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Argonne National Laboratory

VIBRATIONS OF DEFECTS IN LATTICES

by

R. J. Elliott

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IN NUCLEAR SCIENCE ABSTRACTS

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VIBRATIONS OF DEFECTS IN LATTICES

Five lectures by

R. J. Elliott

Prepared from notes by

W. M. Hartmann

Solid State Science Division

RELEASED FOR ANNOUNCEMENT

IN NUCLEAR SCIENCE ABSTRACTS

July 1966

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FOREWORD

This report presents the notes from a series of five lectures on the vibrations of defects in crystals, given by Dr. R. J. Elliott of the Department of Theoretical Physics, Oxford, England. The lectures were given at Argonne National Laboratory in the spring of 1966 when Dr. Elliott was a visiting professor at the University of Illinois, Urbana. The lectures review many theoretical ideas current in research on vibrations in imperfect crystals. Principally they relate the classical Green's-function techniques of Lifshitz and others to the more modern thermodynamic Green's-functions methods. Except for additions of minor details and a list of references, the material here is as presented in the lectures.

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VIBRATIONS OF DEFECTS IN LATTICES

by

R. J. Elliott

I. PERFECT AND IMPERFECT CRYSTALS AND GREEN'S FUNCTIONS

A. Introduction

These lectures will deal with the way in which defects, well localized in a crystal but interacting strongly with the other atoms, change the properties of a perfect crystal. The mathematical methods used to treat this problem are quite general and may be applied to changes in the electronic or magnetic properties of a crystal. We shall be primarily concerned with the effects of defects on lattice vibrations.

The overall properties of a crystal with N unit cells and with a defect in one cell will be altered to order $1/N$. In the region of the defect, however, local properties will be altered to order 1. For example, a Mössbauer active atom is typically a defect in a crystal. The Mössbauer intensity is calculated from the mean-square displacement of the defect atom, and the second-order Doppler shift from the mean-square velocity.

To discuss the effects of defects in optical and neutron spectroscopy, clearly a quantum-mechanical treatment of the problem is necessary. However, as long as we remain in the harmonic approximation, which we shall do for the most part, a classical normal-mode analysis is equivalent to the quantum-mechanical discussion. Indeed, defect-vibration problems may first have been discussed by Lord Raleigh in The Theory of Sound.

Since the 1940's, theoretical interest in these problems has increased, with the work of I. M. Lifshitz and E. W. Montroll and others as a basis. Within the last five years, the theories have been refined and applied to many different experiments.

B. Perfect Crystal

All the methods typically used to solve defect problems can be called Green's-function methods; they relate the properties of an imperfect lattice to those of a perfect lattice.

We may write the harmonic vibrational Hamiltonian for a perfect crystal as

$$H = \sum_{\alpha \ell} \frac{p_{\alpha}^2(\ell, t)}{2M_{\alpha}} + \sum_{\alpha \beta \ell \ell'} \phi_{\alpha \beta}(\ell \ell') u_{\alpha}(\ell, t) u_{\beta}(\ell' t), \quad (1.1)$$

where the potential energy is expanded to second power in the displacements u of an atom in the ℓ^{th} unit cell with cell position $\bar{R}(\ell)$. The particular atom of mass M_{α} within a unit cell is labeled with the subscript α , which also labels Cartesian axes. Thus for s atoms in the unit cell, α takes on $3s$ values.

An important feature of the perfect lattice is its translational symmetry, whence the matrix $\phi_{\alpha \beta}(\ell \ell')$ depends only upon the difference $(\ell - \ell')$ and not upon ℓ and ℓ' individually.

We can find the normal modes of the perfect crystal from the classical equation of motion,

$$M_{\alpha} \ddot{u}_{\alpha}(\ell) + \sum_{\beta \ell'} \phi_{\alpha \beta}(\ell \ell') u_{\beta}(\ell') = 0. \quad (1.2)$$

Note that a quantum-mechanical derivation of this equation could be done by writing the equation of motion for an operator X ,

$$i\hbar \frac{\partial X}{\partial t} = [H, X]. \quad (1.3)$$

Solutions of the form $u \sim e^{i\omega t}$ may be found by solving the dynamical-matrix equation,

$$[\phi_{\alpha \beta}(\ell \ell') - \omega^2 M_{\alpha} \delta_{\alpha \beta} \delta(\ell \ell')] u_{\beta \ell'} = 0 \quad (1.4)$$

for eigenvalues $M_{\alpha} \omega^2$.

The translational symmetry of the perfect crystal makes ϕ a circulant. The matrix ϕ may be divided into N blocks of dimension $3s \times 3s$, all of which have the same form; all blocks taken on any diagonal line of ϕ are equal. Physically, this represents unit cells which are entirely equivalent and in which functions of the particle motion may differ at most by a phase factor $e^{i\bar{q} \cdot \bar{R}(\ell)}$. The normal modes of this system may therefore be found by solving only a $3s \times 3s$ matrix and may be written as

$$Q_{\alpha}^j(\bar{q}) = \sum_{\ell} \sigma_{\alpha}^{+j}(\bar{q}) e^{i\bar{q} \cdot \bar{R}(\ell)} u_{\alpha}(\ell) (M_{\alpha}/N)^{1/2}, \quad (1.5)$$

where j , the branch label, and $\bar{q}$ together take on $3sN$ values, the total number of degrees of freedom. The matrix σ characterizes the motion within a unit cell just as the "u"-function in the typical Bloch-wave treatment of electrons in a crystal characterizes the electrons.

