0 \) is equal to \( M_1 \) (monoatomic chain) that expression reduces to:

\[
\left( \frac{\omega_G}{\omega_L} \right)^2 = \frac{1}{1 - \varepsilon^2}
\]

which is a standard result [7].

1.2.2 Second case. — Next-nearest-neighbours. We have solved this case numerically and some results are given in figure 4. We may point out that even in this simple case the Green’s function method has no analytic solution.

1.3 RESULTS AND DISCUSSION FOR THE DIATOMIC CHAIN. — If to obtain the approximate expressions \( \omega_1 \) and \( \omega_2 \) for the localized mode frequency one uses for the perturbation a frequency dependent form such as \( \varepsilon \omega^2 \), (5) and (7) are not useful, because one cannot determine the moments \( \delta \mu_k \) from the traces as in (3.2).

To eliminate this difficulty, one can notice that, if in the eigenvalue problem, one replaces the perturbation term \( \varepsilon \omega^2 \) by its value for the localized mode \( \omega_{\text{loc}} \), one has a new problem to solve for which \( \omega_{\text{loc}} \) is still a solution. In such a case the moment’s technique can be used, because the perturbative potential remains constant depending on \( \omega_{\text{loc}} \) as a parameter.

One can then write for the linear chain with a pure mass defect

\[
\delta \mu_1 = \varepsilon \omega_{\text{loc}}^2,
\]

\[
\delta \mu_2 = \delta \mu_1(\delta \mu_1 + 2 D_{00}).
\]

In the first model, where \( \omega_{\text{loc}} \) is approximated by \( \omega_1 \) given by (5) one obtains

\[
\left( \frac{\omega_1}{\omega_L} \right)^2 = \frac{1 + \lambda}{1 + \eta} \frac{1}{1 - \varepsilon^2}
\]

In the second model, \( \omega_2 \) reduces to

\[
\left( \frac{\omega_2}{\omega_L} \right)^2 = \frac{1 + \varepsilon - \eta + 2 \lambda}{1 + \eta} \frac{1}{1 - \varepsilon^2}
\]

The corresponding results are shown on figures 3 and 4 where they are compared to the exact values. First let us point out that for \( \lambda = 0, \eta = 1 \) (monoatomic chain with nearest neighbour’s interactions only) the expression (14) reduces to

\[
\left( \frac{\omega_2}{\omega_L} \right)^2 = \frac{1}{1 - \varepsilon^2}
\]

![FIG. 3. — Linear diatomic chain with \( \eta = 0.5, \lambda = 0 \).](image-url)
FIG. 4. — Linear diatomic chain with $\eta = 2$, $\lambda = 0.20$.

In this particular case the second model gives the exact values, which is not true for the first one.

In the more general case one can consider two situations:

1) When $\eta < 1$ (the light mass is replaced by $M'$) we have always $\omega_1 < \omega_G < \omega_2$. For $\varepsilon \geq 0.9$ ($M'$ small) the relative error $(\omega_1 - \omega_G)/\omega_G$ is always smaller than 2%. On the other hand the error is larger when $\varepsilon \to 0$. For $\varepsilon \geq 0.9$ the relative error $(\omega_2 - \omega_G)/\omega_G$ for the second model is always smaller than 0.1% and for other values of $\varepsilon$, even when $\omega_2$ approaches $\omega_1$ (band limit) the error remain smaller than 1.8%.

2) When $\eta > 1$ (the heavy mass is replaced by $M'$) the error on $\omega_1$ increases and the formula (13) becomes a poor approximation. On the other hand $\omega_2$ provides an approximate value with an error less than 2%, when $\eta = 2$, for any value of $\varepsilon$. When $\varepsilon \geq 0.9$ the error introduced by $\omega_2$ is 0.2% maximum, for $0 < \lambda < 0.30$.

From this, one can derive the preliminary conclusion that, although one can believe that the two models are opposite extremes and should give comparable errors, the second one gives a very good approximation on the whole range of values of $\varepsilon$, at least for the linear chain.

