Effect of Defects on Lattice Vibrations*

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The theory of the effect of localized defects such as impurities, holes, and interstitials on the vibrations of crystal lattices is developed. Although most of the analysis is concerned with one-dimensional chains, the general approach to defects in three-dimensional lattices is outlined through the example of a simple cubic lattice with nearest-neighbor interactions.

Many types of defects cause localized normal modes whose effect dies out rapidly with distance from the defect. Mathematical techniques, which involve the use of Green's functions, are discussed for the theory of these localized modes. The vibrational frequencies of these modes are displaced out of the band of frequencies of a perfect lattice.

The theory of interaction of two defects as a function of their distance of separation is developed for the range of very low temperatures through the calculation of the change of zero-point energy of a lattice as a result of the introduction of a defect pair. Defects attract each other in a monatomic lattice. The attraction between two mass defects in a linear chain is inversely proportional to the cube of their distance of separation.

The effect of a localized defect mode in a simple cubic lattice diminishes as with the distance r as $r^{-1}\exp(-Ar)$.

INTRODUCTION

LOCAL defects such as impurities, holes, interstitials, etc., in crystals make their existence apparent in many striking ways. The impurity levels of semiconductors are the seat of those electrons which can easily make transitions into the conduction band and hence (with the holes which behave in an analogous manner) are to a large degree the dominant influence in the electrical behavior of semiconductors. Impurities are known to change relaxation times in magnetic materials by many orders of magnitude. Transport processes such as electrical and heat conduction are frequently controlled by the scattering of electrons or phonons by defects.

An enormous literature exists which gives a semi-empirical or phenomenological theory of the effects mentioned above as well as of the diffusion of defects. A proper basis for the systematic discussion of the effect of impurities on electrons in solids has been given by Slater and Koster[1] through the use of localized Wannier[2] wave functions. The effect of defects on electrons in a linear chain has also been discussed by Saxon and Hutner.[3] There is considerable similarity between the behavior of electrons in semiconductors, spin waves in magnetic materials and lattice vibrations in crystals in general. Since lattice vibrations are the most amenable of these three phenomena to mathematical analysis, the authors have felt that a detailed investigation of the effect of lattice defects on lattice vibrations might shed some light on the general defect problem.

It is not only in solid state physics that defects are important. Any discussion of the interaction of particles with a field is really one of localized defects in the field. Since the theory of lattice vibrations is mathematically equivalent to that of a discrete quantum field, an analogy might be made between lattice defects and particles coupled to discrete quantum fields. Fortunately a natural fundamental length, the lattice spacing, is sufficient to immunize the theory of lattice vibrations from the divergences which are the curse of continuum quantum fields. It is hoped that some of the results on the discrete model may contribute to the understanding of some of the difficulties in the continuum case. Lattice theories of quantum fields have been discussed recently by Schiff[4] and Rosenstock.[5]

A local defect influences the vibrational spectrum in two ways. With the exception of a small number of frequencies which normally lie near the band edges, the possible frequencies are displaced by amounts of order $O(1/N)$ (N being the total number of lattice points). The exceptional frequencies, which might suffer a considerable displacement, are associated with localized normal modes which die out rapidly with distance from the defect. A typical such mode is that associated with a lattice vacancy. It corresponds to a pulsation (similar to that of an explosion bubble in a fluid) whose influence dies out as $r^{-1}\exp(-Ar)$ at large distances. The large class of slightly displaced modes can be discussed through perturbation theory, but the exceptional localized modes must be handled by a separate exact calculation. The theory of these modes has been briefly outlined by Lax and Smith[6] and is essentially the same as that proposed by Koster and Slater[1] for electrons in solids. Although the approach used in the present paper follows in similar lines, it was first suggested to the

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[1] G. F. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954); G. F. Koster, Phys. Rev. **95**, 1436 (1954).

[2] G. H. Wannier, Phys. Rev. **52**, 191 (1937).

[3] D. S. Saxon and R. A. Hutner, Philips Research Repts. **4**, 81 (1949).

[4] L. I. Schiff, Phys. Rev. **92**, 764 (1953).

[5] H. B. Rosenstock, Phys. Rev. **93**, 331 (1954).

[6] M. Lax, Phys. Rev. **94**, 1391 (1954).

authors by a mathematical investigation of discrete potential theory by Duffin.[7]

Every lattice defect has a "self-energy." This corresponds to the difference in bond energy between the imperfect and perfect lattice plus the differences in vibrational zero-point energy, the $\frac{1}{2}h\nu$'s associated with each frequency.

An interesting feature of defects in a monatomic lattice is their clustering tendency. The short-range preference for pairing of vacancies due to the lowering of total bond energies is well known. We shall show that a longer-range attractive force also exists between defects. If the defects are light isotopes imbedded in a matrix of heavier isotopes, this attractive force gives rise to a separation of the isotopic mixture into two phases at very low temperatures. This point has been discussed by perturbation theory by Prigogine, Bingen, and Jeener.[8]

The authors feel that this attraction between defects is a rather general property of locally perturbed fields. In this case it would give rise to the following mechanism: defects might be created by some means of excitation, as they are formed they would cluster together so that when they exist in sufficiently large numbers they might condense in a manner analogous to that in which a gas condenses.

There are three phases of the theory of defects which must be investigated. First, the statics or the energetic considerations such as their self-energies and the interactions between defects; second, the dyamics or motions of defects through the lattice, and finally the statistical mechanics or the effect of thermal excitation on defect formation and interaction. This paper is concerned with the statics. The authors hope to discuss the other two phases later. Stripp and Kirkwood[9] have analyzed the statistical mechanics of holes and impurities in lattices but this work deals only with perturbation theory and neglects the effect of the localized modes which in some situations might be extremely important.

1. DESCRIPTION OF THE MODEL

Our detailed analysis will be carried out for linear chains and simple cubic lattices with nearest neighbor interactions only. Other lattices can be handled in an analogous manner but require somewhat more cumbersome mathematics. We describe our model in this section.

(a) Lattice or Field

Let us consider a simple cubic lattice of N^3 identical particles each of mass M and coupled to its nearest neighbors through both central and noncentral forces. The forces are postulated as harmonic so that the total potential energy of the lattice is

$$\Phi=\Phi_0+\Delta\Phi,$$

where Φ_0 is the potential energy of the lattice at equilibrium, $\Phi_0=3N^3v_0$ (v_0 being the binding energy per pair of particles) and

$$\begin{aligned}\Delta\Phi=&\frac{1}{2a^2}\beta_1\sum_{l,m,n}[(x_{l,m,n}-x_{l+1,m,n})^2\\&+(y_{l,m,n}-y_{l,m+1,n})^2+(z_{l,m,n}-z_{l,m,n+1})^2]\\&+\frac{1}{2a^2}\beta_2\sum_{l,m,n}[(x_{l,m,n}-x_{l,m+1,n})^2\\&+(y_{l,m,n}-y_{l,m,n+1})^2+(z_{l,m,n}-z_{l+1,m,n})^2]\\&+\frac{1}{2a^2}\beta_3\sum_{l,m,n}[(x_{l,m,n}-x_{l,m,n+1})^2\\&+(y_{l,m,n}-y_{l+1,m,n})^2+(z_{l,m,n}-z_{l,m+1,n})^2],\end{aligned}\tag{1.1}$$

when the set of displacements $\{x_{l,m,n},y_{l,m,n},z_{l,m,n}\}$ from equilibrium positions exist at the lattice points $\{l,m,n\}$. The lattice spacing is a. We generally let $\gamma_j=\beta_j/a^2$. The constant γ_1 represents the central force constant while we usually write $\gamma_2=\gamma_3$ for the noncentral force constants. Since a simple cubic lattice with nearest neighbor central force interactions only is unstable to shear we must introduce the noncentral forces to give the system a realistic character.

We shall have occasion to discuss a discrete scalar field whose potential energy can be described as a special case of (1.1). We characterize this field by one parameter $x_{l,m,n}$ associated with each lattice point (l,m,n) and by the potential energy function (1.1) with $\beta_1=\beta_2=\beta_3=\beta$ and $y=z=0$.

We shall first give a classical mechanical discussion of our system and later analyze it quantum mechanically. It is to be recalled that in the case of harmonic operators the quantum mechanical energy levels are $E=\Sigma(n_j+\frac{1}{2})h\nu_j$, where the n_j's are integers and ν_j's the classical frequencies of the normal modes of vibration of the system. Our system of particles is of course equivalent to a triply periodic set of springs and masses. We shall sometimes refer to it as the "field."

Since the motions in the x, y, and z directions are independent of each other in our model we need only analyze the behavior of a lattice with one degree of freedom per lattice point. Newton's equations of motion for such a system are

$$\begin{aligned}M\ddot{x}_{l,m,n}=&(\beta_1/a^2)[x_{l+1,m,n}-2x_{l,m,n}+x_{l-1,m,n}]\\&+(\beta_2/a^2)[x_{l,m+1,n}-2x_{l,m,n}+x_{l,m-1,n}]\\&+(\beta_3/a^2)[x_{l,m,n+1}-2x_{l,m,n}+x_{l,m,n-1}].\end{aligned}\tag{1.2}$$

Similar equations exist for the y's and z's. The equations of motion of our model of a discrete scalar field are the special case of (1.2) with $\beta_1=\beta_2=\beta_3=\beta$.

[7] R. J. Duffin, Duke Math. J. **20**, 233 (1953).

[8] Prigogine, Bingen, and Jeener, Physica **20**, 383 (1954); **20**, 516 (1954).

[9] K. F. Stripp and J. C. Kirkwood, J. Chem. Phys. **22**, 1579 (1954).

We shall choose our system to be composed of $N\times N\times N=N^3$ particles and use periodic boundary conditions

$$x_{l,m,n}=x_{l+N,m,n}=x_{l,m+N,n}=x_{l,m,n+N}, \quad \text{etc.} \tag{1.3}$$

Then the normal modes can be expressed as

$$x_{l,m,n}=u(l,m,n)\exp-i\omega t, \tag{1.4a}$$

where

$$u(l,m,n)=\exp i(\varphi_1 l+\varphi_2 m+\varphi_3 n), \tag{1.4b}$$

and

$$\varphi_j=2\pi a_j/N; \quad a_1,a_2,a_3=1,2,\cdots,N$$

or

$$-\tfrac{1}{2}N, \cdots, \tfrac{1}{2}N. \tag{1.4c}$$

The circular frequencies of the normal modes of vibration of our "field" are

$$a^2M\omega^2=2\sum_1^3\beta_j(1-\cos\varphi_j); \tag{1.5a}$$

if $a\to 0$, $\beta\to\infty$, $M\to 0$ in such a way that $\beta/M=\alpha$ = constant and $L=Na=$ length of an edge of our lattice, we find

$$\omega^2\to 4\pi^2L^{-2}(\alpha_1a_1^2+\alpha_2a_2^2+\alpha_3a_3^2) \tag{1.5b}$$

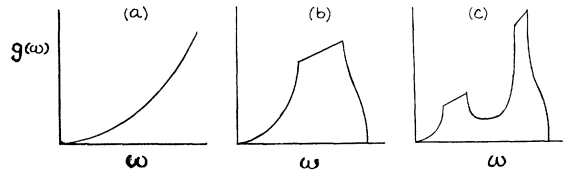


FIG. 1. The distribution function $g(\omega)$ for the number of normal frequencies between ω and $\omega+d\omega$. (a) continuum, (b) $\gamma_1=\gamma_2=\gamma_3$, (c) $\gamma_1>\gamma_2=\gamma_3$.

the square of a typical frequency of a normal mode of the continuum. It is to be recalled that our equations of motion (1.2) reduce to the wave equation (when $\alpha_1=\alpha_2=\alpha_3=\alpha$)

$$\nabla^2u=\alpha^{-2}\partial^2u/\partial t^2. \tag{1.6}$$

An important difference between the continuum and a discrete lattice is that the largest frequency in the discrete lattice is

$$\omega_L^2=4M^{-1}(\gamma_1+\gamma_2+\gamma_3), \tag{1.7}$$

while the set of normal modes of the continuum is unbounded. It is this unboundedness that leads to many of the divergences in field theories.

The distribution function $g(\omega)$ defined so that $g(\omega)d\omega$ is the number of frequencies between ω and $\omega+d\omega$ is quadratic in ω in the continuum [Fig. 1(a)] and has the same character at low frequencies in a lattice, but vanishes at high frequencies [see Figs. 1(b) and 1(c)].

The distribution function of ω^2 is found from its characteristic function

$$f(v)=E(\exp iv\omega^2)$$
$$=\frac{1}{N^3}\sum_{a_1,a_2,a_3=1}^{N}\exp\{2ivM^{-1}\sum_1^3\gamma_j(1-\cos\varphi_j)\}, \tag{1.8}$$

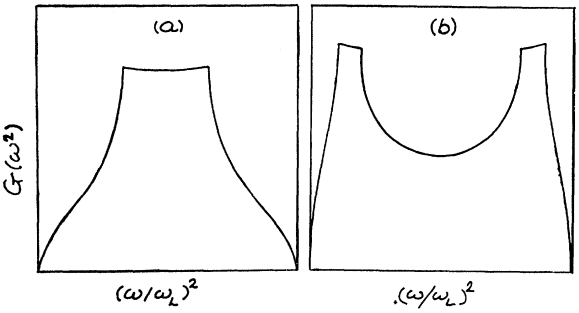


FIG. 2. The distribution function $G(\omega^2)$ for the number of frequencies between ω^2 and $\omega^2+d\omega^2$. (a) $\gamma_1=\gamma_2=\gamma_3$, (b) $\gamma_1>\gamma_2=\gamma_3$. $G(\omega^2)$ has the same shape as the energy distribution function for the tight binding model of electrons in semiconductors.

so that as $N\to\infty$

$$f(v)=\pi^{-3}\prod_{j=1}^{3}\int_0^{\pi}\exp[2ivM^{-1}\gamma_j(1-\cos\varphi_j)]d\varphi_j$$
$$=\prod_{j=1}^{3}\{\exp(2ivM^{-1}\gamma_j)\}\{J_0(2vM^{-1}\gamma_j)\}, \tag{1.9}$$

where $J_0(x)$ is the zeroth-order Bessel function.