We may adopt the following orthonormalization:

$$\begin{aligned} \sum_{\alpha} \sigma_{\alpha}^{+j}(\bar{q}) \sigma_{\alpha}^{j'}(\bar{q}) &= \delta_{jj'}; \\ \sum_j \sigma_{\alpha}^{+j}(\bar{q}) \sigma_{\beta}^j(\bar{q}) &= \delta_{\alpha\beta}. \end{aligned} \quad (1.6)$$

Three values of j label acoustic phonon branches, and $3(s-1)$ values label optic phonon branches, which are quasicontinuous in $\bar{q}$; the actual modes for a given branch are uniformly distributed in $\bar{q}$ -space with an average spacing $1/N$.

In principle, then, we have all the information about the perfect crystal. The normal modes account for all the spectroscopic properties of the vibrations, and averages over these modes will give us thermodynamic relationships. Group theoretically, the simplicity of the perfect-crystal vibrations may be explained by the fact that the translation group has N elements, corresponding to moving a single unit cell to the positions of all other cells in the crystal, leaving the crystal invariant. There are, therefore, N irreducible representations of the translation group; hence, the symmetry types are largely nondegenerate.

C. Imperfect Crystal

When a defect is put into a crystal, all translational symmetry is destroyed in a single blow. The crystal symmetry is reduced from a structure with N operations of the translation group to a structure that retains only the point symmetry around the defect with ~ 10 operations. The simplifying feature of such a problem is that the defect is localized in a small region of space.

Formally we may write the dynamical equation for the imperfect crystal

$$-\omega^2 M'_{\alpha}(\ell) u_{\alpha}(\ell) + \sum_{\beta \ell'} \phi'_{\alpha\beta}(\ell\ell') u_{\beta}(\ell') = 0, \quad (1.7)$$

with M' and ϕ' including a few changes from M and ϕ due to imperfections. Now the mass is a function of cell index ℓ , and the force constant

depends upon ℓ and ℓ' individually. We define the mass-change parameter

$$\epsilon_{\alpha}(\ell) = \frac{M_{\alpha} - M'_{\alpha}(\ell)}{M_{\alpha}}, \quad (1.8)$$

which will be nonzero for only so many values of ℓ as there are defect atoms in the crystal. The change in force constant is also realistically localized to the region of the defect. If, for example, nearest-neighbor force constants are changed in an fcc crystal, the defect looks like a "molecule" of 13 atoms imbedded in the crystal. The modes of such a "molecule" are characterized by the solutions of a matrix C , defined such that

$$-\omega^2 M' + \phi' = -\omega^2 M + \phi + C. \quad (1.9)$$

Of course, C may contain many such defect molecules; but we shall assume that the defect concentration is small enough so that the defect "blocks" of C are well separated. All other elements of C are zero. Then

$$C_{\alpha\beta}(\ell\ell') = \phi'_{\alpha\beta}(\ell\ell') - \phi_{\alpha\beta}(\ell\ell') + \epsilon_{\alpha}(\ell) M_{\alpha} \omega^2 \delta_{\alpha\beta} \delta(\ell\ell'). \quad (1.10)$$

The modes of C , however, are strongly coupled to the modes of the rest of the crystal.

Formally we may write the normal modes of the entire imperfect crystal as

$$Q(f) = \sum_{\alpha\ell} \chi_{\alpha}(f, \ell) u_{\alpha}(\ell). \quad (1.11)$$

The normal modes of the imperfect crystal are no longer characterized by a wave vector $\bar{q}$ and branch j . In general, the defect mixes phonons of different wave vectors; the label f takes on $3sN$ values to label the imperfect crystal normal modes. We may normalize

$$\sum_{\alpha\ell} M_{\alpha}(\ell) |\chi_{\alpha}(f, \ell)|^2 = 1. \quad (1.12)$$

If we can find the $\chi(f)$'s and eigenvalues $\omega^2(f)$, we shall once again have complete information about the imperfect crystal.

D. Classical Green's Functions

The classical Green's functions correspond to those used in electromagnetic theory. For the perfect crystal they are defined as the inverse of the dynamical equation so that

$$(\omega^2 M - \phi) g = 1, \quad (1.13)$$

or

$$\omega^2 M_{\alpha} g_{\alpha\beta}(\ell\ell') - \sum_{\gamma\ell''} \phi_{\alpha\gamma}(\ell\ell'') g_{\gamma\beta}(\ell''\ell') = \delta_{\alpha\beta} \delta_{\ell\ell'}. \quad (1.14)$$

The dynamical equation that we wish to solve for the imperfect crystal is given by (1.9) as

$$\sum_{\beta\ell'} [-M_{\alpha}\omega^2(f) \delta_{\alpha\beta} \delta(\ell\ell') + \phi_{\alpha\beta}(\ell\ell') + C_{\alpha\beta}(\ell\ell')] \chi_{\beta}(f, \ell') = 0. \quad (1.15)$$

From (1.13), however,

$$g(\omega^2 M - \phi - C) = 1 - gC, \quad (1.16)$$

and (1.15) may be written as

$$\left[\delta_{\alpha\gamma} \delta(\ell\ell'') - \sum_{\beta\ell'} g_{\alpha\beta}(\ell\ell', \omega) C_{\beta\gamma}(\ell'\ell'') \right] \chi_{\gamma}(f, \ell'') = 0. \quad (1.17)$$

To solve this equation we must therefore diagonalize the matrix gC . The eigenvalues are given by the determinant $|1 - gC| = 0$. However, C is a small matrix, and the determinant to be solved is only that of a small block of the size of the defect "molecules." The defect problem can thus be solved exactly and often simply. Since the eigenvalues of the defect "molecules" in isolation would be given by $|C| = 0$, the Green's function serves to couple the defect to the rest of the lattice. The Green's function is a useful object.

