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Impurity Induced Infrared Lattice Vibration Absorption

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Impurities are known to affect vibrational properties of crystals by modifying the distribution of normal mode frequencies and altering the nature of the atomic displacements in the neighborhood of the impurities. We have calculated the effects of isotopic impurities on the lattice vibrational optical absorption of both monatomic and diatomic linear chains of alternately charged particles. It is found that even with the harmonic approximation and the use of the cyclic boundary condition, the presence of impurities leads to a broad absorption of the low frequency side of the main maximum. This is in contrast with the delta-function type of absorption at the optical frequency predicted by these models in the absence of impurities. For those cases in which discrete frequencies associated with localized vibrational modes occur, absorption at these isolated frequencies also occurs. This latter absorption can take place at frequencies higher than that of the main maximum. A discussion will be given of the relation between the results of our calculations and available experimental data.

§ 1. Introduction

Various examples are known of optical absorption lines in solids which are due to the effect of impurities on the lattice vibrations. For example silicon containing oxygen impurities exhibits[1] an infrared absorption line which has been qualitatively associated with a Si-O stretching vibration. Pick[2] has observed an infrared absorption line in each of several alkali halide crystals containing hydride ions and has attributed these lines to vibrations localized at the hydride ions. Recently Braunstein[3] has observed infrared impurity absorption lines in a series of germanium-silicon alloys.

In the present paper a theoretical investigation based on lattice dynamics is given of the effect of impurities on the infrared lattice-vibrational optical absorption. Qualitatively, introduction of an impurity can lead to a change in mass and a change in force constants associated with a given site. In addition, polarizabilities and effective charges may be modified. Of these changes only the change in mass

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can be controlled precisely and predictably, so we have restricted our attention to effects due to the change in mass of the impurity.

In a series of papers Montroll, Potts, Maradudin and collaborators[4),5),6),7)] have investigated the effect of impurities on the normal vibrational modes of crystal lattices. We summarize some of their qualitative results which have special interest. First let us consider a monatomic linear chain of atoms with mass M and coupled by nearest neighbor Hooke's law forces.[4)] If one of the atoms is replaced by an atom of mass $M'=(1-\varepsilon)M$ with the force constants unchanged, the normal mode frequencies can be described schematically as in Fig. 1. For a lighter impurity atom, $0<\varepsilon<1$, a discrete frequency associated with a mode localized about the impurity separates from the top of the allowed band of frequencies. For a heavier impurity atom, $\varepsilon<0$, no discrete frequency exists. In both cases the distribution function for the in-band frequencies is modified.[5)]

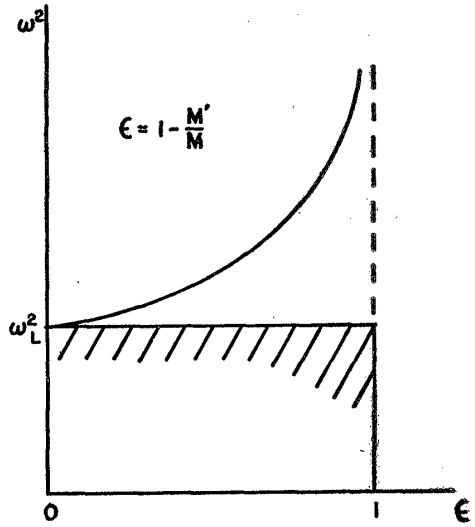

Fig. 1. The variation of the impurity frequency associated with a light isotope defect in a monatomic linear chain is plotted as a function of the impurity mass.

Turning now to the diatomic linear chain[6)] the introduction of an isotopic impurity atom may lead to one or two discrete frequencies associated with localized modes depending on which host atom is replaced and on the relative change in mass. A diagram of the situation is shown in Fig. 2. Of particular interest is the case in which one of the heavier host atoms is replaced by a lighter atom. One then gets a discrete frequency above the top of the optical branch and a second discrete frequency in the forbidden gap between the acoustical and optical branches. As in the monatomic case the frequency distribution function for the in-band modes is modified by the presence of impurity atoms.

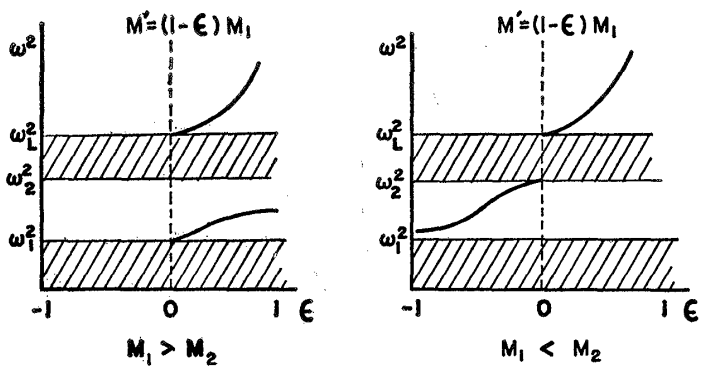

Fig. 2. The dependence on the impurity mass of the frequencies of the localized vibration modes in a linear diatomic chain when a heavy mass and a light mass atom are replaced by an isotopic impurity, respectively.

In this paper we study the effects of isotopic impurities on optical absorption associated both with localized modes and with the ordinary in-band modes. Monatomic and diatomic one and three dimensional cubic lattices of

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the sodium chloride type are considered.

§ 2. The monatomic lattice, cyclic boundary conditions

We study the following simple model of a one-dimensional ionic lattice. We have a linear chain of N ions of alternating charge each of whose mass is M, and each of which interacts only with its nearest neighbors through Hooke's law forces with force constant γ. The time-independent equation of motion for the nth ion is

$$Lu_n = M\omega^2 u_n + \gamma(u_{n+1} - 2u_n + u_{n-1}) = 0, \tag{2·1}$$

whose general solution is

$$u_n = A\cos n\theta + B\sin n\theta, \tag{2·2}$$

provided that

$$M\omega^2 = 2\gamma(1-\cos\theta). \tag{2·3}$$

If we impose the cyclic boundary condition on the displacements,

$$u_{n+N} = u_n, \tag{2·4}$$

we find that

$$\theta = \frac{2\pi s}{N}\,;\ s = 1, 2, 3, \cdots, N. \tag{2·5}$$

When defects are introduced into the lattice, the time-independent equations assume in general the form

$$Lu_n = \sum_p c_{np} u_p. \tag{2·6}$$

Equation (2·6) can be solved formally if we introduce the Green's function $g(n)$ which satisfies the equation

$$Lg(n) = \delta_{n0} \tag{2·7}$$

and also the cyclic boundary condition

$$g(n+N) = g(n). \tag{2·8}$$

With the aid of this function the solution to Eq. (2·6) is

$$u_n = \sum_{m,p} g(n-m)\, c_{mp} u_p. \tag{2·9}$$

If the ion at $n=0$ is replaced by one of the same charge but whose mass is $M' = (1-\varepsilon)M$ the coefficients c_{np} in Eq. (2·6) become

$$c_{np} = \varepsilon M\omega^2 \delta_{np}\delta_{n0}, \tag{2·10}$$

so that Eq. (2·9) becomes

$$u_n = \varepsilon M\omega^2 g(n)\, u_0. \tag{2·11}$$

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Since Eq. (2·11) holds for all n, it must hold for $n=0$, and we thus obtain the eigenvalue equation for the normal mode frequencies of the perturbed lattice:

$$1=\varepsilon M\omega^2 g(0). \tag{2·12}$$

An expression for $g(n)$ which satisfies Eqs. (2·7) and (2·8) is

$$g(n)=\frac{1}{N}\sum_{s=1}^{N}\frac{\exp(2\pi isn/N)}{M\omega^2-2\gamma+2\gamma\cos(2\pi s/N)}=g(-n). \tag{2·13}$$

The sum in Eq. (2·13) is evaluated in the Appendix with the result that

$$g(n)=g(0)\cos n\varphi+\frac{\sin|n|\varphi}{2\gamma\sin\varphi}\,;\quad n=0,\,1,\,2,\,\cdots,\,N-1 \tag{2·14}$$

$$g(0)=\frac{\cot(N\varphi/2)}{2\gamma\sin\varphi} \tag{2·15}$$

where we have put

$$\frac{\omega^2}{\omega_L{}^2}=f^2=\sin^2(\varphi/2),\quad 0<\varphi<2\pi. \tag{2·16}$$