Section 2

Application to the cubic zinc-blende crystals. — Experimentally one can observe localized modes in doped GaP-type-crystals by infrared absorption measurements [8] to [13]. Some experimentalists use an empirical formula with a parameter $\alpha$ to evaluate the localized-mode frequency due to the impurity [14]:

$$\omega_1 = A \left( \frac{1}{M_1} + \frac{1}{\alpha M_1} \right).$$

Here $M_i$ is the impurity-mass, $M_1$ the nearest-neighbour’s mass, $A$ a constant depending upon the maximum optical-mode-frequency in the perfect crystal.

Other attempts have been made to approach the problem theoretically, such as the Green’s-function method [15] or a modified-molecular-model [16]. As the results in [15] were given for all values of $\varepsilon$ in the pure mass defect case, we shall be able to have another test of our models for these three dimensional diatomic systems.

We discuss the results and finally show in some cases how our formulae can very easily give an idea of the changes in force-constants near a defect.

2.1 The equations of motion. — We can write the equations in the form (1), taking account of the interactions between the replaced atom and its nearest and next-nearest-neighbours, and the symmetry-properties of the zinc-blende structure [17]. The force-constants-matrix between the (0, 0, 0)-cation and the $(a/4, a/4, a/4)$-anion (where $a$ is the lattice-constant) can be written:

$$\begin{bmatrix}
\alpha & \beta & \beta \\
\beta & \alpha & \beta \\
\beta & \beta & \alpha
\end{bmatrix}.$$ (17)

For the next-nearest neighbours $(a/2, a/2, 0)$ the matrix is:

$$\begin{bmatrix}
\mu & \mu & 0 \\
\mu & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}.$$ (18)

if we suppose the interactions to be central, and equal between anions and between cations. There are four nearest-neighbours and twelve next-nearest-neighbours, and the corresponding matrices are deduced from (17) and (18) by the classical symmetry matrices for the zinc-blende structure. Finally we obtain the intra-atomic term under the form:

$$D_{00} = \frac{4 \alpha + 8 \mu}{M_0}.$$ (19)

The $\alpha$, $\beta$ and $\mu$ force-constants can be derived from the elastic constants $C_{11}$, $C_{12}$, $C_{44}$ [18] and from the expressions of the optical-frequencies in the long wavelength limit [19] i.e.:

$$C_{11} = \frac{\alpha + 8 \mu}{2 r_0^2} + 0.125 5 Z$$

$$C_{12} = \frac{2 \beta - \alpha + 4 \mu}{2 r_0^2} - 1.324 Z$$

$$C_{44} = \frac{\alpha + 4 \mu}{2 r_0^2} - 0.063 Z - \frac{(2.519 \frac{Z}{r_0} - \frac{\beta}{r_0^2})^2}{2 \alpha^2 + 2 \pi Z \frac{r_0^2}{3 \r_0^2}}$$ (20)

$$\omega_{L0}^2 = \frac{1}{M} \left( 4 \alpha + \frac{8 \pi e^2}{3 V_a} \right)$$

$$\omega_{L0}^2 = \frac{1}{M} \left( 4 \alpha - \frac{4 \pi e^2}{3 V_a} \right)$$
where we have put:

\[ 2 r_0 = a, \quad Z = \frac{z^2 e^2}{2 r_0^2}, \quad \frac{1}{M} = \frac{1}{M_0} + \frac{1}{M_1} \]

and \( V_a \) is the volume of the unit-cell, \( z \) being the effective ionic-charge.

One has in fact five equations to solve, with four variables. The system is solved numerically by a least-square method [19]-[20].