To calculate the Green's function, we recall that its inverse $(M\omega^2 - \phi)$ was diagonalized by a transformation

$$S_{\ell\alpha} = \sigma_{\alpha}^{+j}(\bar{q}) e^{i\bar{q}\cdot\bar{R}(\ell)} (M_{\alpha}/N)^{-1/2}. \quad (1.18)$$

Then

$$g_{jj'}(\bar{q}, \bar{q}', \omega) \equiv \frac{1}{N} \sum_{\alpha\beta\ell\ell'} \sigma_{\alpha}^j(\bar{q}) e^{-i\bar{q}\cdot\bar{R}(\ell)} g_{\alpha\beta}(\ell, \ell', \omega) \times \sigma_{\beta}^{+j'}(\bar{q}') e^{i\bar{q}'\cdot\bar{R}(\ell')} (M_{\alpha}M_{\beta})^{1/2} \quad (1.19)$$

is equal to

$$\frac{\delta_{jj'} \delta(\bar{q}, \bar{q}')}{-\omega_j^2(\bar{q}) + \omega^2} \quad (1.19)$$

and

$$g_{\alpha\beta}(\ell\ell') = \sum_{j\bar{q}} \frac{\sigma_{\alpha}^{+j}(\bar{q}) \sigma_{\beta}^j(\bar{q}) e^{i\bar{q} \cdot (\bar{R}(\ell) - \bar{R}(\ell'))}}{-\omega_j^2(\bar{q}) + \omega^2} \left(\frac{1}{M_{\alpha} M_{\beta} N^2} \right)^{1/2} \quad (1.20)$$

II. SOLUTIONS OF THE PERTURBED DYNAMICAL MATRIX; ELECTRON AND MAGNON ANALOGIES

A. Introduction

In Section I we developed a technique by which the normal modes of vibration and frequencies of a crystal with a single localized imperfection could be found. Before using the technique to solve a problem of a particular defect in a particular type of crystal, let us examine the form of the solutions we expect and also consider the analogous electron and magnon defect problems.

B. Spectrum of Perturbed Modes

The frequencies of the perturbed modes in the defect crystal were shown to be given by the roots of the determinant

$$|1 - gC| = 0. \quad (2.1)$$

The elements of this determinant have the form

$$1 - \sum_{j\bar{q}} \frac{1}{\omega_j^2(\bar{q}) - \omega^2} f(\omega, \bar{q}) = 0, \quad (2.2)$$

where f is some function and the determinant will involve various products of such terms. Without losing much generality, we may consider the case in which the matrix C is only a single number and the solution of (2.2) is

$$\sum_{j\bar{q}} [\omega_j^2(\bar{q}) - \omega^2]^{-1} = f^{-1}(\omega, \bar{q}). \quad (2.3)$$

A conceptual plot of the two sides of this equation appears in Fig. 1. The poles on the left-hand side occur at the frequencies of the modes of the perfect crystal, of which only a few of the total $3sN$ have been shown. The intersections are at the frequencies of imperfect-crystal modes, which are seen to intersperse the modes of the perfect crystal, covering the same band. The exception occurs for the possible intersection outside the band where there may be isolated solutions.

Fig. 1. A Conceptual Plot of Condition (2.3) for Perturbed Solutions of the Defect Problem

These two types of solution are quite different. The "in-band" modes are modes covering the entire

crystal, which are perturbed only in the region of the defect and have their frequencies altered by $O(1/N)$. The modes outside the band are at a frequency

that the perfect crystal will not propagate. If the perfect crystal is thought of as a filter, one may say that the high frequency is outside the pass band of the filter. The defect vibrations of this frequency are localized in space at the defect and fall off exponentially away from the defect; they are called localized modes.*

The localized modes are the more dramatic and are more easily seen experimentally. The perturbed-band modes, altered to $O(1/N)$ in the crystal as a whole, are nevertheless important in the region of the defect where they are altered to $O(1)$. They are therefore important in situations in which the modes are probed by the defect.

As a simple example, consider the case of a single defect mass at the origin, coupled to the rest of the crystal with perfect-crystal force constants. Then, from Eq. (1.10),

$$C_{\alpha\beta}(\ell\ell') = \begin{pmatrix} \epsilon\omega^2 M_\alpha & & \\ & \epsilon\omega^2 M_\alpha & \\ & & \epsilon\omega^2 M_\alpha \end{pmatrix} \delta_{\ell\ell'} \delta_{\ell 0} \delta_{\alpha\beta}. \quad (2.4)$$

We shall see later that for a cubic crystal with such a defect, $f(\bar{q}, \omega)$ of Eq. (2.3) is equal to $-\epsilon\omega^2$. If the defect is a light atom ($\epsilon > 0$), its natural vibrations will be at a frequency above those of the unperturbed band, since $\omega \sim \sqrt{K/M}$, where K is a generalized force constant. If the defect is heavy ($\epsilon < 0$), the natural defect vibrations will be of lower frequencies. The appropriate curve for $f(\bar{q}, \omega)$ drawn on Fig. 1 would intersect outside the band for $\epsilon > 0$, but only inside for $\epsilon < 0$.