The distribution function $G(\omega^2)$ of ω^2 is then

$$G(\omega^2)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp(-iv\omega^2)f(v)dv. \tag{1.10}$$

It is related to the frequency distribution function $g(\omega)$ by $2\omega G(\omega^2)=g(\omega)$. The integration of (1.10) has been discussed by Rosenstock and Newell[10] and one of the authors.[11] It is plotted in Fig. 2.

We shall, in the usual language of solid state physics, frequently refer to the continuum of possible frequencies of our lattice as the "frequency band." We shall see later that localized disturbances in the lattice sometimes give rise to new discrete frequencies which are displaced out of the band (Fig. 3).

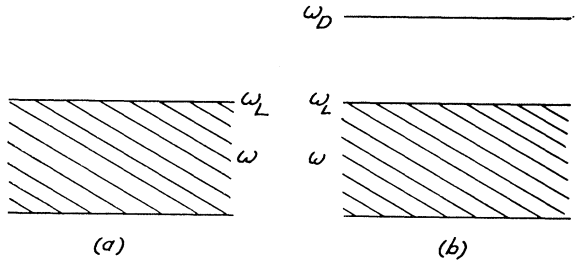


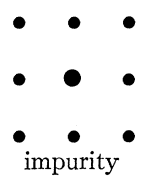
FIG. 3. Frequency spectrum of (a) perfect lattice, (b) lattice with defect. $\omega_L=$ maximum frequency, $\omega_D=$ discrete frequency for localized mode.

[10] H. B. Rosenstock and G. F. Newell, J. Chem. Phys. **21**, 1607 (1953).

[11] E. W. Montroll, Proceedings of the Third Berkeley Symposium on Mathematical Statistics and Probability (University of California Press, Berkeley, 1955).

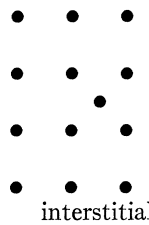
(b) Defects

We now introduce three kinds of disturbances into our perfect lattice or field. Our first local disturbance is the replacement of a normal lattice particle by an impurity atom of mass M'. Since the interaction of this mass with its neighbors differs from the normal interactions, we shall replace the normal central force constant γ_1 by a new one γ_1'. Generally we shall characterize the impurity by the two parameters



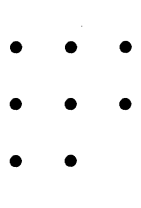
$$P=\gamma_1'/\gamma_1 \quad \text{and} \quad Q=M'/M.$$

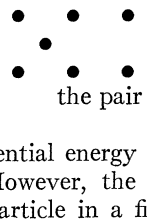
Our second type of local variation is the interstitial, a normal or impurity atom inserted between normal lattice points.



Generally the static distortion caused by the insertion of an interstitial or an impurity extends over several lattice spacings. However, since our first aim is to get a qualitative understanding of the influence of local disturbances, we shall suppose that only nearest neighbors are directly influenced (of course more distant neighbors will be affected indirectly through new localized modes of vibration or from scattering of waves by the disturbance).

Our third type of field singularity is the hole or the omission of an atom from the lattice. It is to be noted that a hole and interstitial would generally be created together (say by radiation damage in a crystal). This might be the analog of pair production in a quantum field. Indeed in a neutral ionic lattice (or in the corresponding discussion of electron levels in semiconductors) the pair is characterized by two regions of space with average charges of opposite sign.





At first glance one would be tempted to characterize a hole by $P=Q=0$, since the original lattice mass is removed and therefore no potential energy of interaction exists with its neighbors. However, the hole forms an interesting model of a particle in a field if we characterize it by $P>1$ and $Q=0$. This choice of P is seen to resemble a hole in a crystal lattice if one examines what happens when an atom is removed from a lattice site in a monatomic lattice. The repulsive force which kept its neighbors in their places is removed so that a tendency exists for them to fall into the hole. We characterize this tendency by coupling the neighbors of the hole to the hole's lattice point by a stronger than normal spring ($\gamma_1'>\gamma_1$), or by an alternative model in which the neighbors on opposite sides of the hole are coupled together with a spring constant $\gamma_1''=\frac{1}{2}\gamma_1'>\frac{1}{2}\gamma_1$.

An interesting property of a hole is that it is the source of a pulsating mode. In a quantum mechanical system there exists a nonvanishing probability (even when the motion of the lattice is its zero-point oscillations) for a neighboring particle to fall into a hole (see Fig. 4). It will be assumed that even though it may take a long time for a neighboring particle to decide to jump into a hole, the time required for the jump to occur, when once started, is small compared to the period of the pulsating mode of the lattice. Hence the motion of a hole does not change the structure of the mode (see Fig. 4) but eventually causes a readjustment of the amplitude of the vibrations of neighboring lattice points. This readjustment is propagated through the lattice with a finite velocity. We see that the motion of a hole is a random process. In a very small time the hole either remains stationary or jumps to one of its neighboring lattice positions. The existence of an external field or other holes might give a preference to jump in a particular direction.

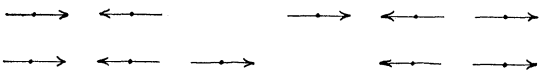


FIG. 4. The pulsating localized mode for a hole. The motion of the hole (illustrated above as a displacement of one lattice spacing to the right) does not alter the character of the mode.

Classically this random process corresponds to the random walk of a particle on a lattice. In the limit of very small lattice spacings its motion can sometimes be described through the diffusion equation. If, however, the lattice and hole are disturbed by the measurements required for the determination of transition probabilities of various jumps, a Schrödinger equation yields a more appropriate description in this limit. The effective mass of the hole would be assigned in the manner that is used to define the effective mass of an electron in a metal or semiconductor or of a bubble in a fluid. This paper is mainly concerned with one-dimensional systems. Although formulas will be given for many three-dimensional situations, the details of these more lengthy calculations will be reserved for a subsequent paper.

2. GENERAL EQUATIONS FOR A ONE-DIMENSIONAL LATTICE

The equations of motion of a one-dimensional ring of N atoms are

$$M\ddot{x}_j-\gamma(x_{j+1}-2x_j+x_{j-1})=D_jx_j, \qquad j=-\tfrac{1}{2}N+1, \cdots, \tfrac{1}{2}N, \quad (2.1a)$$

$$x_{N+j}=x_j. \quad (2.1b)$$

Here x_j represents the displacement of the jth atom from its equilibrium position and D_j is a difference differential operator which characterizes the lattice defects.

In the perfect lattice ($D_j \equiv 0$) of lattice spacing a, the displacements can be expressed as a linear combination of the normal modes

$$x_j = A_k a \exp i(t\omega_k + j\varphi_k); \quad \varphi_k = 2\pi k/N \tag{2.2a}$$

(and those with exponentials of $-t\omega_k$). Here

$$\omega_k = 2(\gamma/M)^{\frac{1}{2}} \sin\tfrac{1}{2}\varphi_k = \omega_L \sin\tfrac{1}{2}\varphi_k, \tag{2.2b}$$

where ω_L is the largest frequency,

$$M\omega_L^2 = 4\gamma. \tag{2.2c}$$

The dimensionless constants $\{A_k\}$ are to be chosen to satisfy initial conditions in the lattice.

The quantum mechanical zero-point energy of our perfect lattice is

$$E_0 = \tfrac{1}{2}\hbar\omega_L \sum_{k=1}^{N} \sin(\pi k/N) \simeq \hbar\omega_L N/\pi, \tag{2.3}$$

so that the zero-point per lattice point is $\epsilon_0 = \hbar\omega_L/\pi$.

When lattice defects exist the normal modes divide into two classes; those whose frequencies suffer slight variations in the band, and those whose frequencies are displaced out of the band. This latter group corresponds to modes localized around the defects and must be analyzed separately. The former group can be discussed by perturbation theory. The detailed manner in which this division into classes occurs is presented in Appendix I.

When perturbation theory is not appropriate we assume that

$$x_j = aAu(j) \exp -i\omega t, \tag{2.4}$$

where $u(j)$ is a set of dimensionless numbers which in an infinite lattice are defined by

$$\begin{aligned} Lu(j) &= M\omega^2 u(j) + \gamma[u(j+1) - 2u(j) + u(j-1)] \\ &= \sum_k w^{(k)}(k+j)u(k+j) \qquad (2.5a) \\ & j = 0, \pm 1, \pm 2, \cdots, \end{aligned}$$

and which are localized around defects so that

$$u(j) \to 0 \quad \text{as} \quad j \to \pm\infty. \tag{2.5b}$$

The operator L is defined so that $Lu(j)$ gives the middle quantity in (2.5a). It has the differential representation $L = M\omega^2 - 2\gamma(1 - \cosh D)$; $D = d/dj$. The $w^{(k)}(j+k)$'s characterize the lattice defects and vanish as $j \to \pm\infty$.

The general solution of (2.5a) can be obtained in terms of the Green's function $g(j)$ which is defined by

$$Lg(j) = \begin{cases} \gamma & \text{if } j = 0 \\ 0 & \text{otherwise.} \end{cases} \tag{2.6}$$

It is easy to see that the solution of (2.6) is

$$u(j) = \gamma^{-1} \sum_k \sum_l g(j+k-l) w^{(k)}(l) u(l) \tag{2.7a}$$

for, if we apply the L operator to $u(j)$ we find

$$\begin{aligned} Lu(j) &= \gamma^{-1} \sum_k \sum_l w^{(k)}(l) u(l) Dg(j+k-l) \\ &= \sum_{k,l} w^{(k)}(l) u(l) \delta(j+k-l) = \sum_k w^{(k)}(j+k) u(j+k). \end{aligned}$$

If the disturbance has an influence on lattice points $l_1, l_2, \cdots, l_s$ then the new frequencies and normal modes are found by successively setting j (in 2.7) equal to $l_1, l_2, \cdots, l_s$ and finding the values of ω for which this set of homogeneous equations has solutions. It is to be noted that the Green's function $g(j)$ depends on ω. When the solutions of these equations have been found, we see that

$$u(j) = \gamma^{-1} \sum_{\beta=1}^{s} \sum_k g(j+k-l_\beta) w^{(k)}(l_\beta) u(l_\beta). \tag{2.7b}$$

The Green's function which satisfies (2.6) is

$$\begin{aligned} g(j) &= (\gamma/\pi) \int_0^\pi \frac{\cos\varphi j d\varphi}{2\gamma(\cos\varphi - 1) + M\omega^2} \\ &= \frac{1}{2\pi} \int_0^\pi \frac{\cos j\varphi d\varphi}{\cos\varphi + \cosh z}, \end{aligned} \tag{2.8a}$$

$$= \frac{\exp\{-|j|(z+i\pi)\}}{2\sinh z} = \frac{(-1)^j \exp(-|j|z)}{2\sinh z}, \tag{2.8b}$$

where, defining f as $f = \omega/\omega_L$,

$$\cosh\tfrac{1}{2}z = \omega/\omega_L = f > 1. \tag{2.9}$$

Note that (2.5b) implies

$$g(j) \to 0 \text{ as } j \to \infty \text{ and therefore that } z > 1. \tag{2.10a}$$

Also, since $z \to \infty$ as $f \to \infty$,

$$g(j) \to 0 \text{ as } f \to \infty \text{ for fixed } j. \tag{2.10b}$$

This means that the higher the frequency of a localized mode, the more rapidly it decays spacewise. Note also

$$g(j) = g(-j). \tag{2.10c}$$

Similar formulas can be derived for the discussion of the propagation of a plane wave through our lattice. Let us assume that in the absence of local disturbances a plane wave

$$x_j = aA \exp i(j\varphi_0 - \omega t), \tag{2.11a}$$

with

$$M\omega^2 = 2\gamma(1 - \cos\varphi_0) \quad \text{or} \quad \omega = 2(\gamma/M)^{\frac{1}{2}} \sin\tfrac{1}{2}\varphi_0 \tag{2.11b}$$

is propagated through the lattice. Here Aa represents a length which is a fraction A of a lattice spacing. If the "scattering" of the plane wave by the disturbance is elastic, the complete displacement of the jth lattice

particle is

$$x_j = Aae^{-i\omega t}[u(j)+\exp ij\varphi_0], \tag{2.12}$$

where $u(j)$ is the solution of the equations

$$Lu(j) = M\omega^2 u(j)+\gamma[u(j+1)-2u(j)+u(j-1)]$$
$$= \sum_k w^{(k)}(k+j)[u(k+j)+\exp i(k+j)\varphi_0], \tag{2.13}$$

the disturbance again being introduced through the set of numbers $\{w^{(k)}(k+j)\}$. The solution of this set of equations is obtained as before, through the use of the Green's function $g(j)$ which satisfies (2.6). In this case the denominator of (2.8a) has a pole (since now $0<\omega<\omega_L$). Hence we must use the Cauchy principal value of (2.8a) to find

$$g(j) = (\gamma/\pi)\oint_0^\pi \frac{\cos\varphi j d\varphi}{2\gamma(\cos\varphi-1)+M\omega^2}$$
$$= \frac{1}{2\pi}\oint_0^\pi \frac{\cos\varphi j d\varphi}{\cos\varphi-\cos\varphi_0} = -\frac{1}{2}\frac{\sin(|j|\varphi_0)}{\sin\varphi_0}. \tag{2.14}$$