The eigenvalue equation (2·12) becomes

$$\tan(N\varphi/2)=\varepsilon\tan(\varphi/2). \tag{2·17}$$

From Eqs. (2·11) and (2·13) we see that the isotope defect affects only the symmetric modes, i. e., those for which $u_n=u_{-n}$, while the antisymmetric modes, for which $u_{-n}=-u_n$, are unaffected by the presence of the defect. Thus we can classify the solutions to the perturbed equations as follows:

$$\text{symmetric:}\quad u_n=\varepsilon M\omega^2 g(n)u_0,\quad \omega=\omega_L\sin(\varphi/2) \tag{2·18a}$$

$$\tan(N\varphi/2)=\varepsilon\tan(\phi/2) \tag{2·18b}$$

$$\text{antisymmetric:}\quad u_n=B\sin(2\pi ns/N),\quad \omega=\omega_L\sin(\varphi/2) \tag{2·19a}$$

$$\varphi=\frac{2\pi s}{N}. \tag{2·19b}$$

In each of these cases we can restrict φ to the interval $(0,\pi)$ since we gain no new normal modes from the interval $(\pi,2\pi)$, and this restriction gives the correct number of normal mode vibrations.

We now turn to the calculation of the dipole moment of the lattice associated with each normal mode. This is defined by

$$M(s)=\sum_{n=0}^{N-1}e_n u_n(s) \tag{2·20}$$

where $u_n(s)$ is the displacement of the nth ion in the sth normal mode of vibration and e_n is the charge on the nth ion. In the present case $e_n=e(-1)^n$, and we find for the antisymmetric modes that

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$$M(s)=eB\sum_{n=0}^{N-1}(-1)^n\sin\frac{2\pi ns}{N}=0. \tag{2·21}$$

Thus we see that the antisymmetric modes do not contribute to the optical absorption of the lattice.

To calculate the contribution of the symmetric modes to the dipole moment it is convenient to proceed as follows. From Eqs. (2·18a) (2·20) and (2·13) we find that

$$M(s)=\varepsilon eM\omega_s^2u_0\sum_{n=0}^{N-1}(-1)^n g(n)=\frac{\varepsilon e\omega_s^2}{\omega_s^2-\omega_L^2}u_0 \tag{2·22}$$

where ω_s is the sth root of Eq. (2·18b).

The displacement u_0 is obtained from the normalization condition

$$\sum_{n=0}^{N-1}M_n u_n^2(s)=M\sum_{n=0}^{N-1}u_n^2(s)-\varepsilon Mu_0^2(s)=1. \tag{2·23}$$

This equation can be rewritten as

$$\begin{aligned}1+\varepsilon Mu_0^2(s)&=\varepsilon^2M^3\omega_s^4u_0^2(s)\sum_{n=0}^{N-1}g^2(n)\\&=\frac{MN}{2}\varepsilon^2u_0^2(s)\tan^2\frac{\varphi_s}{2}\csc^2\frac{N\varphi_s}{2}\left\{1+\frac{1}{N}\cot\varphi_s\sin N\varphi_s\right\}\end{aligned} \tag{2·24}$$

where this result is obtained from Eqs. (2·13) and (2·15) by a differentiation with respect to φ. With the aid of the eigenvalue equation, Eq. (2·17), this expression can be simplified to

$$\frac{MN}{2}u_0^2(s)\left\{1+\varepsilon^2\tan^2\frac{\varphi_s}{2}-\frac{\varepsilon}{N}\left(1+\tan^2\frac{\varphi_s}{2}\right)\right\}=1. \tag{2·25}$$

Combining the results expressed by Eqs. (2·22) and (2·25) we finally obtain for the dipole moment associated with the sth normal mode

$$M(s)=-\frac{\sqrt{2}\,\varepsilon e}{\sqrt{MN}}\frac{\tan^2(\varphi_s/2)}{\sqrt{1+\varepsilon^2\tan^2(\varphi_s/2)-(\varepsilon/N)[1+\tan^2(\varphi_s/2)]}} \tag{2·26a}$$

$$=-\frac{\sqrt{2}\,\varepsilon e}{\sqrt{MN}}\frac{f_s^2}{\sqrt{(1-f_s^2)[1-(1-\varepsilon^2)f_s^2-\varepsilon/N]}}. \tag{2·26b}$$

Ordinarily, the term of $O(1/N)$ in the denominator of Eq. (2·26b) is negligible compared to the rest of the denominator, and we have the approximate result that

$$M(s)\simeq-\frac{\sqrt{2}\,\varepsilon e}{\sqrt{MN}}\frac{f_s^2}{\sqrt{(1-f_s^2)[1-(1-\varepsilon^2)f_s^2]}}. \tag{2·27}$$

We have so far not considered explicitly the contribution to the dipole moment due to localized impurity modes of vibration. It is known from the work of Montroll and Potts[4] that such a mode exists if $0<\varepsilon<1$ but not if $\varepsilon<0$. In the

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former case, which is the more interesting one, there is a solution to Eq. (2·17) with $f>1$. This special case is included in the general treatment just presented, and is obtained by replacing φ by

$$\varphi=\pi+iz \tag{2·28}$$

so that now

$$f^2=\cosh^2(z/2)>1. \tag{2·29}$$

If Eq. (2·28) is substituted into Eq. (2·17) the eigenvalue equation for the impurity frequency becomes

$$\varepsilon\coth(z/2)=\tanh(Nz/2)\to 1 \text{ as } N\to\infty. \tag{2·30}$$

In the large N limit the solution of Eq. (2·30) is

$$z=\ln\frac{1+\varepsilon}{1-\varepsilon} \tag{2·31}$$

which together with Eq. (2·29) gives the Montroll-Potts result

$$f_{imp}^2=\frac{1}{1-\varepsilon^2} \tag{2·32}$$

If this result is substituted into Eq. (2·26b), or, alternatively, if Eqs. (2·28) and (2·31) are substituted into Eq. (2·26a), we obtain for the dipole moment associated with the impurity mode

$$M_{imp}=\frac{\sqrt{2}\,e}{\sqrt{M}}\frac{1}{\sqrt{\varepsilon}\sqrt{1-\varepsilon^2}}. \tag{2·33}$$

The absorption coefficient is proportional to $M^2(f)g(f)$ where $g(f)$ is the frequency distribution function for the perturbed lattice. It has the form

$$g(f)=g_0(f)+\Delta g(f) \tag{2·34}$$

where $g_0(f)$ is the distribution function for the perfect lattice,

$$g_0(f)=\frac{2}{\pi}\frac{1}{\omega_L\sqrt{1-f^2}}, \tag{2·35}$$

and $\Delta g(f)$ is the change in $g_0(f)$ due to an isotope defect[5]:

$$\Delta g(f)=-\frac{\varepsilon}{2N}\frac{g_0(f)}{[1+(\varepsilon^2-1)f^2]}-\frac{1}{2N\omega_L}\delta(f-1)+\frac{1}{N\omega_L}\delta\left(f-\frac{1}{\sqrt{1-\varepsilon^2}}\right),$$

$$0<\varepsilon<1, \tag{2·36a}$$

$$=\frac{|\varepsilon|}{2N}\frac{g_0(f)}{[1+(\varepsilon^2-1)f^2]}-\frac{1}{2N\omega_L}\delta(f-1),\quad \varepsilon<0. \tag{2·36b}$$

For the more interesting case of $0<\varepsilon<1$ we find that

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$$M^2(f)g(f)=\frac{2e^2}{MN}\frac{\varepsilon^2 f^4}{(1-f^2)[1-(1-\varepsilon^2)f^2]}$$
$$\times\left\{\frac{2}{\pi\omega_L}\frac{1}{\sqrt{1-f^2}}-\frac{\varepsilon}{N\pi\omega_L}\frac{1}{\sqrt{1-f^2}[1-(1-\varepsilon^2)f^2]}-\frac{1}{2N\omega_L}\delta(f-1)\right\}$$
$$+\frac{2e^2}{M}\frac{1}{\varepsilon(1-\varepsilon^2)}\frac{1}{N\omega_L}\delta\left(f-\frac{1}{\sqrt{1-\varepsilon^2}}\right). \tag{2·37a}$$

For the case $\varepsilon<0$, we have

$$M^2(f)g(f)=\frac{2e^2}{MN}\frac{\varepsilon^2 f^4}{(1-f^2)[1-(1-\varepsilon^2)f^2]}$$
$$\times\left\{\frac{2}{\pi\omega_L}\frac{1}{\sqrt{1-f^2}}+\frac{|\varepsilon|}{N\pi\omega_L}\frac{1}{[1+(\varepsilon^2-1)f^2]\sqrt{1-f^2}}-\frac{1}{2N\omega_L}\delta(f-1)\right\}. \tag{2·37b}$$

These results are exact.