C. Analogies between Defect Problems

1. Electron Problem (Energy-band Theory)

As a first analogy to the vibration of defects, let us consider the motion of electrons, as opposed to phonons, in a crystal with a defect. Mathematically the analogy holds very well. Consider the electron Hamiltonian

$$H = \frac{p^2}{2m} + V, \quad (2.5)$$

with the Bloch-wave solutions $\psi = u_{\bar{k}} e^{i\bar{k} \cdot \bar{r}}$ and energies $\epsilon_{\bar{k}}$.

---

*Some confusion in terminology is occasionally found in the literature where "localized mode" or "quasilocalized mode" is used to designate defect modes in general, including perturbed-band modes.

If we define annihilation and creation operators for an electron in the $\bar{k}$ state by their operations on states of n such particles,

$$\begin{aligned} a_{\bar{k}}^- | n_{\bar{k}} \rangle &= \sqrt{n_{\bar{k}}} | n_{\bar{k}} - 1 \rangle, \\ a_{\bar{k}}^\pm | n_{\bar{k}} \rangle &= \sqrt{n_{\bar{k}} + 1} | n_{\bar{k}} + 1 \rangle, \end{aligned} \quad (2.6)$$

then

$$H = \epsilon_{\bar{k}} a_{\bar{k}}^\pm a_{\bar{k}}^-. \quad (2.7)$$

From (2.6), clearly $a_{\bar{k}}^\pm a_{\bar{k}}^-$ is the number operator, diagonal on states $| n_{\bar{k}} \rangle$ and counting the number of such electrons. In terms of the Fourier transforms,

$$\begin{aligned} a_{\bar{R}}^- &= \frac{1}{\sqrt{N}} \sum_{\bar{k}} a_{\bar{k}}^- e^{i\bar{k} \cdot \bar{R}}, \\ a_{\bar{R}}^\pm &= \frac{1}{\sqrt{N}} \sum_{\bar{k}} a_{\bar{k}}^\pm e^{-i\bar{k} \cdot \bar{R}}, \end{aligned} \quad (2.8)$$

and

$$H = V_0 \sum_{\bar{R}} a_{\bar{R}}^\pm a_{\bar{R}}^- + \sum_{\bar{\delta}} V_{\bar{\delta}} \sum_{\bar{R}} a_{\bar{R}}^\pm a_{\bar{R}+\bar{\delta}}^-, \quad (2.9)$$

whereupon

$$\epsilon_{\bar{k}} = V_0 + \sum_{\bar{\delta}} V_{\bar{\delta}} e^{i\bar{k} \cdot \bar{\delta}}. \quad (2.10)$$

The eigenfunctions of (2.9) are Wannier functions, where the electron is localized about $\bar{R}$ and hence are well suited to a treatment of localized perturbations. The two summands in (2.9) are, respectively, the energy of an electron localized at $\bar{R}$ and an electron migration energy $V_{\bar{\delta}}$.

The eigenvalues of the perfect crystal are simply those of the matrix $V(\bar{R}, \bar{R} + \bar{\delta})$. Because of the translational symmetry, $V(\bar{R}, \bar{R} + \bar{\delta})$ depends only upon the difference $\bar{\delta}$ and is a circulant like the dynamical matrix ϕ . The electron problem is then equivalent to the vibrational problem.

The additional potential seen by an electron due to an isolated defect atom may be written as

$$\sum_{\bar{R}_1 \bar{R}_2} U_{\bar{R}_1 \bar{R}_2} a_{\bar{R}_1}^+ a_{\bar{R}_2}, \quad (2.11)$$

where the sum is over a few values $\bar{R}_1 \bar{R}_2$. The additional potential U is completely analogous to the defect matrix C in the vibrational case, and the method of solution is again the same.

For example, consider a single defect at the origin in the simple case in which the perfect crystal is described by a single band of free electrons $\epsilon_{\bar{k}} = \hbar^2 k^2 / 2m$. Then the defect potential is the only potential in the whole problem, and we simply need solutions for an electron in a potential well. The solutions are of two types. The positive-energy wave functions are not changed except for a phase shift, and the only appreciable difference occurs in the region of the well (defect). If the well is of sufficient complexity that there is a state in the well with the energy of some state outside, we may find a resonance, where electrons tend to pile up in the defect region tunneling out into the potential free region. These states are then likewise continuum states but with strong enhancement near the defect. On the other hand, the well may have a proper bound state, of an energy outside the band of continuum states. Clearly, the first solution corresponds to the perturbed-band modes of the vibrational problem with the possibility of resonance behavior, and the second corresponds to the localized mode.