The solution of (2.13) is easily seen to be

$$u(j) = \gamma^{-1}\sum_{k,l} g(j+k-l)w^{(k)}(l)[u(l)+\exp il\varphi_0]. \tag{2.15}$$

Since the postulated disturbance is chosen to be localized, $w^{(k)}(l)$ vanishes for only a small number of values of l, and the displacements in the summand of (2.15) range over only a small set of l's. If these be l_1, l_2, $\cdots$, l_s then we must determine $u(l_1)$, $\cdots$, $u(l_s)$ by succesively letting j be l_1, $\cdots$, l_s and solving the resulting s inhomogeneous equations for $u(l_1)$, $\cdots$, $u(l_s)$. Then the final solution of (2.15) is

$$u(j) = \gamma^{-1}\sum_k\sum_\beta g(j+k-l_\beta)w^{(k)}(l_\beta)[u(l_\beta)+\exp i\varphi_0 l_\beta]. \tag{2.16}$$

If we let u be a vector with components $u(l_\beta)$, $\beta=1, \cdots, s$ we see that the s equations derived from (2.16) for $u(l_1)$, $\cdots$, $u(l_s)$ can be written in the matrix form

$$u = Gu+Gv, \tag{2.17}$$

where v is a known vector and G a known matrix. Then, if ψ_μ and ζ_μ are the characteristic vectors of G defined by

$$G\psi_\mu = \lambda_\mu\psi_\mu \quad \text{and} \quad \zeta_\mu G = \lambda_\mu\zeta_\mu \tag{2.18a}$$

$$\zeta_\mu\cdot\psi_\nu = \delta_{\mu\nu}, \tag{2.18b}$$

where $\{\lambda_\mu\}$ is the set of eigenvalues of G, we can expand the known vector v as

$$v = \sum v_\mu\psi_\mu; \quad v_\mu = \zeta_\mu\cdot v. \tag{2.19}$$

Then it is easily seen that

$$u = \sum_\mu[\lambda_\mu v_\mu/(1-\lambda_\mu)]\psi_\mu. \tag{2.20}$$

It is to be noted that the characteristic values and vectors of G can also be used to find the frequencies of localized modes. Equation (2.7b) is equivalent to

$$u = Gu,$$

when $j=l_1, l_2, \cdots, l_s$. Hence if we express u as $u=\sum u_\mu\psi_\mu$ the condition for the existence of solutions of $u=Gu$ is

$$\sum u_\mu(1-\lambda_\mu)\psi_\mu = 0 \quad \text{or} \quad u_\mu(1-\lambda_\mu)=0 \text{ for all } \mu. \tag{2.21}$$

We shall now apply the various formulas derived in this section to the investigation of the effect of an isolated defect in a one-dimensional lattice.

3. ISOLATED POINT DEFECT

This section is concerned with the theory of localized modes associated with isolated defects. The amplitude of lattice displacements due to these modes diminishes exponentially with distance from the defect. The types of defects analyzed are

(a) The variation of the mass of a single particle and of the force constants associated with that particle and its nearest neighbors. If the force constants are not changed this corresponds to the introduction of an isotope into the lattice.

(b) The interstitial.

(c) The changing of a single force constant.

The topology of a linear chain is such that the localized modes of an interstitial can be deduced from those of a normal impurity, and that of a hole can be deduced from the results of (c).

In general the localized modes associated with impurities are either symmetrical or antisymmetrical about the position of the impurity (particles to the left being either in or 180° out of phase with those to the right). As the mass of the impurity is reduced the frequency of the symmetric mode increases and its range of influence on its neighbors decreases; in the limit of zero mass the effect of this mode is no longer propagated through the lattice. The only mode associated with a hole is the antisymmetric one; this mode exists independently of the mass of the impurity provided the new spring constant is sufficiently large (in fact if $\gamma'/\gamma = P > 2$). The impurity frequencies are plotted in Fig. 7.

A brief discussion of the scattering by an isotope is given at the end of the section.

Let us insert an impurity atom of mass M' in the lattice point "0" in a chain of $2N+1$ atoms, and let γ' be the force constant of the "spring" which connects this atom to atoms "1" and "−1." Then Eqs. (2.5) become

$$Lu(j) = 0 \text{ except when } j=0, \pm 1, \tag{3.1a}$$

$$Lu(0) = (M-M')\omega^2 u(0) + (\gamma-\gamma')[u(1)-2u(0)+u(-1)], \tag{3.1b}$$

$$Lu(-1) = (\gamma'-\gamma)[u(-1)-u(0)], \tag{3.1c}$$

$$Lu(1) = (\gamma'-\gamma)[u(1)-u(0)], \tag{3.1d}$$

and the w's of (2.5) are

$$w^{(k)}(k+j)=0, \quad \text{for all } k \text{ and } j \text{ except} \tag{3.2a}$$

$$w^{(0)}(0)=(M-M')\omega^2-2(\gamma-\gamma'); \qquad w^{(\pm1)}(\pm1)=\gamma-\gamma', \tag{3.2b}$$

$$w^{(1)}(0)=w^{(-1)}(0)=\gamma-\gamma'; \quad w^{(0)}(\pm1)=\gamma'-\gamma. \tag{3.2c}$$

The solution of Eqs. (2.5) from which localized normal modes are to be determined is

$$\begin{aligned} u(j)=\gamma^{-1}u(0)\{&g(j)[(M-M')\omega^2-2(\gamma-\gamma')] \\ &+(\gamma-\gamma')[g(j+1)+g(j-1)]\} \\ &+u(1)(1-P)[g(j)-g(j-1)] \\ &+u(-1)(1-P)[g(j)-g(j+1)], \end{aligned} \tag{3.3}$$

where we set

$$P=\gamma'/\gamma \quad \text{and} \quad Q=M'/M, \quad f=\omega/\omega_L. \tag{3.4}$$

Since the coefficient of $u(0)$ will appear in many places we employ the definition of $g(j)$ [Eq. (2.6)] to derive it in a more compact form:

$$\begin{aligned} &\gamma^{-1}\{g(j)[(M-M')\omega^2-2(\gamma-\gamma')] \\ &\qquad +(\gamma-\gamma')[g(j+1)+g(j-1)]\} \\ &\qquad =\begin{cases} 4f^2g(j)(P-Q) & \text{if } j\neq0 \\ 4f^2g(0)(P-Q)+(1-P) & \text{if } j=0. \end{cases} \end{aligned} \tag{3.5}$$

The matrix G defined in (2.17) is

$$G=\begin{bmatrix} (1-P)[g(1)-g(0)] & 4f^2g(1)(P-Q) & (1-P)[g(1)-g(2)] \\ (1-P)[g(0)-g(1)] & 4f^2g(0)(P-Q)+(1-P) & (1-P)[g(0)-g(1)] \\ (1-P)[g(1)-g(2)] & 4f^2g(1)(P-Q) & (1-P)[g(1)-g(0)] \end{bmatrix}. \tag{3.6}$$

One of the characteristic vectors of G is

$$\psi_1=\{1, 0, -1\} \text{ with } \lambda_1=(1-P)[g(2)-g(0)]. \tag{3.7a}$$

The adjoint (left-hand characteristic vector of G) is

$$\zeta_1=\tfrac{1}{2}(1, 0, -1), \text{ so that } \zeta_1\cdot\psi_1=1. \tag{3.7b}$$

This is a pulsating mode

$$\leftarrow \cdot \rightarrow. \tag{i}$$

It is the one-dimensional analog of a periodically expanding and contracting spherical bubble.

The other solutions are easily found when $P=1$ (the case of an impurity such as an isotope which does not distort the lattice, $\gamma'=\gamma$). Then

$$\psi_2=\{1, g(0)/g(1), 1\}; \quad \lambda_2=4f^2(1-Q)g(0), \tag{3.8}$$

and

$$\zeta_2=(0, g(1)/g(0), 0). \tag{3.9}$$

Finally

$$\psi_3=\{1,0,1\}, \quad \lambda_3=0, \tag{3.10}$$

$$\zeta_3=\tfrac{1}{2}(1, 2g(1)/g(0), 1). \tag{3.11}$$

The modes in this case are

$$\rightarrow\leftarrow\rightarrow, \tag{ii}$$

$$\rightarrow \cdot \rightarrow. \tag{iii}$$

In the general case the roots λ_2 and λ_3 satisfy the characteristic equation

$$\begin{aligned} \lambda^2-\lambda((1-P)\{&[g(1)-g(2)]+3[g(1)-g(0)]\} \\ &+(1-Q)\{1-2[g(1)-g(0)]\}) \\ &+4f^2g(1)(1-P)(1-Q)=0. \end{aligned} \tag{3.12}$$

The characteristic vectors are of the form

$$\psi=\{a,b,a\}, \tag{3.13a}$$

with an a/b ratio

$$\frac{a}{b}=\frac{\lambda+P-1-4f^2g(0)(P-Q)}{2(1-P)[g(0)-g(1)]}. \tag{3.13b}$$

The left characteristic vectors are of the form

$$\zeta=(2ac+bd)^{-1}(c,d,c), \tag{3.14a}$$

with

$$\frac{c}{d}=\frac{\lambda+P-1-4f^2g(0)(P-Q)}{8f^2g(1)(P-Q)}. \tag{3.14b}$$

Since there are two roots of our characteristic equation these are the vectors of the form (3.13) and (3.14).

The frequencies associated with our isolated defect modes are determined by referring back to (2.21). In order that

$$u=\{u(-1), u(0), u(1)\} \tag{3.15a}$$

be expressible as

$$u=\sum u_\mu\psi_\mu, \tag{3.15b}$$

the condition $(1-\lambda_\mu)u_\mu=0$ must be satisfied for all μ. Hence if $u\not\equiv0$ then $\lambda_\mu=1$. The frequency ω associated with the symmetrical pulsating mode (i) [Eq. (3.7a)] is then determined by

$$(1-P)[g(2)-g(0)]=1. \tag{3.16}$$

When $\omega/\omega_L>1$, $g(j)$ is given by (2.8b). Therefore we have

$$\tfrac{1}{2}(1-P)(e^{-2z}-1)/\sinh z=1 \quad \text{with } z>1 \tag{3.17}$$

so that $\exp(-z)=1/(P-1)$. This quantity is <1 as is required only when $P=\gamma'/\gamma>1$. Then

$$(\omega/\omega_L)^2=\cosh^2\tfrac{1}{2}z=\frac{1}{4}\frac{P^2}{(P-1)} \quad \text{when } P>2; \tag{3.18}$$

as $P\rightarrow2$ this mode returns to the band.

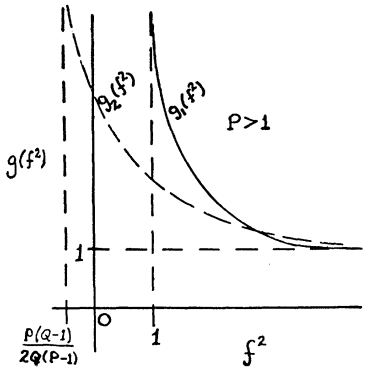


FIG. 5. The intersection of $g_1(f^2)$ and $g_2(f^2)$ represents the solution of Eq. (3.22). $P>1$.

The displacement of the jth lattice point of a system oscillating in this mode is [see Eq. (2.76)]

$$u(j)=(1-P)u(1)[1/(1-P)]^j, \quad j\geqslant 1 \tag{3.19a}$$

$$u(j)=-u(-j) \quad \text{for } j<0. \tag{3.19b}$$

Note that large values of P correspond to high frequencies and a rapid drop in $|u(j)|$ as $|j|$ increases. Also, the frequency is independent of the mass of the defect particle.

The symmetric mode (ii) $[u(j)=u(-j)]$ has an easily determined frequency when $P=1$ (the isotope case). Then (3.8) implies

$$4(\omega/\omega_L)^2=1/g(0)(1-Q),$$

or

$$(\omega/\omega_L)^2=1/Q(2-Q) \quad \text{with } 0<Q<1. \tag{3.20}$$

This mode goes back into the band as $Q\to 1$. It has the property

$$u(j)=u(-j)=[Q/(Q-2)]^{|j|}u(0) \quad \text{when } 0<Q<1. \tag{3.21}$$

It is interesting to note that the frequency (3.20) is the same as that of the pulsating mode of a hole if one replaces P by $2/Q$.

The frequency of the symmetric mode (ii) is obtained as a general function of P and Q by setting $\lambda=1$ in Eq. (3.12). If one uses (2.8b), (2.9), and the equivalent of (2.9), $\sinh\frac{1}{2}z=(f^2-1)^{\frac{1}{2}}$ with $f=\omega/\omega_L$ some algebraic manipulation yields the following equation for the frequency of our required symmetrical mode:

$$\left(\frac{f^2}{f^2-1}\right)^{\frac{1}{2}}=1+\frac{QP}{P(1-Q)+2Q(P-1)f^2}, \tag{3.22}$$

while the factor (b/a) in (3.13) becomes

$$a/b=-Qf(f-[f^2-1]^{\frac{1}{2}}). \tag{3.23}$$

An asymptotic expression for the frequency $f=\omega/\omega_L$ can easily be obtained in the limit of very small mass of the impurity $Q=\epsilon\simeq 0$. Here we assume $f^2=a/Q$ and find a by noting that

$$[f^2/(f^2-1)]^{\frac{1}{2}}\simeq 1+Q/2a+O(Q^2), \tag{3.24}$$

so that (3.22) becomes

$$Q/2a=O(Q^2)=QP/[P+2a(P-1)]+O(Q^2),$$

or $a=\frac{1}{2}P$ and as $Q\to 0$

$$f^2\sim\tfrac{1}{2}P/Q+O(Q). \tag{3.25}$$

Hence as the relative mass $Q=M'/M$ of an impurity vanishes, the frequency of the local mode becomes very large while the effective range vanishes. In the limit $a=0$ the neighboring lattice points do not feel the effect of this mode and the particle of mass M' disappears leaving a hole. One degree of freedom of our chain then disappears. Then the only localized mode associated with a hole is the antisymmetric or pulsating mode (i). It can be shown that a/b in Eq. (3.23) satisfies $-1<a/b<0$ when $f>1$ and $1>Q>0$.