2.2 Comparison of our approximate frequencies with the exact results. — A treatment quite similar to that of the linear chain in section 1.3, using (19) immediately gives:

\[
\begin{align*}
\omega_1 &= \frac{4 \pi + 8 \mu}{M_0(1 - \varepsilon)} \\
\omega_2 &= \frac{\omega_0^2}{1 + \varepsilon} + \frac{2 \varepsilon}{1 - \varepsilon^2} \frac{4 \pi + 8 \mu}{M_0} \\
\end{align*}
\]  

where \( M_0 \) is the mass of the replaced atom and \( \varepsilon \) the mass defect. We have made the calculations for: GaP, GaAs, GaSb, InP, InAs, InSb, AlSb, ZnS, ZnSe, ZnTe, CdTe, HgTe and SiC, \( \varepsilon \) running from 0.05 to 0.95, and \( M_0 \) being the first or the second atom in the crystal under consideration. We only present a selection of the characteristic cases in figures 5 and 6.

The results for \( \omega_G(\varepsilon) \) computed by the Green’s function method have been presented by Gaur et al. [15] and we can compare our approximate values \( \omega_1 \) and \( \omega_2 \) with theirs [20]. We have verified that, when \( \varepsilon \) is large (light impurity) \( \omega_1 \) and \( \omega_2 \) are close to \( \omega_G \), by defect and by excess respectively. The exact values of the localized-mode frequencies are then located between our analytic formulae \( \omega_1 \) and \( \omega_2 \) (21).

When \( \varepsilon \) decreases the values \( \omega_1 \) obtained from the first-model are rapidly in disagreement with \( \omega_G \) values; but the corrected values \( \omega_2 \) provide a good approximation. It is convenient to consider three cases:

1) The two masses \( M_0 \) and \( M_1 \) of the crystal are of the same order of magnitude. In this case we have \( \omega_1 < \omega_G < \omega_2 \) the maximum error on \( \omega_2 \) being about 1 or 2%.

2) When \( M_0 < M_1 \), i.e. the light mass is replaced, the agreement between \( \omega_1, \omega_G, \omega_2 \) is better, and the average value \( (\omega_1 + \omega_2)/2 \) is practically indistinguishable from the exact value \( \omega_G \).

3) On the contrary, when \( M_0 > M_1 \), i.e. the heavy mass is replaced, the disagreement between \( \omega_1 \) and \( \omega_G \) becomes greater and the first model has no interest. But on the other hand \( \omega_2 \) is still useful and gives a good approximation to the exact frequency.

2.3 Evaluation of the changes in force-constants. — Experimental data on the localized

\[ \begin{align*}
\omega_1 &= \frac{4 \pi + 8 \mu}{M_0(1 - \varepsilon)} \\
\omega_2 &= \frac{\omega_0^2}{1 + \varepsilon} + \frac{2 \varepsilon}{1 - \varepsilon^2} \frac{4 \pi + 8 \mu}{M_0} \\
\end{align*}
\]
vibrational modes due to impurities in crystals with the zinc-blende structure are rather scarce, and thus we cannot arrive at very general conclusions. The case of Al is however interesting, since we have seven experimental values available [21]-[24]. In table I we give the values of \( \omega_1 \) (band-limit), \( \omega_G \) (Green's-functions method), \( \omega_{\text{exp}} \) (experimental values), \( \omega_1 \) (first model), \( \omega_2 \) (second model).

The difference between \( \omega_{\text{exp}} \) and the pure mass-defect theoretical frequencies can obviously be interpreted as due to local changes in force-constants. To evaluate them roughly we shall only take into account the change of the intraatomic term on the impurity site. Such a description can only become exact for highly localized states but it gives an order of magnitude of the true change in force constant.