2. Magnon Problem

We shall indicate very briefly how an identical formalism may be applied to find the magnon spectrum of an imperfect magnetic crystal. The Hamiltonian is given by the exchange interaction

$$H = - \sum_{i \neq j} J_{ij} \bar{S}(\bar{R}_i) \cdot \bar{S}(\bar{R}_j). \quad (2.12)$$

In the ferromagnetic ground state ψ_0 , all spins $\bar{S}(\bar{R})$ are aligned with maximum spin S along the negative z -axis. The magnon represents a deviation from this perfect alignment. We may call an excited state with one spin, the k^{th} , turned up ψ_k . This state is not an eigenfunction of the Hamiltonian, which may be seen by writing it in terms of spin-raising and -lowering operators S^+ and S^- , where

$$\begin{aligned} S_i^+ &= S_i^x + i S_i^y, \\ S_i^- &= S_i^x - i S_i^y, \end{aligned} \quad (2.13)$$

and

$$H = - \sum_{i \neq j} J_{ij} \left[S_i^z S_j^z + \frac{1}{2} (S_i^+ S_j^- + S_i^- S_j^+) \right]. \quad (2.14)$$

Then

$$(H - E_0) \psi_k = 2S \sum_j J_{kj} \psi_k - 2S \sum_{j \neq k} J_{kj} \psi_j, \quad (2.15)$$

where E_0 is the ground-state energy

$$-S^2 \sum_{i \neq j} J_{ij}.$$

The proper spin-deviation states are magnon states in which the spin deviation propagates with a wave vector $\bar{q}$; they may be found by the usual technique of Fourier transforming ϕ_k into $\bar{q}$ -space. A localized defect is once again treated in the "site" representation as a change ΔJ in J_{kj} , the analog of the dynamical matrix. Again, solutions of perturbed-band modes are found in the band of the perfect crystal and solutions of localized modes are at frequencies beyond the perfect magnon cutoff.

III. RESPONSE OF A SYSTEM TO A FORCE AND DOUBLE-TIME GREEN'S FUNCTIONS

A. Introduction

In Sections I and II we showed that the normal vibrational modes and frequencies of a crystal with a single defect could be obtained from the solution of the determinantal equation $|1 - gC| = 0$. The solutions were of two types: localized modes, at a frequency above the maximum frequency of the perfect-crystal modes; and "in-band" modes, which covered the entire crystal with possible enhancement near the defect. In principle, then, the problem was solved.

However, a solution in terms of normal modes is not always useful. In particular, experiments to detect changes in the band modes will not observe normal modes but physical quantities, such as the thermal conductivity or the electrical susceptibility. It is, therefore, more useful to solve the defect problem for the changes in actual physical quantities than for normal modes. We shall show how the Green's-function g acts to give the response of a system to an external force. We shall then develop a quantum-mechanical Green's-function technique, which will lead directly to thermally averaged observable quantities.

B. Response of a System to a Force

Consider a time-dependent force $F_\alpha(\ell, t)$ applied in a certain direction to an atom (α) in the ℓ th cell, for example, an electromagnetic field $\bar{E}$ applied to a charge e , where $\bar{F} = e\bar{E}$. The response of the system then will measure the dielectric constant. With the equation of motion for a perfect crystal

$$M_\alpha \ddot{u}_\alpha(\ell, t) + \sum_{\ell' \beta} \phi_{\alpha\beta}(\ell\ell') u_\beta(\ell', t) = F_\alpha(\ell, t), \quad (3.1)$$

we seek solutions of a certain frequency and Fourier transform (3.1). The driving term becomes

$$\bar{F}(\omega) = \int \bar{F}(t) e^{i\omega t} dt, \quad (3.2)$$

and in matrix form

$$(-M\omega^2 + \phi) \bar{u} = \bar{F}. \quad (3.3)$$

From the definition of g in (1.13),

$$-\bar{u} = g\bar{F}, \quad (3.4)$$

or

$$-u_{\alpha}(\ell\omega) = \sum_{\ell'\beta} \sum_{j\bar{q}} \frac{\sigma_{\alpha}^{+j}(\bar{q}) \sigma_{\beta}^j(\bar{q})}{\omega^2 - \omega_j^2(\bar{q})} \frac{e^{i\bar{q} [\bar{R}(\ell) - \bar{R}(\ell')]} N(M_{\alpha}M_{\beta})^{1/2}}{F_{\beta}(\ell', \omega)}. \quad (3.5)$$

The Green's function, originally introduced to couple a defect to the rest of the crystal, serves as well to relate the displacement in the crystal to an applied force.

Consider another example in which the applied force $\bar{F}$ is proportional to some normal displacement coordinate of the system $\bar{Q}^j(\bar{q}, \omega)$; then the response will occur only in this normal coordinate because, by (1.19),

$$-\bar{Q}^{j'}(\bar{q}', \omega) = g_{jj'}(qq', \omega) \bar{F} \quad (3.6)$$

$$= \frac{\delta_{jj'} \delta_{qq'}}{\omega_j^2(\bar{q}) - \omega^2} \bar{F}. \quad (3.7)$$

The response is of the familiar resonant form.

Equations (3.5) and (3.7) have singular behavior at resonances. These singularities may be handled by a mathematical trick, which is also physically significant. If a small imaginary part γ is added to ω , then g becomes a complex function. We then let γ tend to zero applying the rule

$$\lim_{\gamma \rightarrow 0} \frac{1}{\chi + i\gamma} = P\left(\frac{1}{\chi}\right) - i\pi\delta(\chi), \quad (3.8)$$

where P denotes the principal part. Then the real and imaginary parts of a Green's function

$$\frac{1}{\omega^2 - \omega_j^2(\bar{q})}$$

are given by

$$\frac{1}{\omega^2 - \omega_j^2(\bar{q})} = P \frac{1}{\omega^2 - \omega_j^2(\bar{q})} - \frac{i\pi}{2\omega} \{\delta[\omega - \omega_j(\bar{q})] - \delta[\omega + \omega_j(\bar{q})]\}. \quad (3.9)$$

The physical significance of γ may be seen by realizing that in a realistic system a displacement $\bar{u}(\ell, t)$ will be damped in time by anharmonic vibrations or another mechanism. Then $\bar{u} \sim e^{i\omega t - \gamma t}$, i.e., $\omega \rightarrow \omega + i\gamma$, whence g is complex. The system response to a radiation field, for example, will then be complex. From (3.4),

$$\bar{u} = g e \bar{E}. \quad (3.10)$$

Since the dipole moment $\bar{\mu}$ is equal to $e\bar{u}$, we have for the polarizability α

$$\alpha_{\alpha\beta}(\omega) = e^2 g_{\alpha\beta}. \quad (3.11)$$

The polarizability is now a complex function, the imaginary part of which represents the absorption of radiation.