The physically most interesting case is one where the crystal contains a finite number n of defects, and not just one. In this case we can expand $M^2(f)g(f)$ in powers of the concentration of impurities,

$$c=\frac{n}{N} \tag{2·38}$$

in the form

$$M^2(f)g(f)=I(f)=I_0(f)+cI_1(f)+\cdots. \tag{2·39}$$

In this expansion $I_0(f)$ is the value of $I(f)$ in the absence of impurities, I_1, is the change in $I(f)$ due to the addition of a single impurity, and so on[7]. In the present case $I_0(f)$ is just a delta-function centered at $f=1$, and we will neglect it here since it contributes at one frequency only. This means that to terms linear in the concentration of impurities we obtain

$$I(f)\simeq c\cdot\frac{2e^2}{M\omega_L}\left\{\frac{2}{\pi}\frac{\varepsilon^2 f^4}{(1-f^2)^{3/2}[1-(1-\varepsilon^2)f^2]}\right.$$
$$\left.+\frac{1}{\varepsilon(1-\varepsilon^2)}\delta\left(f-\frac{1}{\sqrt{1-\varepsilon^2}}\right)\right\},\quad 0<\varepsilon<1, \tag{2·40a}$$
$$\simeq c\cdot\frac{2e^2}{M\omega_L}\cdot\frac{2}{\pi}\frac{\varepsilon^2 f^4}{(1-f^2)^{3/2}[1-(1-\varepsilon^2)f^2]},\quad \varepsilon<0. \tag{2·40b}$$

Thus in this approximation there is no formal difference between the in-band absorption in the two cases $0<\varepsilon<1$, and $\varepsilon<0$.

In Fig. 3 a plot is given of the integrated absorption coefficient in arbitrary units as a function of the fractional change in mass ε for the localized mode of vibration. One sees that the absorption is strong both when ε is close to zero

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and to unity. In Fig. 4 the absorption coefficient in arbitrary units is plotted as a function of frequnency for the in-band modes when $\varepsilon=1/2$. For the perfect lattice the absorption is zero except at ω_L. The presence of impurities leads to an increase in absorption at in-band frequencies when cyclic boundary conditions are employed.

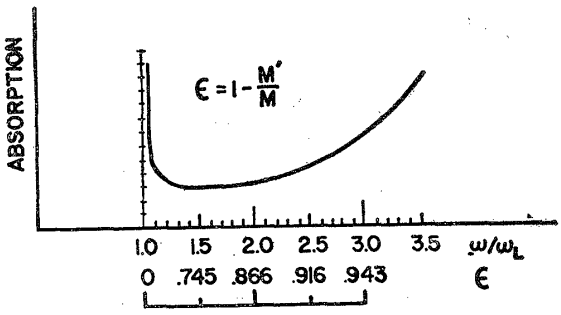

Fig. 3. Absorption (in arbitrary units) due to the localized vibration mode associated with a light isotope impurity in a monatomic linear chain plotted as a function of the impurity mass.

§ 3. A pair of isotope defects in a monatomic chain

It is of interest to investigate the effect of increasing concentration of impurities on the optical absorption. One would like to carry out a calculation for a system with n impurities, but the computational problems become rather severe. We therefore consider the case in which two ions of the same kind are replaced by heavier or lighter impurities. The time independent equations of motion become

$$Lu_n=\varepsilon M\omega^2(u_{-m}\delta_{n,-m}+u_m\delta_{n,m}). \tag{3·1}$$

The solution to this equation is

$$u_n=\varepsilon M\omega^2[g(n+m)u_{-m}+g(n-m)u_m]. \tag{3·2}$$

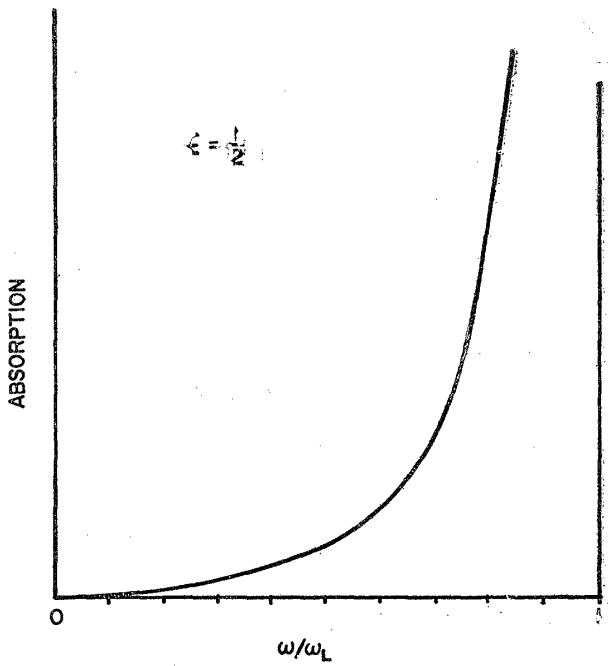

Fig. 4. The in-band absorption (in arbitrary units) due to a single light isotope impurity in a monatomic linear chain plotted as a function of the frequency.

Setting n equal to $-m$ and m respectively, we obtain the following set of equations for the amplitudes u_{-m} and u_m:

$$\begin{pmatrix} \varepsilon M\omega^2 g(0)-1 & \varepsilon M\omega^2 g(2m) \\ \varepsilon M\omega^2 g(2m) & \varepsilon M\omega^2 g(0)-1 \end{pmatrix}\begin{pmatrix} u_{-m} \\ u_m \end{pmatrix}=0. \tag{3·3}$$

The solubility condition leads to the eigenvalue equations for the normal mode frequencies

$$\varepsilon M\omega^2 g(0)=1\pm\varepsilon M\omega^2 g(2m). \tag{3·4}$$

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If we substitute the solution corresponding to the plus sign in Eq. (3·4) back into Eq. (3·3) we find that

$$u_{-m}+u_m=0, \tag{3·5}$$

i.e. this choice corresponds to antisymmetric modes of vibration. Similarly, the solution of Eq. (3·4) with the minus sign leads to the condition

$$u_{-m}-u_m=0, \tag{3·6}$$

and hence to symmetric vibration modes. The displacement components in each case are given by

$$\text{antisymmetric}: \quad u_n=\varepsilon M\omega^2[g(n-m)-g(n+m)]u_m \tag{3·7a}$$

$$\text{symmetric}: \quad u_n=\varepsilon M\omega^2[g(n-m)+g(n+m)]u_m. \tag{3·7b}$$

It is straightforward to show that for the antisymmetric modes the dipole moment of the lattice vanishes, so that we need to consider only the symmetric modes in computing the absorption spectrum of the lattice. Furthermore, we shall restrict our attention to the localized modes, because the in-band modes lead to extremely complicated expressions for the absorption coefficient from which it is difficult to extract simple physical results.