Let us then call \( \theta \) the constant \( 4 \pi + 8 \mu \). We evaluate a new constant \( \theta' \) in order to make \( \omega_1 \) or \( \omega_2 \) coincide with \( \omega_{\text{exp}} \). In the first model we can easily show that the new frequency is:

\[
\omega'_1 = \frac{\theta'}{M_0(1 - \varepsilon)}.
\]

Fitting this frequency \( \omega'_1 \) to the experimental value \( \omega_{\text{exp}} \) gives (Appendix B)

\[
\frac{\theta'}{\theta}_1 = \left( \frac{\omega_{\text{exp}}}{\omega_1} \right)^2
\]

where \( \omega_1 \) is the value obtained for the pure mass defect. We obtain for the second-model a force-constants-ratio given by (Appendix B):

\[
\frac{\theta'}{\theta}_2 = \left[ \frac{\omega_G^2}{2} - \varepsilon \omega_{\text{exp}}^2 + \frac{1}{2} \{ (\omega_G^2 - 2 \omega_{\text{exp}}^2) \}^2 + 4 D_{00}(D_{00} - \omega_G^2)^{1/2} \right] / D_{00}.
\]

The corresponding numerical values are given in table I. To use (23) and (24) care must be taken that \( (\omega_1 - \omega_G)/\omega_G \) or \( (\omega_2 - \omega_G)/\omega_G \) are sufficiently small compared to \( (\omega_{\text{exp}} - \omega_G)/\omega_G \) in order to obtain meaningful results for \( \theta'/\theta \).

If Al replaces an atom of the same groups in the periodic table of elements (here Ga or In) the pure mass-defect values are very close to the experimental data. Consequently we need a strong modification for the force constant \( \theta \) (ratio 1.4 to 1.8). The two models become valid and give similar results. A detailed theoretical study should certainly be worth doing, to give an interpretation of the decrease of \( \theta'/\theta \) in table I. However, for the model to be coherent, it would be necessary to introduce interatomic changes in force constants related to \( \theta' - \theta \).

### Table I

**Localized-mode frequencies (in \( 10^{13} \) s\(^{-1} \)) for Al, and force-constant changes. (The replaced atom is underlined.)**

<table>
<thead>
<tr>
<th>Al-replaced atom</th>
<th>( \omega_1 )</th>
<th>( \omega_{\text{exp}} )</th>
<th>( \omega_1 )</th>
<th>( \omega_2 )</th>
<th>( \omega_1 )</th>
<th>( \theta'/\theta )</th>
<th>( \theta'/\theta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaP</td>
<td>7.59</td>
<td>8.34</td>
<td>6.86</td>
<td>8.45</td>
<td>8.32</td>
<td>1.48</td>
<td>0.93</td>
</tr>
<tr>
<td>GaAs</td>
<td>5.50</td>
<td>6.81</td>
<td>6.47</td>
<td>7.11</td>
<td>6.95</td>
<td>1.10</td>
<td>0.87</td>
</tr>
<tr>
<td>GaSb</td>
<td>4.25</td>
<td>5.97</td>
<td>5.99</td>
<td>6.32</td>
<td>6.27</td>
<td>0.99</td>
<td>0.86</td>
</tr>
<tr>
<td>InSb</td>
<td>3.74</td>
<td>5.57</td>
<td>5.35</td>
<td>5.89</td>
<td>5.78</td>
<td>1.00</td>
<td>0.86</td>
</tr>
<tr>
<td>ZnS</td>
<td>6.61</td>
<td>8.25</td>
<td>5.63</td>
<td>7.14</td>
<td>6.83</td>
<td>2.14</td>
<td>1.80</td>
</tr>
<tr>
<td>ZnSe</td>
<td>4.77</td>
<td>6.76</td>
<td>5.32</td>
<td>5.94</td>
<td>5.67</td>
<td>1.61</td>
<td>1.45</td>
</tr>
<tr>
<td>ZnTe</td>
<td>3.87</td>
<td>5.89</td>
<td>5.26</td>
<td>5.26</td>
<td>5.17</td>
<td>1.40</td>
<td>1.32</td>
</tr>
</tbody>
</table>

### Section 3

**General discussion and application to the U center.**

3.1 ACCURACY OF THE ANALYTIC FORMULAE. — Let us first recall the general features obtained in the comparison of \( \omega_1 \) and \( \omega_2 \) with the exact value \( \omega_G \) in section 1.