The complex frequency allows us to convert the sum

$$\sum_{j\bar{q}} \frac{1}{\omega^2 - \omega_j^2(\bar{q})}$$

to an integral along the real axis from which the poles have been removed. Thus,

$$\begin{aligned} \frac{1}{3sN} \sum_{j\bar{q}} \frac{1}{\omega^2 - \omega_j^2(\bar{q})} &= P \int \frac{\nu(\omega')}{\omega^2 - \omega'^2} d\omega' \\ &- \frac{i\pi}{2\omega} \sum_{j\bar{q}} \{ \delta[\omega - \omega_j(\bar{q})] - \delta[\omega + \omega_j(\bar{q})] \} (3sN)^{-1}, \end{aligned} \quad (3.12)$$

where $\nu(\omega)$ is a density of states (number of states per unit ω) normalized to unity; i.e.,

$$\int_0^{\omega_m} \nu(\omega) d\omega = 1. \quad (3.13)$$

But

$$\frac{1}{3sN} \sum_{j\bar{q}} \delta[\omega - \omega_j(\bar{q})] = \nu(\omega), \quad (3.14)$$

and the sum (3.12) equals

$$P \int \frac{\nu(\omega')}{\omega^2 - \omega'^2} d\omega' - \frac{i\pi}{2\omega} [\nu(\omega) + \nu(-\omega)]. \quad (3.15)$$

Thus far in this section we have been concerned with only perfect crystals. The extension to imperfect crystals will be shown to result in a simple relationship between perfect- and imperfect-crystal Green's functions. The analog of Eq. (3.3) is

$$(-M'\omega^2 + \phi') \bar{u} = \bar{F}. \quad (3.16)$$

We define

$$G = (M'\omega^2 - \phi')^{-1} \quad (3.17)$$

and

$$-\bar{u} = G\bar{F}. \quad (3.18)$$

Now

$$G^{-1} = M'\omega^2 - \phi' = M\omega^2 - \phi - C = (M\omega^2 - \phi)(1 - gC) = g^{-1}(1 - gC) \quad (3.19)$$

or

$$G = g(1 - gC)^{-1}. \quad (3.20)$$

Just as the normal-mode frequencies of the perfect crystal are given by the poles of g , the frequencies of the imperfect crystal are given by the poles of G , where $|1 - gC| = 0$ in agreement with our previous result.

The Green's-function technique used here is only one method for solving problems of this sort. If $\bar{F}$ is due to a thermal fluctuation within the system, the problem can be solved by employing noise theorems such as the generalized Nyquist theorem. In any case, any problem that can be solved with Green's functions can be solved in some other way as well. In many-body theory, the use of Green's functions often suggests new ideas for approximations. In the harmonic approximation, our problem is not a many-body problem, but we shall find many-body-type Green's functions to be useful, particularly in dealing with resonances.

C. Double-time Green's Functions

The modern quantum-mechanical Green's functions are a device used to calculate thermally averaged correlation functions and hence observable quantities with no particular reference to a normal-mode analysis.

The correlation functions may arise in the following way: If a small force $F_\alpha(\ell) e^{i\omega t}$ perturbs a quantum-mechanical system, the perturbed part of the Hamiltonian is

$$H_1 = -u_\alpha(\ell) F_\alpha(\ell) e^{i\omega t} \quad (3.21)$$

The time-averaged expectation value of $u_\beta(\ell')$ in the perturbed system then involves matrix elements between all states m , thermally populated, and n and is proportional to

$$\sum_m e^{-\beta E_m} \sum_n \frac{\langle m | u_\alpha(\ell) | n \rangle \langle n | u_\beta(\ell') | m \rangle}{E_m - E_n + \hbar\omega} / \sum_m e^{-\beta E_m}, \quad (3.22)$$

where $\beta = 1/kT$ and $|m\rangle$ are eigenstates of the unperturbed Hamiltonian. If $\omega \rightarrow \omega + i\gamma$, the imaginary part of (3.22) equals

$$\frac{-\pi \sum_m e^{-\beta E_m} \sum_n \langle m | u_\alpha(\ell) | n \rangle \langle n | u_\beta(\ell') | m \rangle \delta(E_m - E_n + \hbar\omega)}{\sum_m e^{-\beta E_m}}. \quad (3.23)$$

We shall soon see that (3.23) is the Fourier transform of a double-time correlation function.