The eigenvalue equation (3·4) for symmetric modes has a solution corresponding to a localized vibration mode when $0<\varepsilon<1$. Replacing ϕ by $\pi+iz$ in the usual way, we obtain the equation which determines the frequency of the localized mode:

$$\varepsilon \coth\frac{z}{2}=1-\varepsilon \coth\frac{z}{2}e^{-2mz}. \tag{3·8}$$

This equation can be solved by iteration, using the solution for $m\to\infty$ as the starting point. The result is

$$f^2=\frac{1}{1-\varepsilon^2}\left\{1+\frac{2\varepsilon^2}{1-\varepsilon^2}\left(\frac{1-\varepsilon}{1+\varepsilon}\right)^{2m}+\cdots\right\}, \tag{3·9}$$

and corresponds to a value of z given by

$$z=\ln\frac{1+\varepsilon}{1-\varepsilon}+\frac{2\varepsilon}{1-\varepsilon^2}\left(\frac{1-\varepsilon}{1+\varepsilon}\right)^{2m}+\cdots. \tag{3·10}$$

The displacement amplitudes become

$$u_n=\varepsilon \coth\frac{z}{2}(-1)^{n+m}u_m[e^{-|n-m|z}+e^{-|n+m|z}], \tag{3·11}$$

so that the expression for the dipole moment associated with this mode becomes

$$M(z)=(-1)^m eu_m\,\varepsilon\coth\frac{z}{2}\sum_{n=-\infty}^{\infty}[e^{-|n-m|z}+e^{-|n+m|z}]=2(-1)^m e\varepsilon u_m\coth^2\frac{z}{2}. \tag{3·12}$$

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The normalization condition, which determines the amplitude u_m, is

$$M\sum_n u_n^2+2(M'-M)u_m^2=1. \tag{3·13}$$

If we substitute Eq. (3·11) into Eq. (3·13), we can rewrite the latter equation as

$$M\varepsilon^2\coth^2\frac{z}{2}u_m^2\sum[e^{-2|n-m|z}+2e^{-|n-m|z-|n+m|z}+e^{-2|n+m|z}]-2\varepsilon Mu_m^2=1. \tag{3·14}$$

The sums are readily evaluated and we find that

$$2M\varepsilon u_m^2\left\{[\varepsilon\coth z(1+e^{-2mz})+2\varepsilon me^{-2mz}]\coth^2\frac{z}{2}-1\right\}=1. \tag{3·15}$$

However, from the eigenvalue equation we see that

$$1+e^{-2mz}=\frac{1}{\varepsilon}\tanh\frac{z}{2}, \tag{3·16}$$

so that

$$2M\varepsilon u_m^2\left\{\frac{\coth z}{\tanh(z/2)}+2m\coth\frac{z}{2}-2m\varepsilon\coth^2\frac{z}{2}-1\right\}=1. \tag{3·17}$$

If we substitute for z the expression given in Eq. (3·10), and transpose terms we obtain

$$u_m=\frac{\sqrt{\varepsilon}}{\sqrt{M}\sqrt{1-\varepsilon^2}}\left[1-\frac{(2m\varepsilon-1)}{1-\varepsilon^2}\left(\frac{1-\varepsilon}{1+\varepsilon}\right)^{2m}+\cdots\right]. \tag{3·18}$$

This result together with Eq. (3·12) gives us finally that

$$M_{imp}=\frac{2e(-1)^m}{\sqrt{M}\sqrt{\varepsilon}\sqrt{1-\varepsilon^2}}\left[1-\frac{2m\varepsilon+1-2\varepsilon^2}{1-\varepsilon^2}\left(\frac{1-\varepsilon}{1+\varepsilon}\right)^{2m}+\cdots\right]. \tag{3·19}$$

If we compare the results given by Eqs. (2·33) and (3·19) and recall that the absorption is proportional to M^2, we see that although only one of the two impurity modes in the present case is optically active it contributes twice as much to the absorption at the impurity frequency as does the single impurity mode which is associated with a single, isolated impurity. This tends to confirm our statement in the preceding section that if we have n impurities in our lattice, where $n\ll N$ so that they are widely separated, then to the first approximation the absorption at the impurity frequency is n times the absorption due to a single, isolated impurity.

§ 4. A single isotope defect in a monatomic lattice with free ends

In all cases discussed so far the unperturbed lattice has an absorption spectrum which consists only of a single δ-function peak at $\omega=\omega_L$. This result is a direct consequence of the assumption of the cyclic boundary condition on the lattice. It is known from the results of Rosenstock[8] that if more realistic boundary conditions

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are imposed on the lattice, e. g., if the ends of the lattice are allowed to be free, a non-vanishing absorption in the frequency range $(0, \omega_L)$ results. Since in the cyclic boundary case all in-band absorption is due to the impurity, it is of some interest to see how the presence of the impurity affects the in-band absorption in a lattice where it is non-vanishing to begin with.

We choose for this purpose a lattice of (an even number) N atoms which we number from 1 to N. We place an isotope defect whose mass is $M'=(1-\varepsilon)M$ at $p=N/2$ in the lattice. The equations of motion for this lattice become

$$M\omega^2 u_n+\gamma(u_{n+1}-u_n)-\gamma(u_n-u_{n-1})=0, \quad n\neq p \tag{4·1a}$$

$$M'\omega^2 u_p+\gamma(u_{p+1}-u_p)-\gamma(u_p-u_{p-1})=0, \quad n=p. \tag{4·1b}$$

The boundary conditions are

$$\begin{aligned} u_1-u_0&=0 \\ u_{N+1}-u_N&=0. \end{aligned} \tag{4·2}$$

A solution satisfying the boundary condition $u_{N+1}-u_N=0$ and satisfying the equations of motion for $n\geq p$ is

$$u_n=A\cos\left(N-n+\frac{1}{2}\right)\varphi, \quad n\geq p, \tag{4·3}$$

provided that $\omega^2=\omega_L^2\sin^2\varphi/2$, where $\omega_L=\sqrt{4\gamma/M}$ is the largest unperturbed frequency of the lattice. A solution satisfying the boundary condition $u_1-u_0=0$ and satisfying the equations of motion for $n<p$ is

$$u_n=B\cos\left(n-\frac{1}{2}\right)\varphi, \quad n<p, \tag{4·4}$$

provided again that $\omega^2=\omega_L^2\sin^2\varphi/2$. The coefficients A and B are determined by substituting the solutions (4·3) and (4·4) into the equations for the displacement components which are linked by the defect, u_p and u_{p-1}. This leads to the pair of equations

$$A\left\{[2(1-\varepsilon)\sin^2(\varphi/2)-1]\cos\left(\frac{N+1}{2}\right)\varphi+\frac{1}{2}\cos\left(\frac{N-1}{2}\right)\varphi\right\} +\frac{1}{2}B\cos\left(\frac{N-3}{2}\right)\varphi=0 \tag{4·5a}$$

$$\frac{1}{2}A\cos\left(\frac{N+1}{2}\right)\varphi+B\left\{[2\sin^2(\varphi/2)-1]\cos\left(\frac{N-3}{2}\right)\varphi +\frac{1}{2}\cos\left(\frac{N-5}{2}\right)\varphi\right\}=0. \tag{4·5b}$$

The condition that this pair of equations have non-trivial solutions for A and B is that the determinant of the coefficients vanishes. After some manipulations this condition reduces to

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$$1=\varepsilon\tan(\varphi/2)\left[\cot N\varphi+\frac{\cos\varphi}{\sin N\varphi}\right], \tag{4·6}$$

and we also find that

$$B=A\frac{\cos\left(\frac{N+1}{2}\right)\varphi}{\cos\left(\frac{N-1}{2}\right)\varphi}. \tag{4·7}$$

The dipole moment for the sth normal mode is

$$M(s)=\sum_{n=1}^{N}e(-1)^n u_n(s)=\frac{eB}{2\cos(\varphi/2)}[-1+(-1)^{p-1}\cos(p-1)\varphi]$$

$$+\frac{eA}{2\cos(\varphi/2)}[(-1)^p\cos(N-p+1)\varphi+(-1)^N] \tag{4·8}$$

$$=\frac{2eA\sin\frac{\varphi}{2}\sin\frac{N\varphi}{2}}{\cos\frac{\varphi}{2}\cos\frac{N-1}{2}\varphi}\times\begin{cases}\sin^2\frac{N}{4}\varphi, & p \text{ even}\\ \cos^2\frac{N}{4}\varphi, & p \text{ odd.}\end{cases} \tag{4·9}$$