Our frequency ratio f is displaced out of the band only when certain relations exist between P and Q. One way of solving (3.22) is to plot both the left and right hand sides as functions of f^2 and to find their point of intersection (see Fig. 5). We shall denote $[f^2/(f^2-1)]^{\frac{1}{2}}$ by $g_1(f^2)$ and the right hand side by $g_2(f^2)$. Two cases are to be examined separately, namely $P>1$ and $0<P<1$ ($P=1$ having already been disposed of). It will generally be assumed that $Q\geqslant 0$. When $P>1$ the right-hand side of (3.22) approaches $1+P[2f^2(P-1)]^{-1}>1+\frac{1}{2}f^{-2}$. Hence, the function $g_2(f^2)$ eventually lies above $g_1(f^2)$ as $f^2\to\infty$. Since $g_2(f^2)$ forms a hyperbola with one asymptote at $f^2=P(Q-1)/2Q(P-1)$ and the other at $f^2=1$, the condition for the interaction of $g_1(f^2)$ and $g_2(f^2)$ to exist (as it must if our required frequency is to rise out of the band) is that

$$P(Q-1)/2Q(P-1)<1 \quad \text{or} \quad P\geqslant Q(2-P).$$

Otherwise the asymptote of $g_2(f^2)$ lies to the right of that of $g_1(f^2)$ and no intersection or proper value of (3.22) exists.

When $P<1$ the hyperbola which represents $g_2(f^2)$ is twisted by 90° about the intersection of the asymptotes (see Fig. 6). Here an intersection of g_1 and g_2 exists as long as

$$(Q-1)P/2(P-1)Q>1 \quad \text{or} \quad P>Q(2-P)$$

as in the foregoing. It is to be recalled from (3.20) that a solution exists when $P=1$ if $0<Q<1$. Hence, our

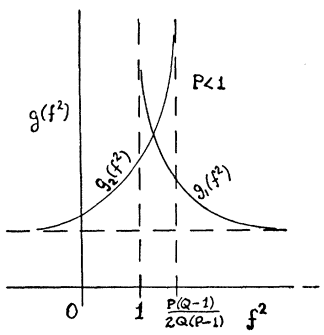


FIG. 6. The intersection of $g_1(f^2)$ and $g_2(f^2)$ represents the solution of Eq. (3.22). $P<1$.

result can be summarized by stating that a normal mode of type (ii) exists with a frequency above the band when all the following conditions are satisfied

$$P>0, \quad P>Q(2-P), \quad \text{and} \quad Q\geqslant 0 \tag{3.26}$$

with the frequency going to infinity as $Q\to 0$.

Equation (3.22) can be squared and rearranged to yield the following quadratic equations for the squares of the normal mode frequencies

$$4Q^2(P-1)f^4+PQf^2(4-PQ-2P)-P^2=0. \tag{3.27}$$

The reader is to be warned that spurious roots generally exist. The only root of significance here has the property $(\omega/\omega_L)^2\geqslant 1$. A root can always be checked for appropriateness by substituting the corresponding values of f^2 back into (3.22). The impurity frequencies are plotted in Fig. 7.

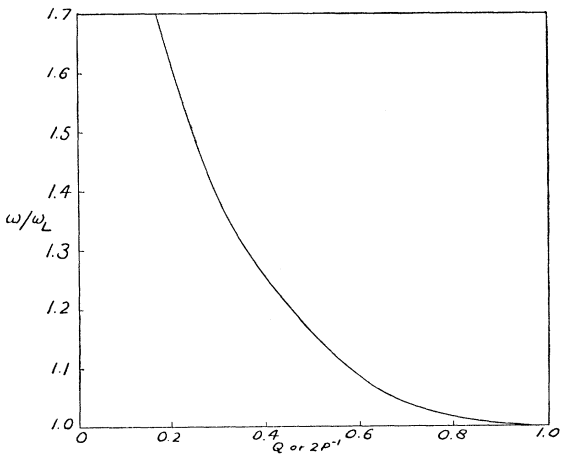


FIG. 7. Variation of impurity frequency ω with impurity parameter ($Q=M'/M$ for an isotope, $P=\gamma'/\gamma$ for a hole). ω_L = maximum frequency for the perfect lattice.

Once the frequencies of modes of type (ii) are known, all displacements can be discussed in terms of $u(0)$ through the equation

$$u(j)=Qu(0)(1+e^z)\exp-|j|(z+i\pi); \qquad \omega/\omega_L=\cosh\tfrac{1}{2}z. \tag{3.28}$$

As $(\omega/\omega_L)\to\infty$, $z\to\infty$ and $u(j)\to 0$ so that high frequencies imply rapid spacewise decay as was mentioned earlier.

The characteristic equation (3.12) may have two roots with $\lambda=1$ when special relations exist between P and Q. However, this is not the case under two conditions of greatest interest; those with either $P=1$ (the "isotope" case) or $Q=0$ (the case of the "hole").

A discussion of the interstitial proceeds along the same line that was followed above for holes and impurities. Since an interstitial does not change the topology of a linear chain one expects the results to be equivalent to those derived in the foregoing (as can indeed be proven to be the case). Since an interstitial in a three dimensional simple cubic lattice gives a local body centered structure, this equivalence disappears in a real lattice.

We shall now give a brief analysis of the interstitial to show how it can be fitted into the mathematical formalism discussed in Sec. 2, even though no unexpected results are obtained.

Consider a linear chain of $2N$ atoms and suppose an atom of mass M'' is inserted at an interstitial site "$\frac{1}{2}$" between the two sites "0" and "1." If γ'' is the force constant of the spring connecting the interstitial to its neighbors, then the fundamental equations (2.5) become

$$Lu(j)=0 \quad \text{except when } j=0,1 \tag{3.29a}$$
$$Lu(j)=(\gamma''-\gamma)u(0)-\gamma''u(\tfrac{1}{2})+\gamma u(1) \quad \text{if } j=0, \tag{3.29b}$$
$$Lu(j)=(\gamma''-\gamma)u(1)-\gamma''u(\tfrac{1}{2})+\gamma u(0) \quad \text{if } j=1, \tag{3.29c}$$

with the additional equation

$$\gamma u(\tfrac{1}{2})=-\gamma''[u(1)-2u(\tfrac{1}{2})+u(0)]+(\gamma-M''\omega^2)u(\tfrac{1}{2}). \tag{3.29d}$$

The form of this last equation is somewhat arbitrary; the present choice is consistent with the definition (2.6) of the Green's function. The w functions are all zero except that, with an obvious extension of the notation

$$w^{(0)}(0)=w^{(0)}(1)=\gamma''-\gamma, \tag{3.30a}$$
$$w^{(1)}(1)=w^{(-1)}(0)=\gamma, \tag{3.30b}$$
$$w^{(\frac{1}{2})}(\tfrac{1}{2})=w^{(\frac{1}{2})}(1)=w^{(-\frac{1}{2})}(\tfrac{1}{2})=w^{(-\frac{1}{2})}(0)=-\gamma'', \tag{3.30c}$$
$$w^{(0)}(\tfrac{1}{2})=2\gamma''+(\gamma-M''\omega^2). \tag{3.30d}$$

The determination of the normal modes and frequencies depends on the solution of the eigenvalue problem for the matrix G, given in the present case by

$$G=\begin{bmatrix}(P_I-1)g(0)+g(1) & -P_I[g(0)+g(1)] & g(0)+(P_I-1)g(1)\\ \tfrac{1}{2}P_I & 1-P_I+2Q_If^2 & \tfrac{1}{2}P_I\\ (P_I-1)g(1)+g(0) & -P_I[g(0)+g(1)] & g(1)+(P_I-1)g(0)\end{bmatrix}, \tag{3.31a}$$

where

$$P_I=\gamma''/\gamma \quad \text{and} \quad Q_I=M''/M. \tag{3.31b}$$

Although this matrix seems quite different from that given by (3.6) for the impurity problem, it leads to the same normal modes and frequencies. For example, one characteristic vector of G is

$$\psi_1=\{1,0,-1\} \text{ with } \lambda_1=(P_I-2)[g(0)-g(1)]. \tag{3.32}$$

The corresponding normal frequency ω is obtained from

$$(P_I-2)[g(0)-g(1)]=1, \tag{3.33a}$$

which is only an alternative form of (3.16) leading to

the same result

$$(\omega/\omega_L)^2=\tfrac{1}{4}[P_I^2/(P_I-1)]. \tag{3.33b}$$

A detailed analysis of the other modes for the interstitial confirms that they also are identical with those for the impurity. For the one-dimensional lattice, therefore, the effects of the impurity and the interstitial are the same; this might well have been inferred from their obvious "topological" similarity and would not be expected for lattices of higher dimensions.

The last type of isolated defect to be examined is the single anomalous force constant. We let the force constant associated with the interaction between the lattices points 0 and 1 be γ'' and the rest be γ as usual and define

$$P'=\gamma''/\gamma. \tag{3.34}$$

The required equations of motion are

$$Lu(j)=0 \quad \text{except when } j=0,\ 1, \tag{3.35a}$$

$$Lu(j)=(\gamma-\gamma'')[u(1)-u(0)] \quad \text{for } j=0, \tag{3.35b}$$

$$Lu(j)=(\gamma-\gamma'')[u(0)-u(1)] \quad \text{for } j=1. \tag{3.35c}$$

Hence,

$$w^{(k)}(k+j)=0 \quad \text{for all } k \text{ and } j \text{ except}$$
$$w^{(1)}(1)=w^{(-1)}(0)=(\gamma-\gamma'')=-w^{(0)}(0)=-w^{(0)}(1). \tag{3.36}$$

The G matrix is

$$G=(1-P')[g(1)-g(0)]\begin{pmatrix}1 & -1\\ -1 & 1\end{pmatrix}. \tag{3.37}$$

The characteristic values of G are

$$\lambda_1=0, \quad \lambda_2=2(1-P')[g(1)-g(0)], \tag{3.38}$$

with characteristic vectors

$$\zeta_1=\tfrac{1}{2}(1,\ 1), \qquad \psi_1=\{1,\ 1\}, \tag{3.39a}$$

$$\zeta_2=\tfrac{1}{2}(1,\ -1), \quad \psi_2=\{1,\ -1\}. \tag{3.39b}$$

The antisymmetrical vector ψ_2 yields a frequency out of the band, for if we let $\lambda_2=1$ and define $g(j)$ by (2.8b) we have

$$f^2=(\omega/\omega_L)^2=(P')^2/(2P'-1), \tag{3.40}$$

which is exactly the same as the frequency of the pulsating mode of a hole [Eq. (3.18)] if we identify P' with $\frac{1}{2}P$. The decay factor $\exp-z$ is

$$\exp-z=1/(2P'-1). \tag{3.41}$$

The theory of scattering of plane waves which is summarized in Eqs. (2.16)–(2.00) can be applied to the problem of scattering by an isolated defect. The simplest case is that of the isotope, $P=1$. Equation (2.16) reduces to

$$u(j)=\gamma^{-1}g(j)\omega^2(M-M')[u(0)+1], \tag{3.42}$$

where $g(j)$ is (see 2.14)

$$g(j)=\tfrac{1}{2}(\sin|j|\varphi_0)/\sin\varphi_0, \tag{3.43}$$

with

$$\omega/\omega_L=f=\sin\tfrac{1}{2}\varphi_0, \tag{3.44}$$

and $u(0)$ is found by setting $j=1$. Since $g(0)=0$, $u(0)=0$ and

$$u(j)=2f^2(1-Q)\sin(|j|\varphi_0)/\sin\varphi_0. \tag{3.45}$$

The total displacement of the jth lattice point from its equilibrium position is (see Eq. 2.12)

$$x_j=aAe^{-i\omega t}[e^{ij\varphi_0}+2f^2(1-Q)\sin(|j|\varphi_0)/\sin\varphi_0]. \tag{3.46}$$

Since the term $\sin|j|\varphi_0$ contains terms with both positive and negative exponents, the scattered wave contains both a reflected and transmitted part.

The full matrix theory must be used when $P\neq 1$.

4. ZERO-POINT OR VIBRATIONAL SELF-ENERGY OF DEFECTS

An important characteristic of a lattice defect is its vibrational self-energy. We define this quantity as the difference between the zero-point energy of the lattice with a defect and that of a perfect lattice. The total potential energy of a lattice can be approximated as a constant term (the sum of the bond energies) plus a term quadratic in relative displacements. Hence the total self-energy is the sum of that required to make the change in the bond energies associated with the introduction of the defect plus the vibrational self-energy.

The vibrational self-energy can be decomposed into two parts; the first being due to the shifting of frequencies in the band, ΔE_b, and the second being due to the removal of frequencies from the band, ΔE_D. If $\{\omega_j^{(0)}\}$ represents the vibrational frequencies of a perfect lattice and $\{\omega_j^{(1)}\}$ those of a lattice with a single defect, the vibrational self-energy is

$$\Delta E=\tfrac{1}{2}\textstyle\sum_j \hbar[\omega_j^{(1)}-\omega_j^{(0)}]=\Delta E_b+\Delta E_D. \tag{4.1}$$

When Q is close to 1, ΔE follows immediately from perturbation theory as well as from an exact analysis of all the normal modes (those inside as well as outside the band).