If the two atoms of the crystal have comparable masses the exact value \( \omega_G \) is greater than \( \omega_1 \) and smaller than \( \omega_2 \) both for the linear chain and the zinc-blende crystals. In all cases \( \omega_2 \) gives a better approximation, \( (\omega_2 - \omega_G)/\omega_G \) remaining smaller than 2\%. This maximum error occurs near the limit of the band. However the values obtained from \( \omega_1 \) are not too bad, so that the average between \( \omega_1 \) and \( \omega_2 \) is better than \( \omega_2 \) itself.

For different masses let us consider first the case where the impurity is substituted for the light mass. Both frequencies are good approximations \( \omega_2 \) remaining better than \( \omega_1 \) and the situation is quite the same as for equal masses. However, in the opposite case when the heavy atom is replaced, \( \omega_2 \) comes quite close to \( \omega_G \) and \( \omega_1 \) becomes a very poor approximation except for highly localized states.

To give a discussion of these results, we first recall that our models are not based on the true perturbative potential \( \omega^2 \) but on the expression \( \omega^2 \) which gives the same result for the frequency of the localized mode. Then the change in density of states \( \delta \omega^2 \) which we shall discuss is not the true one.

Let us first consider the first model giving the frequency \( \omega_1 \). One can easily show (Appendix A) that \( \omega_1 \) must underestimate the exact value \( \omega_G \), by an amount depending on the second moment \( V_2 \) of \( \delta \omega^2 \) inside the band with respect to its bary-center. One can also show that this error tends to
zero as $\omega_2$ tends to infinity. The problem is to know why $\omega_1$ is good in all cases except when heavy atoms are replaced.

It is evident that no rigorous proof of this can be given. We simply suggest the following tentative explanation. From the knowledge of the intersections of the intraatomic Green's function matrix element $G_{oo}(\omega^2)$ with $(\omega_{loc}^2)^{-1}$ one can deduce $\omega_{loc}$ and $\delta\nu(\omega^2)$. For a zinc-blende system with equal masses the real part of $G_{oo}$ has a sharp positive peak near $\omega_L$ due to the optical band and a smaller one due to the acoustical band (these are oversimplified features of $G_{oo}$). For small mass defects one should obtain the conclusion that one lososes one state in the optical band and none in the acoustical band. In this limit $\omega_1$ should provide a good approximation, $V_2$ remaining small.

For different masses, if the light atom is replaced the optical part of $G_{oo}(\omega^2)$ will increase corresponding to a decrease of the acoustical contribution. The preceding argument remains valid with perhaps an enhanced accuracy because the frequency gap increases, narrowing the optical band and then $V_2$. On the other hand if the heavy atom is replaced, the acoustical part is enhanced. For small mass defects one could obtain a localized state in the gap and lose another state in the acoustical band. The situation could become even more complicated. The result is that $V_2$ increases and $\omega_1$ gives an appreciable error.

Such conclusions do not hold for $\omega_2$ because the two delta-functions take some account of the correction due to $V_2$ and generally lead to an overestimation of the frequency. However in the case where the heavy mass is replaced the model leading to $\omega_2$ is certainly more appropriate than one delta function to take account of the complex situation. It is then not surprising that $\omega_2$ is a good approximation in all cases.

### 3.2 The U-Center Treated as a Pure Mass-Defect

— In diatomic cubic crystals of the Na-Cl type the substitution of a H- or D- ion into the place of Cl- gives rise to a localized high-frequency mode [25]. It is known that the localized mode is triply degenerate [26], [27] and one can treat each component separately.

In order to calculate the force-constants, we take account, after Kellermann [28]:

a) of the Coulomb-interaction-forces between anions and cations,

b) of the short-range repulsive interactions between an atom and its nearest-neighbours.

One finds that the intraatomic force-constant $a$ of the dynamical matrix $D$ can be written

$$a = \frac{6}{K} \frac{R_0}{6} \quad (25)$$

where $R_0$ is the distance between nearest-neighbours, and $K$ the experimental value of the compressibility.