The constant A is determined by the normalization condition

$$\sum_{n=1}^{N}Mu_n^2+(M'-M)u_p^2=1. \tag{4·10}$$

The first term on the left-hand side of Eq. (4·10) is summed as follows:

$$\sum_{n=1}^{N}Mu_n^2=M\left\{\sum_{n=1}^{p-1}B^2\cos^2\left(n-\frac{1}{2}\right)\varphi+\sum_{n=p}^{N}A^2\cos^2\left(N-n+\frac{1}{2}\right)\varphi\right\}$$

$$=\frac{1}{2}MB^2\left[\frac{N}{2}-1+\frac{\sin(N-2)\varphi}{2\sin\varphi}\right]$$

$$+\frac{1}{2}MA^2\left[\frac{N}{2}+1+\frac{\sin(N+2)\varphi}{2\sin\varphi}\right]. \tag{4·11}$$

The normalization condition, Eq. (4·10) becomes

$$1=\frac{1}{2}MA^2\left\{\frac{\cos^2\left(\frac{N+1}{2}\right)\varphi}{\cos^2\left(\frac{N-1}{2}\right)\varphi}\left[\frac{N}{2}-1+\frac{\sin(N-2)\varphi}{2\sin\varphi}\right]+\frac{N}{2}+1+\frac{\sin(N+2)\varphi}{2\sin\varphi}\right\}$$

$$-\varepsilon MA^2\cos^2\left(\frac{N+1}{2}\right)\varphi$$

$$\simeq\frac{MNA^2}{4\cos^2\left(\frac{N-1}{2}\right)\varphi}[1+\cos N\varphi\cos\varphi] \tag{4·12}$$

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where we have retained only the terms proportional to N. It can be shown that this approximation is permissible for all φ in $(0, \pi)$, i. e. for the in-band modes. We finally obtain

$$A=\frac{2\cos\left(\frac{N-1}{2}\right)\varphi}{\sqrt{NM}}\frac{1}{\sqrt{1+\cos N\varphi\cos\varphi}}. \tag{4·13}$$

The dipole moment can be rewritten as

$$M(s)=\frac{2e}{\sqrt{NM}}\frac{\sin\frac{\varphi}{2}\sin\frac{N}{2}\varphi}{\cos\frac{\varphi}{2}\sqrt{1+\cos N\varphi\cos\varphi}}\left[1\pm\cos\frac{N\varphi}{2}\right],\begin{cases}p \text{ odd}\\ p \text{ even.}\end{cases} \tag{4·14}$$

It is a rather difficult matter to eliminate φ from Eq. (4·14) in favor of the frequency ω. We have therefore evaluated $M(s)$ numerically for the particular case in which $N=20$ and $\varepsilon=1/2$. One finds that as s increases, $M(s)$ undergoes oscillations which become extremely rapid when N is large. In any physically resolvable frequency interval, however, these oscillations will be averaged out so that the absorption is a smoothly varying function of ω. We have therefore averaged $M(s)$ over small ranges of s to smooth out these physically unimportant oscillations. The absorption coefficient is plotted as a function of frequency in Fig. 5. One sees that when a lighter impurity atom is present, the in-band absorption is less than that for the perfect lattice. This result is the opposite of that obtained with cyclic boundary conditions. We believe that the free boundary condition gives the more reliable result since it seems physically more realistic than the cyclic boundary condition.

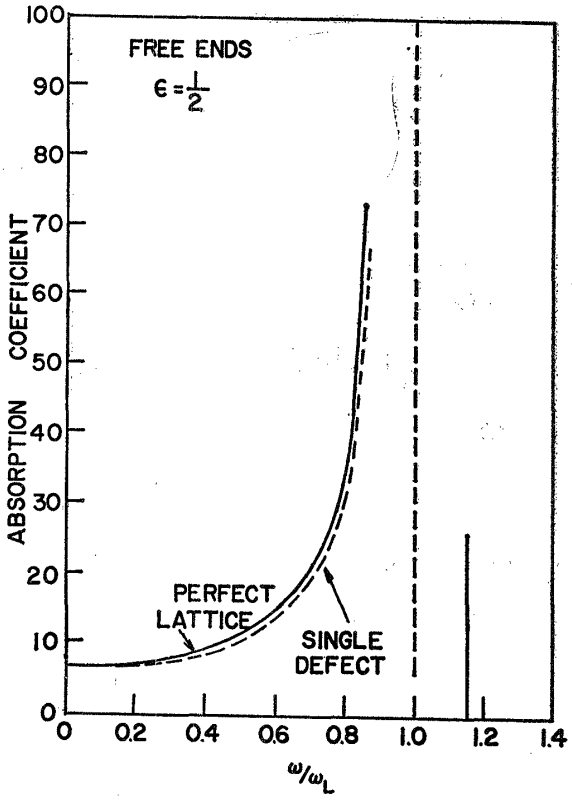

Fig. 5. The absorption in a monatomic linear chain with free ends is plotted both for the case of no impurity and for the case of a single light mass impurity.

In the case that $0<\varepsilon<1$, the eigenvalue equation (4·6) has a solution which corresponds to a mode of vibration which is localized about the defect. This solution is obtained by replacing φ by $\pi+iz$ in Eq. (4·6) :

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$$1=\varepsilon \coth \frac{z}{2}\left(\coth Nz-\frac{\cosh z}{\cos N\pi \sinh Nz}\right). \tag{4·15}$$

In the limit as $N\to\infty$ this equation reduces to the eigenvalue equation for the impurity frequency in a lattice satisfying the cyclic boundary condition, Eq. (2·30).

The expressions for the displacement components u_n associated with the localized mode become

$$\begin{aligned} u_n &= iA(-1)^n \sinh\left(n-N-\frac{1}{2}\right)z, \quad n\geq p \\ &= iB(-1)^n \sinh\left(n-\frac{1}{2}\right)z, \qquad n<p \end{aligned} \tag{4·16}$$

provided that

$$\frac{\omega^2}{\omega_L^2}=\cosh^2\frac{z}{2}. \tag{4·17}$$

In the limit as $N\to\infty$ we find that

$$B=-Ae^z. \tag{4·18}$$

The expression for the dipole moment associated with the localized mode is

$$M(z)=-i\frac{eA}{2\varepsilon}e^{(N+1)z/2}. \tag{4·19}$$

The normalization condition for the localized mode becomes (in the limit of large N)

$$\sum_n M|u_n|^2+(M'-M)|u_p^2|=-\frac{1}{8}MA^2e^{(N+1)z}\left(\frac{1-\varepsilon^2}{\varepsilon}\right)=1, \tag{4·20}$$

so that

$$A^2=-\frac{8\varepsilon}{M(1-\varepsilon^2)}e^{-(N+1)z}. \tag{4·21}$$

Combining Eqs. (4·19) and (4·21) we finally obtain for the dipole moment associated with the localized vibration mode

$$M(z)=\frac{\sqrt{2}\,e}{\sqrt{M}\sqrt{\varepsilon}\sqrt{1-\varepsilon^2}}. \tag{4·22}$$

This expression is identical with the corresponding result for a lattice obeying the cyclic boundary condition, Eq. (2·33).

§ 5. A single defect in a diatomic lattice

We consider an alternating diatomic linear chain composed of N atoms with mass M_1 and N atoms with mass M_2 interacting with nearest neighbor Hooke's law forces. Our discussion will be limited to the case in which a heavier host

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atom is replaced by a lighter isotopic impurity atom with mass M'. As stated in the introduction this case exhibits the maximum number of localized vibrational modes and thus can provide an indication of the principal effects to be expected in diatomic lattices.