In order to avoid the necessity of using perturbation theory of degenerate characteristic values, we shall use the solutions of

$$Lu(n)=0 \quad \text{with} \quad u(N)=u(-N)=0 \tag{4.2a}$$

as the unperturbed characteristic vectors. The fixed particles at the end of the chain lead to normalized solutions

$$u(n)=N^{-\frac{1}{2}}\sin(N-n)\varphi$$

with

$$\varphi=\pi j/2N, \quad j=0,\ 1,\ 2,\ \cdots,\ 2N, \tag{4.2b}$$

with normal mode frequencies

$$M\omega^2=2\gamma(1-\cos\pi j/2N)=4\gamma\sin^2\pi j/4N. \tag{4.2c}$$

The first-order perturbation in $M\omega^2$ for an isolated defect at $n=0$ is

$$M\Delta\omega_k^2=\{u(-1),u(0),u(1)\}\begin{bmatrix}(\gamma'-\gamma) & (\gamma-\gamma') & 0\\ (\gamma-\gamma') & (M-M')[\omega_k^{(0)}]^2-2(\gamma-\gamma') & (\gamma-\gamma')\\ 0 & (\gamma-\gamma') & (\gamma'-\gamma)\end{bmatrix}\begin{bmatrix}u(-1)\\ u(0)\\ u(1)\end{bmatrix}$$
$$=(\gamma'-\gamma)\{[u(0)-u(-1)]^2+[u(0)-u(1)]^2\}+(M-M')[\omega_k^{(0)}]^2u^2(0)$$
$$=4(\gamma'-\gamma)N^{-1}\sin^2\tfrac{1}{2}\varphi_k[\cos^2(N-\tfrac{1}{2})\varphi_k+\cos^2(N+\tfrac{1}{2})\varphi_k]+(M-M')[\omega_k^{(0)}]^2N^{-1}\sin^2N\varphi_k, \quad (4.3)$$

where $\omega_k^{(0)}$ is the unperturbed frequency given by (4.2c).

The vibrational self-energy is (each frequency contributing $\frac{1}{2}\hbar\omega$ to the zero-point energy of the lattice)

$$\Delta E=\tfrac{1}{2}\hbar\sum\Delta\omega_k=\tfrac{1}{2}\hbar\sum[\omega_k-\omega_k^{(0)}]$$
$$=\tfrac{1}{4}\hbar\sum\omega_k^{(0)}\{\Delta\omega_k^2/[\omega_k^{(0)}]^2\}. \quad (4.4)$$

We see that (4.3) breaks into two subsets

$$\Delta\omega_k^2=\begin{cases}2(P-1)\omega_L^2N^{-1}\sin^2\dfrac{k\pi}{4N}\cos^2\dfrac{k\pi}{4N} & k \text{ even}\\ 2(P-1)\omega_L^2N^{-1}\sin^2\dfrac{k\pi}{4N}\sin^2\dfrac{k\pi}{4N} & \\ \qquad+[\omega_k^{(0)}]^2N^{-1}(1-Q) & k \text{ odd.}\end{cases}$$

Then

$$\Delta E=\tfrac{1}{4}\hbar N^{-1}\Big\{2(P-1)\Big[\sum_{k\text{ even}}\omega_k^{(0)}\cos^2\frac{k\pi}{4N}+\sum_{k\text{ odd}}\omega_k^{(0)}\sin^2\frac{k\pi}{4N}\Big]+(1-Q)\sum_{k\text{ odd}}\omega_k^{(0)}\Big\}.$$

In the limit as $N\to\infty$, $\omega_k^{(0)}$ for a given odd k is practically equal to its value for the even number $k+1$. Hence, as $N\to\infty$,

$$\Delta E=\tfrac{1}{8}\hbar N^{-1}[2(P-1)+(1-Q)]\sum_{k=0}^{2N}\omega_k^{(0)}$$
$$=\tfrac{1}{2}\hbar\omega_L\pi^{-1}[2(P-1)+(1-Q)]. \quad (4.5)$$

Second-order perturbation theory gives terms of order $(P-1)^2$ and $(Q-1)^2$ to ΔE so that (4.5) is merely the beginning of a series in $(P-1)$ and $(Q-1)$.

The contribution of the localized defect modes to the vibrational self-energy of a defect are

$$\Delta E_D=\tfrac{1}{2}\hbar\textstyle\sum_j(\omega_j-\omega_L)=\tfrac{1}{2}\hbar\omega_L\sum_j(f_j-1), \quad (4.6)$$

where the summation extends over all defect modes which go out of the band. The assumption is made that the defect mode is the displacement of a mode which was very close to the top of the band in the perfect lattice. We shall give an explicit formula only in the case of the "isotope." When $P=1$ (the "isotope" case $\gamma=\gamma'$) the only mode which escapes from the band is the symmetric one with frequency

$$f=\omega/\omega_L=[1/Q(2-Q)]^{\frac{1}{2}}.$$

Hence

$$\Delta E_D=\tfrac{1}{2}\hbar\omega_L([Q(2-Q)]^{-\frac{1}{2}}-1)$$
$$=\tfrac{1}{2}\hbar\omega_L[\{1-(1-Q)^2\}^{-\frac{1}{2}}-1]$$
("isotope" case). (4.7)

The exact evaluation of the total vibrational self-energy can be achieved through the application of the following theorem[12] on contour integration: Let $g(z)$ be a function analytic inside a contour C and $f(z)$ be a function with zeros at $z_1, z_2, \cdots, z_n$ inside C. Then, if $f(z)$ has no poles inside or on the boundary of C

$$\frac{1}{2\pi i}\int_C\frac{f'(z)}{f(z)}g(z)dz=\sum_i g(z_j). \quad (4.8)$$

Those zeros of $f(z)$ which lie on C are given a weight $\frac{1}{2}$ in the sum.

It is shown in the Appendix that the possible normal mode frequencies of a perfect chain are

$$\omega=\omega_L\sin\tfrac{1}{2}\varphi, \quad (4.9)$$

where the φ's are zeros of the two functions

$$f_1^{(0)}(\varphi)=\sin N\varphi \quad \text{and} \quad f_2^{(0)}(\varphi)=\cos N\varphi \quad (4.10)$$

in the range $0<\mathrm{Re}\,\varphi\leqslant\pi$. A lattice with a single isotopic defect of mass $M'=QM$ also has frequencies given by (4.9) where the φ's are the zeros of

$$f_1(\varphi)=\sin N\varphi, \quad (4.11a)$$

$$f_2(\varphi)=\cos N\varphi+(1-Q)\tan\tfrac{1}{2}\varphi\sin N\varphi. \quad (4.11b)$$

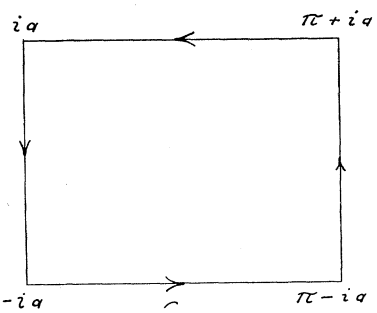


FIG. 8. The contour C which is the path of integration used in (4.12).

[12] See E. C. Titchmarsh, *Theory of Functions* (Oxford University Press, Oxford, 1932), p. 116.

The application of (4.8) implies that

$$\Delta E=\frac{\hbar\omega_L}{4\pi i}\int_C \sin\tfrac{1}{2}z\frac{d}{dz}[\log f_2(z)-\log f_2^{(0)}(z)]dz, \quad (4.12)$$

where the contour C (see Fig. 8) contains the zeros of both $f_2(z)$ and $f_2^{(0)}(z)$. As is discussed in the Appendix, the zeros of $f_2^{(0)}(z)$ and $f_2(z)$ which correspond to normal modes in the band are located on the real axis in the interval $(0,\pi)$. The frequency of the localized mode corresponds (as $N\to\infty$) to the points on the line $z=\pi+iy$ at $y=\pm\log[(2-Q)/Q]$. We take our contour, C, through both of these points since each (being on the boundary) contributes only one half of the required zero-point energy to (4.12).

It is easy to show that

$$\Delta E=\frac{\hbar\omega_L(Q-1)}{4\pi i}\int_C\left\{\frac{N\sin\frac{1}{2}z\cos\frac{1}{2}z+\frac{1}{2}\cos Nz\sin Nz}{\cos Nz\cos\frac{1}{2}z-(Q-1)\sin\frac{1}{2}z\sin Nz}\right\}\times\sin\tfrac{1}{2}z dz/\cos\tfrac{1}{2}z\cos Nz. \quad (4.13)$$

This integral can be decomposed into the sum of four integrals, one for each side of the rectangle in Fig. 8. The integrand of (4.13) is an odd function of y along the line $z=\pi+iy$ from $(-a,\pi)$ to (a,π). In the limit of very long chains, as $N\to\infty$, the two integrals along the longitudinal parts of the contour combine to give a contribution

$$[\hbar\omega_L(Q-1)/8\pi]\left\{\int_0^\pi \frac{\sin\frac{1}{2}(x-ia)dx}{\cos\frac{1}{2}(x-ia)[\cos\frac{1}{2}(x-ia)+i(Q-1)\sin\frac{1}{2}(x-ia)]}+\int_0^\pi \frac{\sin\frac{1}{2}(x+ia)dx}{\cos\frac{1}{2}(x+ia)[\cos\frac{1}{2}(x+ia)-i(Q-1)\sin\frac{1}{2}(x+ia)]}\right\}.$$

These integrals can be transformed easily into elementary real integrals and are found to be (in the case $\sinh\frac{1}{2}a+[Q-1]\cosh\frac{1}{2}a>0$)

$$\frac{1}{2\pi}\hbar\omega_L\{-\tan^{-1}(1/\sinh\tfrac{1}{2}a)+[1-(1-Q)^2]^{-\frac{1}{2}}\tan^{-1}([1-(1-Q^2)]^{\frac{1}{2}}/\times[\sinh\tfrac{1}{2}a+(Q-1)\cosh\tfrac{1}{2}a])\}. \quad (4.14)$$

Hence, for any fixed value of Q, the contribution of this term to (4.13) vanishes as $a\to\infty$.

The only remaining contribution to (4.13) in the limit $a\to\infty$ comes from the imaginary axis. As $N\to\infty$ the term $\frac{1}{2}\cosh Ny\sinh Ny$ in (4.13) dominates $N\sinh\frac{1}{2}y\times\cosh\frac{1}{2}y$ in this line contribution to (4.13). Hence, after applying the appropriate large N asymptotic formulas for $\cosh Ny$ and $\sinh Ny$, and letting $a\to\infty$ we reduce (4.13) to

$$\Delta E=\frac{\hbar\omega_L}{4\pi}(1-Q)\int_0^\infty\frac{\sinh\frac{1}{2}ydy}{\cosh\frac{1}{2}y[\cosh\frac{1}{2}y-(1-Q)\sinh\frac{1}{2}y]}=\frac{\hbar\omega_L}{4\pi}\left\{\int_0^\infty\frac{dy}{\cosh\frac{1}{2}y-(1-Q)\sinh\frac{1}{2}y}-\int_0^\infty\frac{dy}{\cosh\frac{1}{2}y}\right\}=\tfrac{1}{4}\hbar\omega_L\left\{-1+[1-(1-Q)^2]^{-\frac{1}{2}}\left[1+\frac{2}{\pi}\sin^{-1}(1-Q)\right]\right\}. \quad (4.15)$$

As $(1-Q)\to 0$ this becomes $\frac{1}{2}\pi^{-1}(1-Q)$ which is equivalent to the first-order perturbation result (4.5). This is due entirely to the shift of levels in the band. As $Q\to 0$, $\Delta E\to\frac{1}{2}\hbar\omega_L(2Q)^{\frac{1}{2}}$ which is the limit of (4.7a). To summarize, a very "weak" isotopic defect is described by the intra-band shift of frequencies while a "strong" isotopic defect, a very low mass particle introduced into the lattice, exerts its influence through the localized modes. The complete variation of the self-energy of an isotopic defect is plotted in Fig. 9 as a function of the mass ratio $Q=M'/M$.

Since an interstitial has the same topology as a point defect at a normal lattice position the contribution to its self-energy made by those frequencies which are displaced in the band can be inferred from the equations derived above.

The first-order perturbation theory of the anomalous force constant proceeds as follows:

$$M\Delta\omega_k^2=\{u(0),u(1)\}\begin{pmatrix}\gamma''-\gamma & \gamma-\gamma''\\ \gamma-\gamma'' & \gamma''-\gamma\end{pmatrix}\begin{pmatrix}u(0)\\ u(1)\end{pmatrix}=[u(0)-u(1)]^2(\gamma''-\gamma)=4(\gamma''-\gamma)N^{-1}\sin^2\tfrac{1}{2}\varphi_k\cos^2(N+\tfrac{1}{2})\varphi_k.$$

Hence,

$$\Delta\omega_k^2=4[\omega_k^{(0)}]^2N^{-1}(P'-1)\begin{cases}\cos^2\pi k/4N & \text{if } k \text{ is even}\\ \sin^2\pi k/4N & \text{if } k \text{ is odd}\end{cases}$$

so that by following the reasoning used in the derivation of (4.5) we find

$$\Delta E=\tfrac{1}{2}\hbar(P'-1)\omega_L/\pi+O[(P'-1)^2]. \quad (4.16)$$

The pulsating mode which goes out of the band when $P'>1$ gives the contribution to the self-energy [see (4.6) and (3.40)]:

$$\Delta E_D=\tfrac{1}{2}\hbar\omega_L\{P'(2P'-1)^{-\frac{1}{2}}-1\}. \quad P'\geqslant 1 \quad (4.17)$$

We conclude this section with a determination of the vibrational self-energy of a hole. The contribution from

the localized mode is

$$\Delta E_D=\tfrac{1}{2}\hbar\omega_L\left\{\frac{P}{2(P-1)^{\frac{1}{2}}}-1\right\} \quad \text{if } P>2. \qquad (4.18)$$

The first-order contribution ΔE_b of those frequencies which suffer small displacements in the band can be deduced from various formulas derived above. We take the following steps.