From the same considerations as before, one obtains

$$\omega_1^2 = \frac{a}{M_0(1 - \epsilon)} \quad (26)$$

This result has been derived in a previous work [5] but we reproduce it for comparison with $\omega_2$. $M_0$ is the mass of the replaced atom and $\epsilon$ the mass-defect. For $\omega_2$ we get

$$\omega_2^2 = \frac{\omega_1^2}{1 + \epsilon} + \frac{2\epsilon}{1 - \epsilon^2} \frac{\alpha}{M_0} \quad (27)$$

where $\omega_L$ is the longitudinal-optical mode frequency.

The values for $\omega_1$ and $\omega_2$ are given in table II, in which they are compared with $\omega_{exp}$, the cases of H- and D- impurities. The values of $R_0$, $K$, $\omega_L$, and $\omega_{exp}$ are taken from [6], [25], [29]-[31].

### Table II

| U-center. Numerical values of the localized-mode frequencies for the pure mass-defect case (10$^{13}$ s$^{-1}$) |
|---|---|---|---|---|---|
| H | D- |
| $\omega_1$ | $\omega_2$ | $\omega_{exp}$ | $\omega_1$ | $\omega_2$ | $\omega_{exp}$ |
| NaF | 20.0 | 20.6 | 16.1 | 14.1 | 15.0 |
| KF | 17.2 | 17.6 | 13.6 | 12.1 | 12.8 |
| RbF | 16.5 | 16.8 | 13.2 | 11.7 | 12.1 |
| NaCl | 16.4 | 16.7 | 10.7 | 11.6 | 11.7 | 7.6 |
| KCl | 14.5 | 14.7 | 9.4 | 10.2 | 10.5 | 6.7 |
| RbCl | 14.1 | 14.3 | 8.9 | 10.0 | 10.2 |
| NaBr | 15.2 | 15.4 | 9.3 | 10.7 | 11.1 |
| KBr | 13.9 | 14.0 | 8.4 | 9.8 | 10.0 | 6.0 |
| RbBr | 13.1 | 13.2 | 8.0 | 9.3 | 9.4 |
| NaI | 13.3 | 13.5 | 8.1 | 9.4 | 9.7 |
| KI | 12.5 | 12.6 | 7.2 | 8.8 | 9.0 | 5.2 |
| Rbl | 12.3 | 12.4 | 6.8 | 8.7 | 8.9 |

### 3.3 Changes in Force Constants for the U-Center and Deviation from the $\sqrt{2}$ Law between H- and D-

— We observe on table II that calculated frequencies are greater than experimental ones. We shall try to get some consequences for the changes in force constants necessary to suit those values. We calculate the ratio $(a'\alpha'/a)$ and $(a'/\alpha)_2$ for H- exactly as in (23) and (24). The results are given in table III only in the second model. If we suppose after Fieschi [27] and Tosi [29] the repulsive potential between the H- ion and its neighbours to have the same shape as in the perfect crystal i. e.:

$$\phi(R) = \text{constant} \times \exp \frac{r_- + r_+ - R}{\rho} \quad (28)$$

where $R$ is the nearest-neighbour distance and $r_+$ and $r_-$ are the ionic radii, one can show [5] that...
$\ln \alpha'/\alpha$ is a linear function of $r_\infty$. In order to verify this fact, we have drawn the curve $\ln \alpha'/\alpha$ as a function of $r_\infty$ taken from [29], [33]. The linearity is clear: by a least-square method we obtain the equation: $\ln \alpha'/\alpha = 0.92 \ r_\infty - 0.46$ (Fig. 7).

![Figure 7. Log $\alpha'/\alpha$ for the U-center vs. $r_\infty$.](image)

Similar results are obtained for $D^-$, although we have only four values for the experimental data.

Starting from the new force constants $\alpha'$ calculated above, it is possible to derive the frequencies $\omega_2(D)$ for deuterium (Table III).