The time independent equations of motion can accordingly be written as

$$\begin{aligned} &\omega^2 M_2 u_{2n} + \gamma[u_{2n+1} - 2u_{2n} + u_{2n-1}] = 0 \\ &\omega^2 M_1 u_{2n+1} + \gamma[u_{2n+2} - 2u_{2n+1} + u_{2n}] = \delta_{n,0} \varepsilon M_1 \omega^2 u_1, \end{aligned} \tag{5·1}$$

where $M_2 < M_1$, $\varepsilon M_1 = M_1 - M'$, and $0 < \varepsilon < 1$. By making the transformations

$$\begin{aligned} v_{2n} &= (M_2 \omega^2 - 2\gamma)^{1/2} u_{2n} \\ v_{2n+1} &= (M_1 \omega^2 - 2\gamma)^{1/2} u_{2n+1}, \end{aligned} \tag{5·2}$$

where positive square roots are to be taken, one can write Eqs. (5·1) in the compact form

$$(M^* \omega^2 - 2\gamma) v_n + \gamma (v_{n+1} + v_{n-1}) = \delta_{n,1} \varepsilon M_1 \omega^2 \frac{(M_2 \omega^2 - 2\gamma)^{1/2}}{(M_1 \omega^2 - 2\gamma)^{1/2}} v_1 \tag{5·3}$$

where

$$(M^* \omega^2 - 2\gamma)^{1/2} = (M_1 \omega^2 - 2\gamma)^{1/2} (M_2 \omega^2 - 2\gamma)^{1/2} \tag{5·4}$$

and the atoms have been relabeled.

The Green function solution to Eq. (5·3), assuming cyclic boundary conditions, can be written as

$$v_n = g^*(n-1) \varepsilon M_1 \omega^2 \frac{(M_2 \omega^2 - 2\gamma)^{1/2}}{(M_1 \omega^2 - 2\gamma)^{1/2}} v_1, \tag{5·5}$$

where the Green's function $g^*(n)$ is given by

$$g^*(n) = \frac{1}{2N} \sum_{s=1}^{2N} \frac{\exp(2\pi i s n/2N)}{M^* \omega^2 - 2\gamma + 2\gamma \cos(2\pi s/2N)}. \tag{5·6}$$

The eigenvalue equation, which determines the characteristic values of the frequency ω, is obtained by substituting $n=1$ in Eq. (5·5) yielding

$$1 = \varepsilon M_1 \omega^2 \frac{(M_2 \omega^2 - 2\gamma)^{1/2}}{(M_1 \omega^2 - 2\gamma)^{1/2}} g^*(0). \tag{5·7}$$

Let us consider first the localized mode with frequency above the top of the optical branch. Defining

$$f^2 = \frac{M^* \omega^2}{4\gamma}, \tag{5·8}$$

one can evaluate the Green function and obtain

$$g^*(n) = \frac{(-1)^n}{4\gamma} \frac{[f - \sqrt{f^2 - 1}]^{2|n|}}{f\sqrt{f^2 - 1}}. \tag{5·9}$$

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The characteristic frequency determined by Eqs. (5·7), (5·8) and (5·9) is specified by

$$2\omega^2=\omega_0^2+\frac{2\omega_A^2+\sqrt{(1-\varepsilon^2)^2\omega_0^4+4\varepsilon^2\omega_A^4}}{(1-\varepsilon^2)}, \tag{5·10}$$

where

$$\omega_0^2=2\gamma/M_2 \tag{5·11a}$$

$$\omega_A^2=2\gamma/M_1. \tag{5·11b}$$

The effective dipole moment $M(0)$ can be evaluated using methods similar to those employed for the monatomic lattice. The result is

$$M(0)=-\frac{e\varepsilon u_1}{(1-y^4)}\frac{\omega_0\omega}{(\omega^2-\omega_L^2)^{1/2}\omega_A}\left\{\frac{(\omega^2-\omega_0^2)^{1/2}\omega_A}{(\omega^2-\omega_A^2)^{1/2}\omega_0}[1+y^4]+2y^2\right\} \tag{5·12}$$

where

$$y=f-\sqrt{f^2-1} \tag{5·12a}$$

$$\omega_L^2=2\gamma\left(\frac{1}{M_1}+\frac{1}{M_2}\right), \tag{5·12b}$$

and the amplitude u_1 is determined by the normalizing condition

$$M_1\sum_{n\ \mathrm{odd}}u_n^2+M_2\sum_{n\ \mathrm{even}}u_n^2=1+\varepsilon M_1u_1^2. \tag{5·12c}$$

The result obtained from Eq. (5·12c) is

$$M_1u_1^2=\frac{(1-y^8)(\omega^2-\omega_0^2)}{[(\omega^2-\omega_0^2)(1+y^8)+2y^4(\omega^2-\omega_A^2)]-\varepsilon(1-y^8)(\omega^2-\omega_0^2)}. \tag{5·13}$$

The localized mode with frequency in the "forbidden" gap between acoustical and optical branches will be considered next. The Green function for this case can be written as

$$g^*(n)=\frac{(i)^{|n|-1}}{2\gamma}\frac{\omega_0\omega_A x^{|n|}}{\omega\sqrt{\omega_L^2-\omega^2}(\omega_0\omega_A)^{|n|}} \tag{5·14}$$

where

$$x=\omega(\omega_L^2-\omega^2)^{1/2}-(\omega^2-\omega_A^2)^{1/2}(\omega_0^2-\omega^2)^{1/2}. \tag{5·14a}$$

The value of the frequency in the "forbidden" gap is specified by

$$2\omega^2=\omega_0^2+\frac{2\omega_A^2-\sqrt{(1-\varepsilon^2)^2\omega_0^4+4\varepsilon^2\omega_A^4}}{(1-\varepsilon^2)}. \tag{5·15}$$

The effective dipole moment $M(g)$ may be expressed as

$$M(g)=\frac{e\varepsilon\omega u_1}{(\omega^2-\omega_A^2)^{1/2}(\omega_L^2-\omega^2)^{1/2}(\omega_0^2\omega_A^2+x^2)}\{\omega_0^2(\omega^2-\omega_A^2)^{1/2}2x$$
$$-(\omega_0^2-\omega^2)^{1/2}(\omega_0^2\omega_A^2-x^2)\}, \tag{5·16}$$

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where the amplitude u_1 is determined by the normalization condition Eq. (5·12c) and is given by

$$M_1 u_1^2 = \frac{(\omega_0^2-\omega^2)(\omega_0^4\omega_A^4-x^4)}{2\omega_0^2\omega_A^2(\omega^2-\omega_A^2)x^2+(\omega_0^2-\omega^2)(\omega_0^4\omega_A^4+x^4)-\varepsilon(\omega_0^2-\omega^2)(\omega_0^4\omega_A^4-x^4)}. \tag{5·17}$$

Turning now to the modes with frequencies lying within the acoustical branch we find that the eigenvalue equation (5·7) can be written as

$$1=\varepsilon\frac{\omega^2(\omega_0^2-\omega^2)^{1/2}}{\omega_0\omega_A(\omega_A^2-\omega^2)^{1/2}}\csc\phi\cot N\phi \tag{5·18}$$

where

$$\sin^2\frac{\phi}{2}=f^2=\frac{M^*\omega^2}{4\gamma}. \tag{5·18a}$$

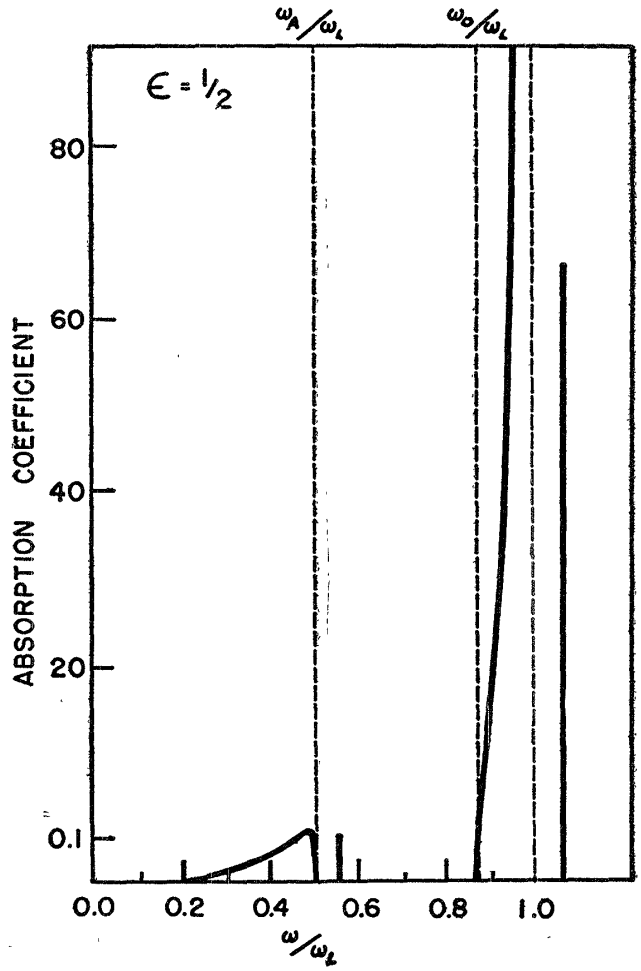

Fig. 6. Absorption in a diatomic linear chain for the case that one of the heavy masses is replaced by a lighter isotope impurity.