(a) Insert an anomalous bond with force constant P' into the lattice at the expense of $\Delta E_b{}^{(1)}\simeq\frac{1}{2}\hbar(P'-1)\omega_L/\pi$.

(b) Remove one particle from the lattice with $\Delta E_b{}^{(2)}=-\hbar\omega_L/\pi$ [since this is the total zero-point energy per particle in a long chain as derived in Eq. (2.3)].

(c) Without changing the topology of the lattice the anomalous "spring" is chosen to span the hole so that it is extended over two lattice spacings rather than the usual one per bond. The choice $P'=\frac{1}{2}P$ is made to correspond to a consistent model of the hole.

Then

$$\Delta E_b=\tfrac{1}{2}\hbar\omega_L\pi^{-1}(\tfrac{1}{2}P-3). \qquad (4.19)$$

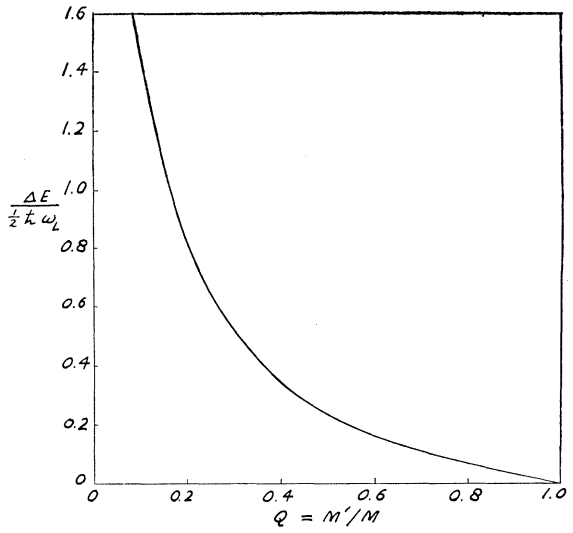


FIG. 9. Self-energy of an isotope mass M' plotted against $Q=M'/M$. ($\frac{1}{2}\hbar\omega_L$ is the zero-point energy corresponding to the maximum frequency of the perfect lattice.)

5. THE DEFECT PAIR

This section is concerned with the interaction of a pair of defects with each other. Several qualitative comments can immediately be made concerning the localized modes. If two defects are very far apart both lead to a localized normal mode of the same frequency. As the defects are brought closer together the degeneracy splits. If the defect coupling is very weak the motion of a given particle located between the two defects can be approximated as a linear combination of the two isolated defect modes. Two independent situations are possible; in the first the motions of the particle of interest due to each defect mode are in phase and in the second they are out of phase. The in-phase motion, which will be called the fitting mode, corresponds to an enhancement of the amplitude of the lattice vibrations while in the out-of-phase motion of the nonfitting case interference occurs. The nonfitting mode has one less node than the fitting one and is associated with the low-frequency member of the split pair.

We now proceed with the detailed analysis of the localized modes of a defect pair.

If a defect is located at lattice point n it induces a displacement from equilibrium at m whose space dependent factor is [generalization of (3.3)]

$$\begin{aligned}u^{(n)}(m)=\gamma^{-1}\{&g(m-n)[(M-M')\omega^2-2(\gamma-\gamma')]\\&+(\gamma-\gamma')[g(m+1-n)+g(m-1-n)]\}u(n)\\&+(1-P)[g(m-n)-g(m-n-1)]u(n+1)\\&+(1-P)[g(m-n)-g(m+1-n)]u(n-1).\end{aligned} \qquad (5.1)$$

Since our differential equations are linear we can apply the superposition principle to find the total displacement which results from defects at $n_1, n_2, \cdots, n_k$:

$$u(m)=\sum_{j=1}^{k}u^{(n_j)}(m). \qquad (5.2)$$

When (5.2) is specialized to a pair of defects, one located at $n_1=0$ and the other at $n_2=n$ the frequencies of normal modes are determined so that the homogeneous equations which relate $u(\pm1)$, $u(0)$, $u(n)$, $u(n\pm1)$ are consistent. These equations are obtained by letting m in (5.2) successively run through $-1, 0, 1, n+1, n, n-1$. The vector u of Eq. (2.17) is

$$u=\{u(-1), u(0), u(1), u(n+1), u(n), u(n-1)\}. \qquad (5.3)$$

The G matrix of Eq. (2.17) has the following form:

$$G=\begin{pmatrix}G_1 & G_2\\ G_2 & G_1\end{pmatrix}, \qquad (5.4a)$$

where

$$G_1=\begin{bmatrix}(1-P)[g(1)-g(0)] & 4f^2(P-Q)g(1) & (1-P)[g(1)-g(2)]\\ (1-P)[g(0)-g(1)] & 4f^2g(0)(P-Q)+(1-P) & (1-P)[g(0)-g(1)]\\ (1-P)[g(1)-g(2)] & 4f^2(P-Q)g(1) & (1-P)[g(1)-g(0)]\end{bmatrix}, \qquad (5.4b)$$

and

$$G_2=\begin{bmatrix}(1-P)[g(n+1)-g(n+2)] & 4f^2(P-Q)g(n+1) & (1-P)[g(n+1)-g(n)]\\ (1-P)[g(n)-g(n+1)] & 4f^2(P-Q)g(n) & (1-P)[g(n)-g(n-1)]\\ (1-P)[g(n-1)-g(n)] & 4f^2(P-Q)g(n-1) & (1-P)[g(n-1)-g(n-2)]\end{bmatrix}. \qquad (5.4c)$$

The matrix

$$R=2^{-\frac{1}{2}}\begin{pmatrix} I & I \\ I & -I \end{pmatrix} \quad \text{with} \quad I=\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{5.5a}$$

transforms G into

$$R^{-1}GR=\begin{pmatrix} G_1+G_2 & 0 \\ 0 & G_1-G_2 \end{pmatrix}. \tag{5.5b}$$

In the "isotope" case, $P=1$, the matrices $G_1 \pm G_2$ are of the form

$$G_1 \pm G_2 = 4f^2(1-Q)\begin{bmatrix} 0 & g(1)\pm g(n+1) & 0 \\ 0 & g(0)\pm g(n) & 0 \\ 0 & g(-1)\pm g(n-1) & 0 \end{bmatrix}, \tag{5.6}$$

with characteristic vectors

$$\psi_1=\{1,0,1\}, \tag{5.7a}$$

$$\zeta_1=\frac{1}{2}\left(1, -\frac{2g(1)\pm 2(1-2f^2)g(n)}{g(0)\pm g(n)}, 1\right)$$

with $\lambda_1=0$, (5.7b)

$$\psi_2=\{1, 0, -1\}, \tag{5.8a}$$

$$\zeta_2=\frac{1}{2}\left(1, \frac{\pm[g(n-1)-g(n+1)]}{g(0)\pm g(n)}, -1\right)$$

with $\lambda_2=0$, (5.8b)

and

$$\psi_3=\{g(1)\pm g(n+1), g(0)\pm g(n), g(1)\pm g(n-1)\}, \tag{5.9a}$$

$$\zeta_3=(0,1,0)/[g(0)\pm g(n)], \tag{5.9b}$$

with

$$\lambda_3=4f^2(1-Q)[g(0)\pm g(n)]. \tag{5.9c}$$

The frequency which corresponds to the mode ψ_3 is obtained by letting $\lambda_3=1$ [see equation below (3.15b)]. If we introduce our usual expression (2.8b) for $g(j)$ and f^2 into (5.9c), we have the characteristic equation

$$e^z-(2-Q)/Q=\pm Q^{-1}(1-Q)(-1)^n(e^z+1)e^{-nz}, \quad 0<Q<1. \tag{5.10}$$

This equation has been obtained on the supposition that $n \geqslant 3$ but it is easy to show that it is also valid when $n=1, 2$. A special analysis is required for these two cases because when $n=2$ the isotopes are next nearest neighbors and when $n=1$ they are nearest neighbors.

Of course in the first approximation as $n\to\infty$, $\exp z=(2-Q)/Q>1$. A series expansion of our required root can be obtained from the Lagrange theorem: Let $f(w)$ and $\psi(w)$ be functions of a complex variable w analytic on and inside a contour c surrounding a point a, and let t be such that the inequality

$$|t\psi(w)|<|w-a| \tag{5.11}$$

is satisfied at all points on the perimeter of C; then the solution

$$\zeta=a+t\psi(\zeta) \tag{5.12}$$

regarded as an equation in ζ, has one root in the interior of C; and further, any function of ζ analytic on and inside C can be expanded as a power series in t by the formula

$$f(\zeta)=f(a)+\sum_{m=1}^{\infty}\frac{t^m}{m!}\frac{d^{m-1}}{da^{m-1}}[f'(a)\{\psi(a)\}^m]. \tag{5.13}$$

In particular the root ζ of (5.12) which lies in C is

$$\zeta=a+\sum_{m=1}^{\infty}\frac{t^m}{m!}\frac{d^{m-1}}{da^{m-1}}[\psi(a)]^m \tag{5.14}$$

If we let $\exp z=\zeta$ then we can apply (5.14) to find

$$e^z=[(2-Q)/Q]\pm 2(-1)^n(1-Q)Q^{-2}[Q/(2-Q)]^n + (2/Q)[(1-Q)/Q]^2 \times\left(\frac{2-Q-2n}{2-Q}\right)\left(\frac{Q}{2-Q}\right)^{2n}+\cdots, \tag{5.15a}$$

and set $f(\zeta)=\frac{1}{4}(\zeta+2+\zeta^{-1})$ in (5.13) to find

$$(\omega/\omega_L)^2=\frac{1}{Q(2-Q)}\pm 2\frac{(-1)^n(1-Q)^3}{Q^2(2-Q)^2}\left(\frac{Q}{2-Q}\right)^n + \frac{(1-Q)^2}{Q^3(2-Q)^3}[4-6Q+3Q^2-4(1-Q)n]\left(\frac{Q}{2-Q}\right)^{2n}+\cdots, \tag{5.15b}$$

so that

$$(\omega/\omega_L)=[Q(2-Q)]^{-\frac{1}{2}}\left\{1\pm\frac{(-1)^n(1-Q)^2}{2(2-Q)}\left(\frac{Q}{2-Q}\right)^n + \frac{1}{2}\frac{(1-Q)^2}{Q^2(2-Q)^2}[3-4Q+2Q^2-4n(1-Q)] \times\left(\frac{Q}{2-Q}\right)^{2n}+\cdots\right\}. \tag{5.16}$$

We see that the frequency of the isolated impurity $f=[Q(2-Q)]^{-\frac{1}{2}}$ is split into two frequencies as two isolated impurities are brought together.

The difference in zero-point energy of the two particle modes associated with a pair of particles n lattice spacings apart and that of two isolated local modes is, as $n\to\infty$

$$\Delta E_D=\tfrac{1}{2}\hbar\sum\Delta\omega = -2n\hbar\omega_L(1-Q)^3[Q/(2-Q)]^{2n}/[Q(2-Q)]^{5/2}, \tag{5.17}$$

since $\frac{1}{2}\hbar[Q(2-Q)]^{-\frac{1}{2}}$ is the zero-point energy per isolated impurity. Hence the localized modes give rise to an attraction between defects. We shall show in the

next section that in three dimensions this attraction is of the Debye or Yukawa type at great distances.

When n is a small integer it is more convenient to solve the characteristic equation (5.10) directly than to employ the Lagrange formula. We have plotted ΔE_D as a function of n in Fig. 10.

The attraction between light isotope defects in a system of a heavy isotopic species leads to a clustering tendency for the light isotope at very low temperatures, and therefore one would expect an ordering into two phases. This separation has been discussed by Prigogine and his collaborators.[8]

The analysis of the interband frequencies of a chain with two isotopic defects is similar to that of the Appendix for the single isotopic impurity. If one impurity is at $-m$ and the other at m in a chain of $2N+1$ atoms (with ends fixed) the equations for the configurational factor of the displacements are

$$M\omega^2u(n)+\gamma[u(n-1)-2u(n)+u(n+1)] = (M-M')\omega^2\delta(n^2-m^2)u(n), \quad (5.18a)$$

$$u(N)=u(-N)=0, \quad (5.18b)$$

where as usual $\delta(s)=0$ unless $s=0$ in which case it is 1. The solution of this equation is

$$u(n)=\begin{cases} B\sin(N+n)\varphi & \text{if } n<-m \\ A\sin(N-n)\varphi & \text{if } n\geqslant m \\ Ce^{in\varphi}+De^{-in\varphi} & \text{if } -m\leqslant n<m \end{cases} \quad (5.19)$$

where

$$M\omega^2=2\gamma(1-\cos\varphi) \quad (5.20)$$

and the parameters A, B, C, D, and φ are determined from the four "connecting" equations which result from successively letting n be $-m-1$, $-m$, m, $m+1$. A bit of elementary algebra yields the four equation relations between A, B, C, D, and φ:

$$(A+B)\sin(N-m)\varphi=2(C+D)\cos m\varphi,$$
$$(A-B)\sin(N-m)\varphi=2i(C-D)\sin m\varphi,$$
$$B\sin(N-m-1)\varphi-A\sin(N-m+1)\varphi +2i(Ce^{-i\varphi}-De^{i\varphi})\sin m\varphi =2(A+B)(1-\cos\varphi)(1-Q)\sin(N-m)\varphi,$$
$$B\sin(N-m-1)\varphi+A\sin(N-m+1)\varphi -2(Ce^{-i\varphi}+De^{i\varphi})\cos m\varphi =2(B-A)(1-\cos\varphi)(1-Q)\sin(N-m)\varphi.$$