### Table III

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\alpha'/\alpha$</th>
<th>$\omega_2(D)$</th>
<th>$\omega_{\exp}(D)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaF</td>
<td>0.536</td>
<td>12.3</td>
<td>7</td>
</tr>
<tr>
<td>KF</td>
<td>0.525</td>
<td>10.3</td>
<td></td>
</tr>
<tr>
<td>RbF</td>
<td>0.570</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>0.339</td>
<td>8.1</td>
<td>7.6</td>
</tr>
<tr>
<td>KCl</td>
<td>0.358</td>
<td>7.0</td>
<td>6.7</td>
</tr>
<tr>
<td>RbCl</td>
<td>0.331</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td>NaBr</td>
<td>0.285</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>KBr</td>
<td>0.305</td>
<td>6.3</td>
<td>6.0</td>
</tr>
<tr>
<td>RbBr</td>
<td>0.322</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td>NaI</td>
<td>0.267</td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>KI</td>
<td>0.279</td>
<td>5.4</td>
<td>5.2</td>
</tr>
<tr>
<td>RbI</td>
<td>0.235</td>
<td>5.2</td>
<td></td>
</tr>
</tbody>
</table>

A further remark has to be made: we have compared the $H^-$ and $D^-$ cases. In the first model the ratio $y = \omega_1(H)/\omega_1(D)$ is equal to $\sqrt{2}$ because the mass-ratio for H and D is 2. On the other hand, the experimentalists have found a ratio of the order of magnitude 1.9 [32] and that fact has not yet been explained by the simple models available for the U-centers [6]. Generally the ratio is found to be $\sqrt{2}$ as in our first model. We have calculated $y$ with our second model. One can see in Table IV that in this case we obtain deviations of $y^2$ from 2 which have the right sign, but are generally overestimated.

### Table IV

<table>
<thead>
<tr>
<th>Compound</th>
<th>Experimental</th>
<th>Model 1</th>
<th>Model 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>1.92</td>
<td>2</td>
<td>1.72</td>
</tr>
<tr>
<td>KCl</td>
<td>1.94</td>
<td>2</td>
<td>1.77</td>
</tr>
<tr>
<td>KBr</td>
<td>1.94</td>
<td>2</td>
<td>1.76</td>
</tr>
<tr>
<td>KI</td>
<td>1.90</td>
<td>2</td>
<td>1.76</td>
</tr>
</tbody>
</table>

The reason for this probably lies in the fact that we have only introduced intraatomic changes in force constants. This is an unphysical approximation and interatomic terms could introduce appreciable changes in this ratio.

A general conclusion about the U-center is that one can easily obtain from $\omega_2$ changes in force-constants along the whole series of alkali-halides. This gives some interesting trends, such as a linearity upon $r_\infty$ which was already pointed out before [5]. The only difference is that here the results are more precise.

**Conclusion.** — Using a method of moments associated with delta function models for the variation in density of states caused by a substitutional light impurity we have been able to derive approximate expressions for the localized mode frequency. We have carefully compared them to the exact values obtained by the Green's function method for the cases of a linear diatomic chain and zinc-blende crystals.

We have been able to show that the simplest model, where one approximates the change in density of states inside the band by only one delta function with weight $-1$ gave good results when the two masses of the host atoms are equal or, if they are different, when the impurity is substituted for the lighter atom. In the opposite situation, when the heavier atom is replaced this model completely fails for small values of the mass defect.

To correct for this we have simulated the change in density of states inside the band by two delta-functions with total weight $-1$. Such a procedure gives a greatly enhanced accuracy with a maximum error of about $2\%$ for any value of the mass defect.
We believe that this second model can be useful for experimentalists because it is a simple and direct way of getting good estimates for any mass defect. From a theoretical point of view it can also be used to determine changes in force constants from the knowledge of the experimental frequencies. We have made simple applications of this in zinc-blende crystals with Al impurities and for the U-center in alkali-halides. This last example shows how an examination of the changes in force constants deduced in this way can give useful informations concerning the trends along series of compounds.

Acknowledgements. — We would like to thank Dr. J. F. Vetelino for kindly sending us the exact values of the frequencies for zinc blende crystals.