Consider a thermally averaged correlation function

$$\langle A(t) B(t') \rangle_T \equiv F_{AB}(t - t'), \quad (3.24)$$

depending only upon the difference in times $t - t'$, where

$$\langle \dots \rangle_T = \frac{\sum_m \langle m | \dots | m \rangle e^{-\beta E_m}}{\sum_m e^{-\beta E_m}}. \quad (3.25)$$

We lose no generality in setting $t' = 0$, and we define

$$\begin{aligned} F_{AB}(t) &\equiv \langle A(t) B(0) \rangle_T; \\ F_{BA}(t) &\equiv \langle B(0) A(t) \rangle_T. \end{aligned} \quad (3.26)$$

We define the Fourier transform

$$F_{AB}(t) = \int J(\omega) e^{-i\omega t} d\omega. \quad (3.27)$$

If we take the time Fourier transform of (3.23), letting $u_\alpha(\ell) = A$, $u_\beta(\ell') = B$, we find

$$\begin{aligned} \int (3.23) e^{i\omega t} dt &= \left(\sum_m e^{-\beta E_m} \right)^{-1} \\ &\times \left(\sum_m e^{-\beta E_m} \sum_n \langle m|A|n\rangle \langle n|B|m\rangle e^{(i/\hbar)(E_n - E_m)t} \right). \end{aligned} \quad (3.28)$$

Since H is diagonal on states $|m\rangle$, or

$$\langle m|e^{iHt/\hbar}|m'\rangle = e^{iE_m t/\hbar} \delta_{mm'}, \quad (3.29)$$

the term inside the sums in (3.28) is

$$\sum_{m'm''} \langle m|e^{-iHt/\hbar}|m'\rangle \langle m'|A|m''\rangle \langle m''|e^{iHt/\hbar}|n\rangle \langle n|B|m\rangle. \quad (3.30)$$

Performing the sums in (3.30) by closure, we find

$$\langle m|e^{iHt/\hbar} A e^{iHt/\hbar}|n\rangle \langle n|B|m\rangle. \quad (3.31)$$

The left-hand bracket contains the Heisenberg operator $A(t)$. We may now sum on n by closure, and (3.28) becomes

$$\left(\sum_m e^{-\beta E_m} \right)^{-1} \sum_m e^{-\beta E_m} \langle m|A(t) B(0)|m\rangle = F_{AB}(t). \quad (3.32)$$

We have thus established the connection between second-order perturbation theory and the correlation function $F_{AB}(t)$.

The correlation function $F_{BA}(t)$ may also be found in terms of $J(\omega)$, simply by interchanging state labels m and n in (3.28). Then, since the Fourier transform of $J(\omega)$ requires $E_n - E_m = \hbar\omega$,

$$F_{BA} = \int J(\omega) e^{-\beta\hbar\omega} e^{-i\omega t} d\omega. \quad (3.33)$$

The observable properties of a physical system now may be calculated from the spectral representation $J(\omega)$. We shall define Green's functions, which will be used to calculate $J(\omega)$ according to a prescription. Define retarded (R) and advanced (A) Green's functions designated by

$$G(t) = \frac{2\pi}{\hbar} \langle\langle A(t); B(0) \rangle\rangle, \quad (3.34)$$

where

$$\frac{\hbar}{2\pi} G_A(t) = i\theta(-t) \langle[A(t), B(0)]\rangle_T, \quad (3.35a)$$

and

$$\frac{\hbar}{2\pi} G_R(t) = -i\theta(t) \langle[A(t), B(0)]\rangle_T, \quad (3.35b)$$

where

$$\begin{aligned} \theta(t) &= 0 & \text{for } t < 0 \\ &= 1 & \text{for } t \geq 0. \end{aligned} \quad (3.36)$$

Using

$$\theta(t) = \lim_{\gamma \rightarrow 0} \int_{-\infty}^t e^{\gamma\tau} \delta(\tau) d\tau, \quad (3.37)$$

and

$$\delta(\tau) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\chi\tau} d\chi, \quad (3.38)$$

whence

$$\theta(t) = \lim_{\gamma \rightarrow 0} \frac{i}{2\pi} \int_{-\infty}^{\infty} \frac{e^{-i\chi t}}{\chi + i\gamma} d\chi, \quad (3.39)$$

we consider the frequency Fourier transform of $G_R(t)$, which by the convolution theorem equals

$$\int d\omega' \int \langle [A(\tau), B(0)] \rangle_T e^{i\omega'\tau} d\tau \int \theta(-\tau') e^{i(\omega-\omega')\tau'} d\tau'. \quad (3.40)$$

Then from (3.39), (3.27), and (3.33),

$$G_R(\omega) = \frac{1}{\hbar} \int_{-\infty}^{\infty} \frac{J(\omega')(1 - e^{-\beta\hbar\omega'})}{\omega - \omega' + i\gamma} d\omega', \quad (3.41)$$

similarly,

$$G_A(\omega) = \frac{1}{\hbar} \int_{-\infty}^{\infty} \frac{J(\omega')(1 - e^{-\beta\hbar\omega'})}{\omega - \omega' - i\gamma} d\omega'. \quad (3.42)$$

In the complex plane of ω , G_R is analytic in the upper half-plane and G_A in the lower half-plane. We may define G , analytic for all ω , as

$$G = \begin{cases} G_R & \text{for } \text{Im } \omega > 0 \\ G_A & \text{for } \text{Im } \omega < 0. \end{cases} \quad (3.43)$$

Then we can show that

$$\lim_{\gamma \rightarrow 0} \text{Im}[G(\omega + i\gamma) - G(\omega - i\gamma)] = \frac{2\pi}{\hbar} (e^{-\beta\hbar\omega} - 1) J(\omega). \quad (3.44)$$

Therefore $J(\omega)$ can be found if Green's functions G are known.