The solutions of this set are of two types

(a) The even solutions, $u(n)=u(-n)$, with

$$A=B, \quad C=D, \quad A\sin(N-m)\varphi=2c\cos m\varphi,$$

so that

$$u(n)=A\frac{\sin(N-m)\varphi}{\cos m\varphi}\cos n\varphi, \quad -m\leqslant n<m$$

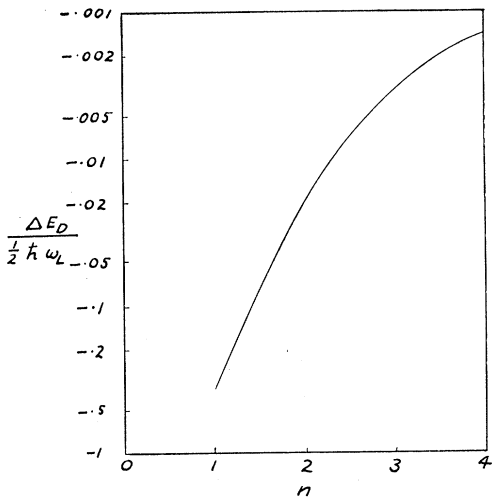


FIG. 10. Contribution of localized modes to the energy of interaction of two isotopes of masses $\frac{1}{2}M$. ($\frac{1}{2}\hbar\omega_L$ is the zero-point energy corresponding to the maximum frequency of the perfect lattice.)

and the characteristic equation for φ is

$$\cot N\varphi=2(Q-1)\tan\tfrac{1}{2}\varphi\cos m\varphi\frac{\sin(N-m)\varphi}{\sin N\varphi}. \quad (5.21)$$

(b) The odd solution, $u(n)=-u(-n)$, with

$$A=-B, \quad C=-D, \quad A\sin(N-m)\varphi=2iC\sin m\varphi,$$

so that

$$u(n)=A\frac{\sin(N-m)\varphi}{\sin m\varphi}\sin n\varphi, \quad -m\leqslant n<m$$

and the characteristic equation for φ is

$$\sin N\varphi=2(Q-1)\tan\tfrac{1}{2}\varphi\sin(N-m)\varphi\sin m\varphi. \quad (5.22)$$

The characteristic equations which correspond to a single defect at m or $-m$ is

$$\sin N\varphi\cos N\varphi=(Q-1)\tan\tfrac{1}{2}\varphi\sin(N-m)\varphi \times\sin(N+m)\varphi, \quad (5.23)$$

which when $m=0$ becomes

$$\sin N\varphi[\cot N\varphi-(Q-1)\tan\tfrac{1}{2}\varphi]=0$$

which is equivalent to (A-7) and (A-8) in the Appendix.

If we combine (5.22) and (5.21) we find that the values of φ which lead to normal mode frequencies are zeros of the function

$$f(\varphi)=\{\cos N\varphi+2\epsilon\tan\tfrac{1}{2}\varphi\cos m\varphi\sin(N-m)\varphi\} \times\{\sin N\varphi+2\epsilon\tan\tfrac{1}{2}\varphi\sin(N-m)\varphi\sin m\varphi\} =A(\varphi)+2\epsilon B(\varphi)+\epsilon^2C(\varphi), \quad (5.24a)$$

where

$$\epsilon=(1-Q), \quad (5.24b)$$

$$A(\varphi)=\cos N\varphi\sin N\varphi=\tfrac{1}{2}\sin 2N\varphi, \quad (5.24c)$$

$$B(\varphi)=\tfrac{1}{2}\tan\tfrac{1}{2}\varphi\{\cos 2m\varphi-\cos 2N\varphi\}, \quad (5.24d)$$

$$C(\varphi)=2\tan^2\tfrac{1}{2}\varphi\sin^2(N-m)\varphi\sin 2m\varphi. \quad (5.24e)$$

The corresponding values of φ associated with an isolated defect at $\pm m$ are zeros of

$$f_0(\varphi)=A(\varphi)+\epsilon\beta(\varphi), \tag{5.25}$$

while those of perfect lattice are zeros of

$$f_1(\varphi)=A(\varphi). \tag{5.26}$$

A generalization of (4.12) leads immediately to a formula for the interaction energy of a pair of defects separated by a distance $2m$ lattice spacings

$$\Delta E=\frac{\hbar\omega_L}{4\pi i}\int_C \sin\tfrac{1}{2}z\frac{d}{dz}\{\log f(\varphi)-2\log f_0+\log f_1\}dz$$

$$=\frac{\hbar\omega_L}{4\pi i}\int_C \sin\tfrac{1}{2}z\left\{\frac{\beta'-[\alpha^2]'+\epsilon(\alpha\beta'-2\beta\alpha')}{(1+\epsilon\alpha)(1+2\epsilon\alpha+\beta\epsilon^2)}\right\}dz, \tag{5.27a}$$

where

$$\alpha=B/A=\tan\tfrac{1}{2}z\left\{\frac{\cos 2mz-\cos 2Nz}{\sin 2Nz}\right\}, \tag{5.27b}$$

$$\beta=C/A=4\frac{\tan^2\tfrac{1}{2}z\sin^2(N-m)z\sin 2mz}{\sin 2Nz}. \tag{5.27c}$$

The contour C is again around the counter clockwise rectangle given in Fig. 8.

It can be shown that in the limit as $N\to\infty$, the integrand is an even function of y along the line $z=iy$ and an odd function along $z=\pi+iy$. Hence the integral from $-\pi+iy$ to $\pi+iy$ vanishes. It can also be shown that as $N\to\infty$, the values of α and β along $z=x+ia$ are

$$\alpha\sim i\tan\tfrac{1}{2}(x+ia)+O(\exp -Na), \tag{5.28a}$$

$$\beta\sim-\tan^2\tfrac{1}{2}(x+ia)+O(\exp -Na). \tag{5.28b}$$

Hence the integrand of (5.27a) along $z=x+ia$ is of $O(\exp -Na)$ and can be neglected. One also finds the integral along $z=x-ia$ to vanish in the same way. Since, as $N\to\infty$

$$\alpha=-\tanh\tfrac{1}{2}y,\quad \beta=(\tanh^2\tfrac{1}{2}y)(1-\exp[-4my]),$$

we finally obtain, after letting $a\to\infty$,

$$\Delta E=-\frac{\epsilon^2\hbar\omega_L}{2\pi}\int_0^\infty \frac{[\sinh\tfrac{1}{2}y\tanh\tfrac{1}{2}y]e^{-4my}}{(1-\epsilon\tanh\tfrac{1}{2}y)}$$

$$\times\left\{\frac{4m\tanh\tfrac{1}{2}y(1-\epsilon\tanh\tfrac{1}{2}y)-\operatorname{sech}^2\tfrac{1}{2}y}{1-2\epsilon\tanh\tfrac{1}{2}y+\epsilon^2\tanh^2\tfrac{1}{2}y[1-\exp(-4my)]}\right\}dy. \tag{5.29}$$

The authors have not been able to evaluate this integral as a function of ϵ and m. However it is easily calculated as $\epsilon\to 0$ and as $\epsilon\to 1$.

The energy of interaction of two weak isotopic defects separated by $2m$ lattice spacings is found by setting $\epsilon=0$ in the integrand of (5.29):

$$\Delta E=\frac{\hbar\omega_L\epsilon^2}{2\pi}\int_0^\infty \sinh\tfrac{1}{2}y\,d\{\tanh^2\tfrac{1}{2}y\exp -4my\} \tag{5.30}$$

$$=-\frac{\epsilon^2\hbar\omega_L}{4\pi}\int_0^\infty e^{-4my}\tanh^2\tfrac{1}{2}y\cosh\tfrac{1}{2}y\,dy$$

$$=-\frac{\epsilon^2\hbar\omega_L}{4\pi}\left\{\frac{4m}{(4m)^2-\frac{1}{4}}-\int_0^\infty \operatorname{sech}\tfrac{1}{2}y\exp(-4my)dy\right\} \tag{5.31}$$

$$=-\frac{\epsilon^2\hbar\omega_L}{4\pi}\left\{\frac{4m}{(4m)^2-\frac{1}{4}}-\psi(\tfrac{3}{4}+2m)+\psi(\tfrac{1}{4}+2m)\right\},$$

where as usual

$$\psi(z)=\frac{d}{dz}\log\Gamma(z)=-\gamma-\frac{1}{z}+\sum_{n=1}^{\infty}\frac{z}{n(z+n)},$$

with $\gamma=0.57721$. The asymptotic formula for large z

$$\psi(z)=\log z-(2z)^{-1}-\sum_{n=1}^{m}B_{2n}z^{-2n}/2z+O(z^{-2m-2}),$$

and Nörlands factorial expansion

$$\psi(a+z)-\psi(a)=\frac{z}{a}-\frac{1}{2}\frac{z(z-1)}{a(a+1)}+\cdots$$

are useful for finding the interaction of two widely separated isotopic defects. A finite series for ΔE is

$$\Delta E=-\frac{\epsilon^2\hbar\omega_L}{\pi}\left\{\frac{4m}{(8m)^2-1}-\frac{\pi}{4}+\left[1-\tfrac{1}{3}+\cdots-\frac{1}{8m-1}\right]\right\}, \tag{5.32}$$

while the first few terms of the asymptotic series for large separations are

$$\Delta E\sim-\frac{(Q-1)^2\hbar\omega_L}{\pi}\left\{\frac{1}{(8m)^3}-\frac{2}{(8m)^5}+\cdots\right\}. \tag{5.33}$$

It is remarkable that the asymptotic formula is valid over the entire range of integral values of m. When $m=1$ it is found that the exact equation (5.32) yields $\Delta E=-1.903\times 10^{-3}\hbar\omega_L\epsilon^2/\pi$ while the first two terms of the asymptotic formula yield $E=-1.89\times 10^{-3}\hbar\omega_L\epsilon^2/\pi$ with even better agreement when $m\geqslant 2$.

The result (5.32) has also been obtained from second-order perturbation theory.

In the limit of a strong defect ($Q=0$) we use the fact that $\epsilon=1$ so that

$$1-\epsilon\tanh\tfrac{1}{2}y=\operatorname{sech}\tfrac{1}{2}y\exp-\tfrac{1}{2}y,$$

which yields

$$\Delta E=-\frac{\epsilon^2\hbar\omega_L}{2\pi}\int_0^\infty \frac{\sinh^2\frac{1}{2}y e^{-(4m-1)y}\{4m\sinh\frac{1}{2}y-e^{\frac{1}{2}y}\}dy}{1-\sinh^2\frac{1}{2}y\exp\{-(4m-1)y\}}. \tag{5.34}$$

With the possible exception of the choice $m=1$, the term $\sinh^2\frac{1}{2}y\exp[-(4m-1)y]$ in the denominator of the integrand can be neglected when compared with 1. Hence the integration becomes elementary and yields

$$\Delta E=-\frac{2\epsilon^2\hbar\omega_L(4m-1)}{\pi(8m-5)(8m-3)(8m-1)(8m+1)}. \tag{5.35}$$

Corrections for small m are easily obtained by expanding the denominator in powers of $\sinh^2\frac{1}{2}y\exp[-(4m-1)y]$.

The first few terms in an asymptotic series for ΔE which is valid for all ϵ when m is large is obtained by expanding all terms in (5.29) as a power series in y. Then

$$\Delta E\sim-\frac{\epsilon^2\hbar\omega_L}{\pi}\frac{1}{(8m)^3}\left\{1+\frac{3}{4m}\epsilon+O(m^{-2})\right\}, \tag{5.36}$$

which is consistent with (5.35) and (5.33). It is to be noted that the first-order term has the same form for all values of $\epsilon=1-Q$.

Note added in proof.—In the case of a pair of holes Q is to be replaced by $2P^{-1}$. If one mass defect corresponds to $\epsilon_1=(1-Q_1)$ and the other to $\epsilon_2=(1-Q_2)$ the first-order term in (5.36) has ϵ^2 replaced by $\epsilon_1\epsilon_2$. Hence the interaction between a heavy and a light defect is repulsive.

6. DEFECTS IN THREE-DIMENSIONAL LATTICES

We now sketch the generalization of the discussion of previous sections to three-dimensional lattices.