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In the limit of large N one can evaluate the effective dipole moment $M_a(s)$ for the sth mode in the acoustical branch in terms of the frequency ω for that mode. The result is

$$M_a(s)=\frac{\sqrt{2}\,e\mathcal{E}}{\sqrt{NM_1}}\frac{\omega^2(\omega_A^2-\omega^2)^{1/2}(\omega_0^2-\omega^2)^{1/2}}{(\omega_L^2-\omega^2)^{1/2}(\omega_L^2-2\omega^2)^{1/2}[\mathcal{E}^2\omega^2(\omega_0^2-\omega^2)+(\omega_A^2-\omega^2)(\omega_L^2-\omega^2)]^{1/2}}. \tag{5·19}$$

The treatment for the optical branch follows in very similar fashion. The expression for the effective dipole moment $M_o(s)$ for the sth mode in the optical branch is given by

$$M_o(s)=\frac{\sqrt{2}\,e\mathcal{E}}{\sqrt{NM_1}}\frac{\omega^2(\omega^2-\omega_A^2)^{1/2}(\omega^2-\omega_0^2)^{1/2}}{(\omega_L^2-\omega^2)^{1/2}(2\omega^2-\omega_L^2)^{1/2}[\mathcal{E}^2\omega^2(\omega^2-\omega_0^2)+(\omega^2-\omega_A^2)(\omega_L^2-\omega^2)]^{1/2}}. \tag{5·20}$$

In order to indicate the qualitative nature of the results for the diatomic case treated above we have made calculations for the specific case in which $M_1=3M_2$ and $\mathcal{E}=1/2$. The absorption coefficient in arbitrary units is plotted as a function of frequency in Fig. 6. One sees that the absorption in the acoustical branch and at the discrete frequency in the "forbidden" gap is quite small. The absorption coefficient increases very rapidly as one approaches the upper bound ω_L of the optical branch. The absorption coefficient at the discrete frequency above the optical branch is relatively large compared to that associated with the mode in the gap.

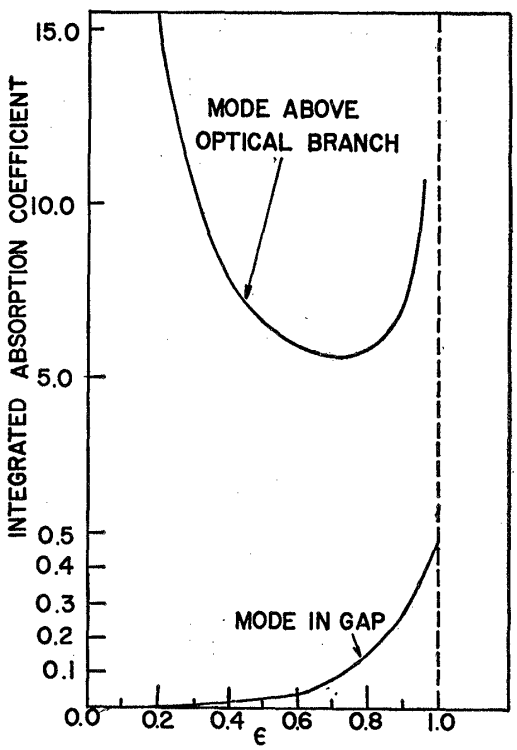

Fig. 7. The integrated absorption coefficient for the two impurity modes in a diatomic linear chain which arise when one of the heavy masses is replaced by a light isotope impurity.

The dependence on $\mathcal{E}$ of the integrated absorption for the localized modes is plotted in Fig. 7 for $M_1=3M_2$. The mode above the optical branch has large absorption for $\mathcal{E}$ near zero and near unity with a minimum at intermediate $\mathcal{E}$. The mode in the gap has continuously increasing absorption as $\mathcal{E}$ increases but the absorption is always very small.

§ 6. Impurity frequencies in three-dimensional lattices

We conclude with a brief discussion of the frequencies associated with localized

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vibration modes due to isotopic impurities in three-dimensional monatomic and diatomic simple cubic lattices having nearest neighbor Hooke's law interactions, both central and non-central.

For a monatomic lattice the eigenvalue equation is

$$1=\varepsilon M\omega^2 g(0,0,0;\omega), \tag{6·1}$$

where

$$g(0,0,0;\omega)=\frac{2+\alpha}{M\omega_L^2}\left\{\frac{1}{\pi^3}\iiint_0^\pi \frac{d\phi_1 d\phi_2 d\phi_3}{(2+\alpha)(2f^2-1)-\alpha\cos\phi_1-\cos\phi_2-\cos\phi_3}\right\}, \tag{6·2}$$

$f^2=\omega^2/\omega_L^2$, and α is the ratio γ_1/γ_2 of central to non-central force constants. The integral in curly brackets has been tabulated for a wide range of the parameters α and f.[9] If we denote it by $I(0,0,0;\alpha;f)$, Eq. (6·1) becomes

$$1=\varepsilon(2+\alpha)f^2 I(0,0,0;\alpha;f). \tag{6·3}$$

For given values of α and ε this equation must be solved numerically.

Although we know experimentally what ω_L is for the alkali-halides we must still determine the value of α in each case. A simple (though not unique) choice is provided by a calculation of the strain energy of our crystal due to a homogeneous deformation. This leads to the following identifications:[10]

$$c_{11}=\frac{\gamma_1}{a_0},\quad c_{12}=0,\quad c_{44}=\frac{\gamma_2}{2a_0}, \tag{6·4}$$

where a_0 is the lattice parameter. These expressions lead to the result

$$\alpha=\gamma_1/\gamma_2=(c_{11}/2c_{44}). \tag{6·5}$$

For the case of KCl, which is reasonably well approximated by a monatomic crystal, we obtain

$$\alpha=\frac{3.98}{2\times 0.625}=3.18. \tag{6·6}$$

If we consider a U-center in KCl which is believed to be an H^- ion replacing a halide ion, $M=36$, $M'=1$, so that $\varepsilon=35/36$. If we now solve Eq. (6·3) for this choice of parameters with the aid of the results of reference 9) we find

$$f=4.26,\quad \frac{\omega_{\rm loc}}{2\pi}=17.9\times 10^{12}\ \mathrm{sec}^{-1}. \tag{6·7}$$

The experimental result of Pick[2] in this case gives

$$f=4.52,\quad \frac{\omega_{\rm loc}}{2\pi}=19\times 10^{12}\ \mathrm{sec}^{-1}. \tag{6·8}$$

In view of the crudeness of the model, the agreement between theory and experiment is striking.