APPENDIX A

We shall recall the evaluation of the error in the first model which was derived in [5]. If one does an exact calculation of the change in density of states $\delta\nu(\omega^2)$ one can write

$$-\omega_0^2 + \omega_0^2 = \delta\mu_1$$  \hspace{1cm} (A.1)

where $\delta\mu_1$ is the first moment of $\delta\nu(\omega^2)$, $\omega_0$ the exact value of the localized frequency, and $\omega_0^2$ the first moment of $\delta\nu(\omega^2)$ inside the band, i.e.

$$\omega_0^2 = \int_0^{\omega_L^2} \delta\nu(\omega^2) \omega^2 d\omega$$ \hspace{1cm} (A.2)

using the fact that

$$\int_0^{\omega_L^2} \delta\nu(\omega^2) d\omega^2 = -1.$$  \hspace{1cm} (A.3)

If one evaluates the second moment of $\delta\nu(\omega^2)$ one can write

$$\delta\mu_2 = \int_0^{\omega_L^2} \delta\nu(\omega^2) \omega^4 d\omega^2 + \omega_0^4$$

$$= -V_2 - \omega_0^4 + \omega_0^2$$ \hspace{1cm} (A.4)

if one defines $V_2$ by

$$V_2 = -\int \delta\nu(\omega^2) (\omega^2 - \omega_0^2)^2 d\omega^2$$ \hspace{1cm} (A.5)

which is the second moment of $\delta\nu(\omega^2)$ inside the band with respect to its barycenter. (A.1) and (A.4) are analogous to the first model except that $\delta\mu_2$ must be changed into $\delta\mu_2 + V_2$. This introduces an error in $\omega_1$ given by

$$\Delta\omega_1^2 = -\frac{V_2}{2\delta\mu_1}.$$ \hspace{1cm} (A.6)

For a pure mass defect $\delta\mu_1$ is equal to $\epsilon\omega_0^2$. The error then decreases when the localized state frequency increases.

APPENDIX B

We shall derive here the formulae for the changes in force constants in an intraatomic approximation. The changes in moments can be written

$$\delta\mu_1 = \epsilon\omega_L^2 + D_{\theta\theta} - D_{\theta\theta}$$

$$\delta\mu_2 = \delta\mu_1(\delta\mu_1 + 2D_{\theta\theta})$$ \hspace{1cm} (B.1)

$D_{\theta\theta}$ being the new intraatomic term equal to $\theta'/M_0$. If one applies the first model, given from (5) replacing $\omega_1$ by its experimental value $\omega_\text{exp}$

$$\omega_\text{exp} = \omega_\text{exp}^2 + D_{\theta\theta}$$ \hspace{1cm} (B.2)

giving

$$\left(\frac{\theta'}{\theta}\right)_1 = \frac{D_{\theta\theta}}{D_{\theta\theta}}$$

$$= \left(\frac{\omega_\text{exp}}{\omega_1}\right)^2.$$ \hspace{1cm} (B.3)

In the second model, with the same definitions for $\delta\mu_1$ and $\delta\mu_2$, one can write, replacing $\omega_2$ by $\omega_\text{exp}$

$$\delta\mu_2 - \omega_\text{exp}^4 = \omega_\text{exp}^2(\delta\mu_1 - \omega_\text{exp}^2).$$ \hspace{1cm} (B.4)

This gives a second order equation for $D_{\theta\theta}$ which leads to

$$\left(\frac{\theta'}{\theta}\right)_2 = \frac{D_{\theta\theta}}{D_{\theta\theta}}$$

$$= \left\{\frac{\omega_1^2 - \omega_\text{exp}^2}{2} + \frac{1}{2} [(\omega_1^2 - 2\omega_\text{exp}^2)^2 + 4D_{\theta\theta}(D_{\theta\theta} - \omega_\text{exp}^2)]^{1/2}\right\}/D_{\theta\theta}.$$ \hspace{1cm} (B.5)
References