The normal frequencies of the perfect three-dimensional simple cubic lattice are defined by

$$M\omega^2=2\sum_{p=1}^{3}\gamma_p\{1-\cos(2\pi r_p/N_p)\};\qquad r_p=1,2,\cdots,N_p, \tag{6.1}$$

with the maximum frequency

$$M\omega_L^2=4(\gamma_1+\gamma_2+\gamma_3). \tag{6.2}$$

The zero-point energy is found to be

$$E=\tfrac{1}{2}\hbar\Sigma\omega=\frac{\hbar}{(2m)^{\frac{1}{2}}}\left\{\prod_{p=1}^{3}\frac{N_p}{2\pi}\right\}\int_0^{2\pi}\int\int\{\sum_{p=1}^{3}\gamma_p(1-\cos\varphi_p)\}^{\frac{1}{2}}\times d\varphi_1 d\varphi_2 d\varphi_3. \tag{6.3}$$

If one component of the displacement of the mass at lattice point j_1, j_2, j_3 is represented by $u(j_1,j_2,j_3)$ then the operator L which is a generalization of that given by (2.5) is

$$\begin{aligned}Lu(j_1,j_2,j_3)&=M\omega^2u(j_1,j_2,j_3)+\gamma_1[u(j_1+1,j_2,j_3)\\&\quad-2u(j_1,j_2,j_3)+u(j_1-1,j_2,j_3)]\\&\quad+\gamma_2[u(j_1,j_2+1,j_3)-2u(j_1,j_2,j_3)\\&\quad+u(j_1,j_2-1,j_3)]+\gamma_3[u(j_1,j_2,j_3+1)\\&\quad-2u(j_1,j_2,j_3)+u(j_1,j_2,j_3-1)].\end{aligned} \tag{6.4}$$

The Green's function satisfying

$$Lg(j_1,j_2,j_3)=\begin{cases}\gamma_1+\gamma_2+\gamma_3 & \text{if } j_1=j_2=j_3=0\\ 0 & \text{otherwise}\end{cases} \tag{6.5a}$$

is readily verified to be

$$g(j_1,j_2,j_3)=-\frac{\gamma_1+\gamma_2+\gamma_3}{2\pi^3}\int_0^{\pi}\int\int\frac{\cos j_1\varphi_1\cos j_2\varphi_2\cos j_3\varphi_3}{\alpha(\gamma_1+\gamma_2+\gamma_3)-\gamma_1\cos\varphi_1-\gamma_2\cos\varphi_2-\gamma_3\cos\varphi_3}d\varphi_1 d\varphi_2 d\varphi_3, \tag{6.5b}$$

where

$$\alpha=1-\tfrac{1}{2}M\omega^2(\gamma_1+\gamma_2+\gamma_3)^{-1} \tag{6.5c}$$

$$=1-2f^2. \tag{6.5d}$$

An extensive program for the computation of this Green's function is being carried out. An interesting asymptotic formula is

$$g\sim-\frac{\gamma_1+\gamma_2+\gamma_3}{(\gamma_1\gamma_2\gamma_3)^{\frac{1}{3}}}\frac{1}{4\pi R}\exp\{-2f(\gamma_1+\gamma_2+\gamma_3)^{\frac{1}{2}}R\} \tag{6.6}$$

valid for large $R=(j_1^2\gamma_1+j_2^2\gamma_2+j_3^2\gamma_3)^{\frac{1}{2}}$. This Green's function has also been discussed by Koster and Slater.[1]

As for the linear lattice, the mode corresponding to a single isotope of mass $M'=QM$ is a symmetric vibration with a discrete frequency which is the solution of the transcendental equation

$$\omega_0^2(M-M')g(0,0,0)=\gamma_1+\gamma_2+\gamma_3, \tag{6.7a}$$

or

$$4f_0^2(1-Q)g(0,0,0)=1. \tag{6.7b}$$

The modes corresponding to a single hole in the lattice are the three antisymmetric pulsating ones with discrete frequency levels given by

$$(\gamma_1-\gamma_1')[g(2,0,0)-g(0,0,0)]=\gamma_1+\gamma_2+\gamma_3, \tag{6.8a}$$

$$(\gamma_2-\gamma_2')[g(0,2,0)-g(0,0,0)]=\gamma_1+\gamma_2+\gamma_3, \tag{6.8b}$$

$$(\gamma_3-\gamma_3')[g(0,0,2)-g(0,0,0)]=\gamma_1+\gamma_2+\gamma_3. \tag{6.8c}$$

The interstitial, placed at the center of a cell of the lattice, is topologically different from a lattice point

as it has eight nearest neighbors. If the force constant for the interactions with these nearest neighbors is taken as γ', then there are four antisymmetric modes with discrete frequencies satisfying

$$\gamma'\{g(0,0,0)-g(1,1,1)+g(1,0,0)-g(0,1,1)+g(0,1,0)-g(1,0,1)+g(1,1,0)-g(0,0,1)\}=\gamma_1+\gamma_2+\gamma_3, \quad (6.9a)$$

$$\gamma'\{g(0,0,0)-g(1,1,1)+g(1,0,0)-g(0,1,1)-g(0,1,0)+g(1,0,1)-g(1,1,0)+g(0,0,1)\}=\gamma_1+\gamma_2+\gamma_3, \quad (6.9b)$$

$$\gamma'\{g(0,0,0)-g(1,1,1)-g(1,0,0)+g(0,1,1)+g(0,1,0)-g(1,0,1)-g(1,1,0)+g(0,0,1)\}=\gamma_1+\gamma_2+\gamma_3, \quad (6.9c)$$

$$\gamma'\{g(0,0,0)-g(1,1,1)-g(1,0,0)+g(0,1,1)-g(0,1,0)+g(1,0,1)+g(1,1,0)-g(0,1,1)\}=\gamma_1+\gamma_2+\gamma_3. \quad (6.9d)$$

If two isotopes occupy lattice sites (0,0,0) and (n_1,n_2,n_3) then, as for the linear lattice, fitting and antifitting modes are possible with normal frequencies satisfying

$$4f^2(1-Q)\{g(0,0,0)\pm g(n_1,n_2,n_3)\}=1. \quad (6.10a)$$

The solutions of this equation give a splitting about the solution for the case of one isotope. The contribution of localized modes to the energy of interaction of the isotopes is estimated from the second term in the Lagrange expansion of f, using (6.10a) in the form

$$\frac{1}{4f^2g(0,0,0)}=1-Q\pm(1-Q)\frac{g(n_1,n_2,n_3)}{g(0,0,0)}. \quad (6.10b)$$

If

$$\zeta^{-1}=4f^2g(0,0,0), \quad (6.11a)$$

$$f(\zeta)=\omega/\omega_L, \quad (6.11b)$$

and

$$\varphi(\zeta)=g(n_1,n_2,n_3)/g(0,0,0), \quad (6.11c)$$

then the second term in the Lagrange expansion of $f(\zeta)$ about $\zeta=1-Q$ (i.e., $f=f_0-\omega/\omega_L$) is

$$\tfrac{1}{2}(1-Q)^2\left[\frac{d}{d\zeta}\{f'(\zeta)\varphi^2(\zeta)\}\right]_{\zeta=1-Q}, \quad (6.12a)$$

which for large n_1, n_2, n_3 becomes

$$\tfrac{1}{2}(1-Q)^2\left[f'(\zeta)\frac{d}{d\zeta}\varphi^2(\zeta)\right]_{\zeta=(1-Q)} \quad (6.12b)$$

$$=\tfrac{1}{2}(1-Q)^2\left[\{f'(\zeta)\}^2\frac{d}{df}\varphi^2(f)\right]_{f=f_0}, \quad (6.12c)$$

$$\sim A\left[\frac{d}{df}\frac{1}{R^2}\exp\{-4f(\gamma_1+\gamma_2+\gamma_3)^{\frac{1}{2}}R\}\right]_{f=f_0}, \quad (6.12d)$$

with

$$R^2=n_1^2\gamma_1+n_2^2\gamma_2+n_3^2\gamma_3; \quad (6.12e)$$

and where A is a positive constant and use has been made of the asymptotic formula (6.6a). The energy of interaction due to localized modes is hence given by

$$V(R)\sim -BR^{-1}\exp -CR, \quad (6.13)$$

where B and C are positive constants (i.e., functions of Q only and independent of n_1, n_2, n_3). The force has the sign of an attraction.

In the case of an isotropic discrete quantum field $\gamma_1=\gamma_2=\gamma_3=\gamma$ so that $R^2=\gamma(n_1^2+n_2^2+n_3^2)$ and the interaction $V(r)$ due to localized modes between our pair of defects is of the Yukawa type at large distances.

Since a crystal lattice corresponds to $\gamma_1\gg\gamma_2=\gamma_3$ the force law (6.13) is not spherically symmetrical and depends on the orientation with respect to crystal axes of the line which connects the two defects.

A more detailed discussion of the three-dimensional lattice will be given in a later publication.

APPENDIX. THE ISOLATED ISOTOPIC IMPURITY IN A LINEAR CHAIN

We shall give a detailed analysis of the "isotopic" impurity in this section. It will serve as an example of how localized modes make their appearance in an exact treatment of the modes in the band. A similar discussion for the electron theory of solids has been given by Koster and Slater,[1] and by Saxon and Hutner.[3]

The equations for the time-independent factor of the displacements are

$$M\omega^2u(n)+\gamma[u(n-1)-2u(n)+u(n+1)]=0, \quad n\neq 0, \quad (A.1a)$$

$$M'\omega^2u(0)+\gamma[u(-1)-2u(0)+u(1)]=0, \quad (A.1b)$$

$$u(N)=u(-N)=0, \quad (A.1c)$$

when one deals with a system of $2N$ particles of mass M and one of mass M' located in the middle of the chain while the end particles are held fixed. One finds

$$u(n)=\begin{cases}A\sin(N-n)\varphi & \text{if } n\geq 0\\ B\sin(N+n)\varphi & \text{if } n<0\end{cases} \quad (A.2)$$

while

$$M\omega^2=2\gamma(1-\cos\varphi). \quad (A.3)$$

One relates the constants A and B by substituting (A.2) into the connecting equations of (A.1) which correspond to $n=0$ and $n=-1$. One finally obtains the following relations between A, B, and φ:

$$B\sin(N-1)\varphi-A\sin(N+1)\varphi=2A(1-Q)(1-\cos\varphi)\sin N\varphi, \quad (A.4)$$

$$(A-B)\sin N\varphi=0. \quad (A.5)$$

Two possible situations arise

$$\text{(a)}\quad A=B \quad (A.6)$$

or

$$\text{(b)}\quad \sin N\varphi=0. \quad (A.7)$$

Condition (b) leads to the odd solutions with $A=-B$ while (a) leads to the even solutions. Since the possible values of φ in the odd solutions are exactly the same as those in the perfect lattice, $\{2\pi j/2N\}$, no shift occurs in the corresponding frequencies.

The even solutions of (A.1) have the characteristic equation

$$\cot N\varphi=(Q-1)\tan\tfrac{1}{2}\varphi, \tag{A.8}$$

for the determination of the φ's. The solutions of (A.8) can be determined by plotting (see Fig. 11) both the left and right hand sides of (A.8) on the same graph and locating their intersection points.

When $Q=1$ the right-hand side of (A.8) vanishes identically so that the possible values of φ are the intersections of the various branches of $\cot N\varphi$ with the φ axis, $\varphi_j=(2j-1)\pi/2N$. When $Q\neq 1$ one intersection occurs in each interval $\{\pi j/N, \pi(j+1)/N\}$ except for the interval $[(N-1)\pi/N, \pi]$ when $Q<1$. No intersection occurs in this interval because the function $(Q-1)\tan\frac{1}{2}\varphi$ always lies below $\cot N\varphi$ in the entire interval.

The introduction of a heavy impurity, $Q>1$, causes a displacement of the various intersections to the left and yields an associated decrease in normal mode frequencies (the largest possible displacement being $\pi/2N$); that of a light impurity $Q<1$ causes displacements to the right with associated increases in normal mode frequencies (with the exception of the "lost mode" the displacement is limited by $\pi/2N$). The lost mode in the light impurity case corresponds to the localized mode which emerges from the band. It is resurrected by assuming that $\varphi=\pi+i\vartheta$ and considering the characteristic equation for ϑ, $\coth N\vartheta=(Q-1)\times\coth\frac{1}{2}\vartheta$. Then in the limit as $N\to\infty$

$$\exp\vartheta=Q/(Q-2), \tag{A.9}$$

while

$$(\omega/\omega_L)^2=\tfrac{1}{2}(1-\cosh z)=1/Q(2-Q), \tag{A.10}$$

which is exactly (3.20).

The change in zero-point energy of the lattice with one isotope has been worked out in detail in Sec. 4; we shall now check this result for the limiting case $Q\to 0$. In this limit, Eq. (A.8) becomes

$$\cot N\varphi=-\tan\tfrac{1}{2}\varphi, \tag{A.11}$$

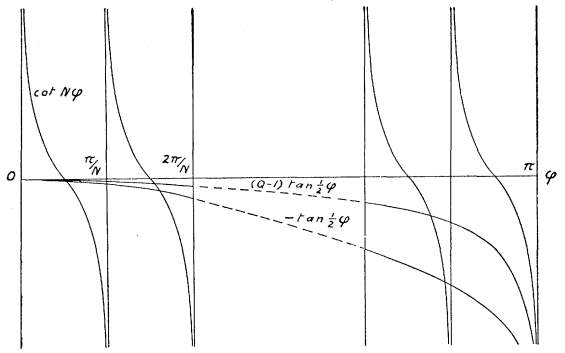


FIG. 11. The solution of Eq. (A.8) can be obtained graphically from the curves sketched above. The right-hand side of (A.8) is sketched for a value $0<Q<1$ and for $Q=0$.

which can be solved exactly:

$$\varphi_j=[(2j-1)\pi/(2N-1)];\ j=1, 2, \cdots, N-1. \tag{A.12}$$

As can be seen in Fig. 11, the first solution

$$\varphi_1=\pi/(2N-1)$$

is near $\pi/2N$ whereas $\varphi_{N-1}=(2N-3)\pi/(2N-1)$ is near $(2N-2)\pi/2N$. The change in zero-point energy contributed by the shifts of the levels in the band is, therefore,

$$\tfrac{1}{2}\hbar\omega_L\left\{\sum_{j=1}^{N-1}\sin\frac{(2j-1)\pi}{2(2N-1)}-\sum_{j=1}^{N}\sin\frac{(2j-1)\pi}{4N}\right\} \tag{A.13}$$

$$=\frac{1}{2}\hbar\omega_L\left\{\frac{1}{2}\operatorname{cosec}\frac{\pi}{2(2N-1)}-\frac{1}{2}-\frac{1}{2}\operatorname{cosec}\frac{\pi}{4N}\right\} \tag{A.14}$$

$$\simeq\frac{1}{2}\hbar\omega_L\left(-\frac{1}{2}-\frac{1}{\pi}\right) \tag{A.15}$$

for large N.

Since the level out of the band contributes

$$\tfrac{1}{2}\hbar\omega_L[Q(2-Q)]^{-\frac{1}{2}}$$

as given by Eq. (4.7a), the change in zero-point energy is thus

$$\frac{1}{2}\hbar\omega_L\left\{[Q(2-Q)]^{-\frac{1}{2}}-\frac{1}{2}-\frac{1}{\pi}+O(Q^{\frac{1}{2}})\right\}. \tag{A.16}$$

This agrees with the expansion given in Eq. (4.15).