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For a diatomic lattice with masses M_1 and M_2 at alternating lattice points where $M_1 > M_2$, the M^* transformation leads to the following eigenvalue equation

$$1=\varepsilon M_1\omega^2\frac{(M_2\omega^2-2\gamma_1-4\gamma_2)^{1/2}}{(M_1\omega^2-2\gamma_1-4\gamma_2)^{1/2}}g^*(0,0,0;\omega) \tag{6·9}$$

in the case that a mass M_1 is replaced by a mass $(1-\varepsilon)M_1$. The function $g^*(0,0,0;\omega)$ is given by

$$g^*(0,0,0;\omega)$$
$$=\frac{1}{\pi^3}\iiint_0^\pi\frac{d\phi_1\,d\phi_2\,d\phi_3}{(M_1\omega^2-2\gamma_1-4\gamma_2)^{1/2}(M_2\omega^2-2\gamma_1-4\gamma_2)^{1/2}+2\gamma_1\cos\phi_1+2\gamma_2\cos\phi_2+2\gamma_2\cos\phi_3}. \tag{6·10}$$

We define the frequencies ω_1^2 and ω_2^2 by

$$\omega_1^2=\frac{2\gamma_1+4\gamma_2}{M_1},\quad \omega_2^2=\frac{2\gamma_1+4\gamma_2}{M_2}. \tag{6·11}$$

In terms of these frequencies $g^*(0,0,0;\omega)$ becomes

$$g^*(0,0,0;\omega)$$
$$=\frac{2+\alpha}{\pi^3M_2\omega_2^2}\iiint_0^\pi\frac{d\phi_1\,d\phi_2\,d\phi_3}{[(\omega^2/\omega_1^2)-1]^{1/2}[(\omega^2/\omega_2^2)-1]^{1/2}(2+\alpha)-\alpha\cos\phi_1-\cos\phi_2-\cos\phi_3}, \tag{6·12}$$

and the eigenvalue equation takes the form

$$1=\varepsilon\frac{\omega^2}{\omega_1^2}\frac{[(\omega^2/\omega_2^2)-1]^{1/2}}{[(\omega^2/\omega_1^2)-1]^{1/2}}(2+\alpha)\left\{\frac{1}{\pi^3}\iiint_0^\pi\frac{d\phi_1\,d\phi_2\,d\phi_3}{[(2+\alpha)/\mu]-\alpha\cos\phi_1-\cos\phi_2-\cos\phi_3}\right\} \tag{6·13}$$

where

$$\mu^{-1}=\left(\frac{\omega^2}{\omega_1^2}-1\right)^{1/2}\left(\frac{\omega^2}{\omega_2^2}-1\right)^{1/2} \tag{6·14}$$

We are interested in those solutions of Eq. (6·13) for which $\omega^2>\omega_L^2=\omega_1^2+\omega_2^2$. Inverting Eq. (6·14) we obtain

$$\frac{\omega^2}{\omega_L^2}=f^2=\frac{1}{2}+\frac{1}{2}\left[1+\frac{4\omega_1^2\omega_2^2}{\omega_L^4}\left(\frac{1}{\mu^2}-1\right)\right]^{1/2}. \tag{6·15}$$

In the case of a U-center in NaCl, $M_1=36$, $M_2=23$, $M'=1$, so that $\varepsilon=35/36$ as before. The value of α is still given by Eq. (6·5) and is

$$\alpha=\frac{5.73}{2\times1.33}=2.154 \tag{6·16}$$

in the present case.

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The solution to Eq. (6·13) is obtained with the aid of the material of reference 9) and is found to be

$$f=3.760$$

which should be compared with the experimental value of

$$f=3.542$$

due to Pick.

§ 7. Discussion

The calculations presented in this paper are restricted to the effects of the mass difference of an impurity atom on the infrared absorption due to lattice vibrations. The most striking result is the appearance of a discrete absorption line associated with the localized mode appearing above the maximum frequency of the optical branch when a host atom is replaced by a lighter atom. This effect disappears if the impurity atom is heavier than the host atom. Thus, if the addition of heavy atom impurities leads to experimentally observed discrete absorption lines, their explanation must lie in a change of force constants or some other mechanism rather than in the mass change. This conclusion applies as well to discrete modes which drop down from the optical branches, since the associated absorption is weak and is masked by the continuous in-band absorption.

For not too large concentrations of impurities there are as many discrete impurity modes above the optical branch as there are degrees of freedom associated with the impurity atoms. Not all of these impurity modes are strongly absorbing, however. In the particular cases studied in sections 2 and 3 only the symmetric modes were optically absorbing. For a general number of impurities the impurity modes can no longer be classified as purely symmetric or antisymmetric, but one can still use a qualitative characterization of symmetric or antisymmetric. Only the discrete modes with a large symmetric character will be expected to lead to strong absorption. The width of the optical absorption line may therefore be relatively narrow compared to the width of the impurity band itself. An extreme case would be that in which every second host atom in an initially monatomic chain is replaced by a lighter impurity atom. The impurity band then becomes a significant fraction of the optical branch, but only the largest frequency is optically absorbing. Experimentally the discrete lines associated with hydride ions in alkali halides are observed by Pick to be very narrow.

The rather good agreement between the calculated values of the impurity frequencies given in section 6 and Pick's experimental results is gratifying but may be fortuitous. Our calculations did not take into account the long range Coulomb forces between ions and the coupling between the x-, y- and z-displacement components. It may be, however, that the relation of the impurity frequency to the reststrahl frequency, which is what we actually calculate, is not sensitive to

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these details, and is given more accurately by our model than either frequency separately.

Appendix

In this appendix we establish Eqs. (2·14) and (2·15) of the text. We begin by evaluating $g(0)$ which is given by

$$g(0)=\frac{1}{2\gamma N}\sum_{s=1}^{N}\frac{1}{\cos(2\pi s/N)-\cos\phi}\qquad 0<\phi<\pi, \tag{A·1}$$

$$=\frac{1}{2\gamma N}\left\{\frac{1}{2\pi i}\int_C\frac{\pi\cot\pi z}{\cos(2\pi z/N)-\cos\phi}dz-\mathrm{Res}\left[z=\frac{N\phi}{2\pi}\right]-\mathrm{Res}\left[z=N-\frac{N\phi}{2\pi}\right]\right\} \tag{A·2}$$

where C is the counterclockwise rectangular contour with corners at $(1/2, -i\alpha)$, $(N+1/2, -i\alpha)$, $(N+1/2, i\alpha)$, and $(1/2, i\alpha)$ which is shown in Fig. A.1. It is easily seen that the contributions to $g(0)$ from BC and DA cancel each other and we are left with

$$g(0)=\frac{\cot[N\phi/2]}{2\gamma\sin\phi}+\frac{\mathrm{Im}}{2\gamma N}\int_{1/2}^{N+1/2}\frac{\cot\pi(x-i\alpha)}{\cos[(2\pi/N)(x-i\alpha)]-\cos\phi}dx \tag{A·3}$$

$$=\frac{\cot[N\phi/2]}{2\gamma\sin\phi} \tag{A·4}$$

in the limit as $\alpha\to\infty$. This is Eq. (2·15).

The recurrence relation satisfied by $g(n)$ can be written as

$$-g(n)\cos\phi+\frac{1}{2}[g(n+1)+g(n-1)]=\frac{\delta_{no}}{2\gamma} \tag{A·5}$$

For $n\neq 0$ the solution to Eq. (A·5) is given by

$$g(n)=A\cos n\phi+B\sin|n|\phi. \tag{A·6}$$

It is clear however, that $A=g(0)$, while from equations (A·5), and (2·13) we find that

$$g(1)=g(-1)=g(0)\cos\phi+\frac{1}{2\gamma}, \tag{A·7}$$

so that $B=1/2\gamma\sin\phi$. Combining these results we obtain finally that

$$g(n)=g(0)\cos n\phi+\frac{\sin|n|\phi}{2\gamma\sin\phi}, \tag{A·8}$$

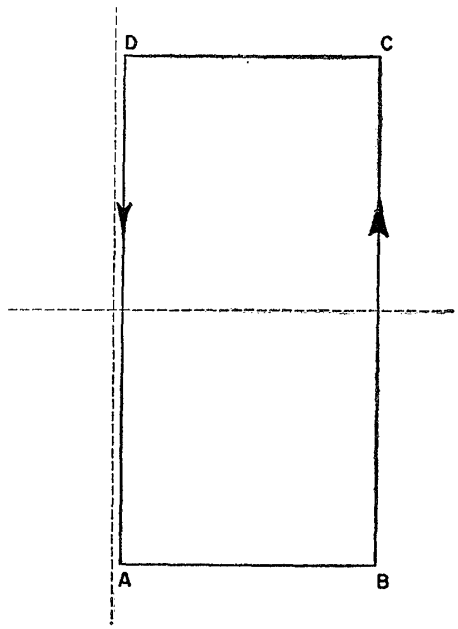

Fig. A.1. The contour for the evaluation of the integral (A·2).

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which is Eq. (2·14). It is readily established that the solution (A·8) satisfies the symmetry condition

$$g(n)=g(N-n) \tag{A·9}$$

which is implied by Eq. (2·13).

An approximate method for evaluating $g(n)$ has been suggested by Lax.[11]

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