G may be determined from the Heisenberg, equation of motion $i\hbar dX/dt = [X, H]$, as follows:

$$\frac{i\hbar^2}{2\pi} \frac{dG}{dt} = \hbar \delta(t) \langle [A, B] \rangle + \langle\langle [A, H]; B \rangle\rangle. \quad (3.45)$$

Generally the equations of motion for a Green's function generate further Green's functions. By successive differentiation, a whole hierarchy of Green's functions can be formed, and in the usual many-body problem some cutoff approximation must be used. But the harmonic-oscillator problem is solvable.

Let us define u - u , u - p , and p - p Green's functions as follows:

$$\begin{aligned}
G_{\alpha\beta}(\ell\ell') &= \frac{2\pi}{\hbar} \langle\langle u_{\alpha}(\ell, t); u_{\beta}(\ell', 0) \rangle\rangle; \\
H_{\alpha\beta}(\ell\ell') &= \frac{2\pi}{\hbar} \langle\langle u_{\alpha}(\ell, t); p_{\beta}(\ell', 0) \rangle\rangle; \\
F_{\alpha\beta}(\ell\ell') &= \frac{2\pi}{\hbar} \langle\langle p_{\alpha}(\ell, t); p_{\beta}(\ell', 0) \rangle\rangle.
\end{aligned} \tag{3.46}$$

We shall use a harmonic Hamiltonian of the form (1.1), except that we need not assume the crystal to be a perfect one at this stage. Accordingly, $M_{\alpha}(\ell)$ will depend upon ℓ and will be designated by $M'_{\alpha}(\ell)$, and the force-constant matrix $\phi_{\alpha\beta}(\ell\ell')$ may depend upon ℓ and ℓ' individually and will be designated by $\phi'_{\alpha\beta}(\ell\ell')$; i.e.,

$$H = H_0 - \bar{u} \cdot C \cdot \bar{u}. \tag{3.47}$$

Then Eq. (3.45) becomes

$$\frac{i\hbar^2}{2\pi} \frac{dG}{dt} = \hbar \delta(t) \langle [u_{\alpha}(\ell, t), u_{\beta}(\ell', 0)] \rangle + \frac{i\hbar}{M'_{\alpha}(\ell)} \langle\langle p_{\alpha}(\ell, t); u_{\beta}(\ell', 0) \rangle\rangle. \tag{3.48}$$

The first term is zero since two displacements at the same time ($t = 0$) commute. If we differentiate a second time, we find

$$\begin{aligned}
& -M'_{\alpha}(\ell) \frac{d^2}{dt^2} G_{\alpha\beta}(\ell\ell', t) \\
& = 2\pi \delta_{\alpha\beta} \delta(\ell, \ell') \delta(t) + \sum_{\gamma\ell''} \phi'_{\alpha\gamma}(\ell\ell'') G_{\gamma\beta}(\ell''\ell', t),
\end{aligned} \tag{3.49a}$$

or

$$(M'_{\alpha} \omega^2 - \phi'_{\alpha}) G = 2\pi. \tag{3.49b}$$

The dynamical equation is then in closed form, expressed only in terms of Green's function G . Equation (3.49b) makes it clear that the Green's function that was introduced in the first two sections is actually the $u - u$ Green's function. (The equations of motion for H and F Green's functions are also in closed form but are different.) To be sure, these complicated Green's functions do not appear to resemble the classical Green's functions of electromagnetic theory, but they have the advantage that through Eq. (3.44) thermally averaged observable properties may be calculated directly.

IV. PHYSICAL RESULTS FROM A DOUBLE-TIME GREEN'S-FUNCTION TREATMENT

A. Introduction

In Section III we presented a prescription for the correlation function of two displacements at different times and places in terms of the Fourier transform of a Green's function,

$$\int e^{i\omega t} \langle\langle u_{\alpha}(\ell, t); u_{\beta}(\ell', 0) \rangle\rangle dt. \quad (4.1)$$

We solved a harmonic quantum-mechanical equation of motion for the $u - u$ Green's function G , which was the same as the response function previously discussed.

In the harmonic approximation, G is temperature-independent [Eq. (3.49b)]. Then from (3.44) the spectral intensity varies like

$$J(\omega) \sim (e^{-\beta\hbar\omega} - 1)^{-1}, \quad (4.2)$$

related to the Bose-Einstein distributions as would be expected for a system of noninteracting bosons.

Recall that for a perfect lattice [Eq. (1.13)],

$$g = (M\omega^2 - \phi)^{-1}, \quad (4.3)$$

and for a lattice with a defect [Eq. (3.20)],

$$G = (1 - gC)^{-1} g. \quad (4.4)$$

Then,

$$G = g + gC(1 - gC)^{-1} g, \quad (4.5)$$

a scattering-matrix form where the second term corresponds to the scattered-wave contribution from a defect C . We may expand

$$X \equiv C(1 - gC)^{-1} = C + CgC + CgCgC + \dots, \quad (4.6)$$

in a perturbation series and notice that since each term of X begins and ends with the small matrix C , the matrix X is equally small, covering only a few values of ℓ and ℓ' .

Then if the defect is only at the origin, $\ell = \ell' = 0$,

$$G(\ell\ell') = g(\ell\ell') + g(\ell 0) X(00) g(0\ell'); \quad (4.7)$$

i.e., the $u(\ell) - u(\ell')$ correlation function in an imperfect crystal is the same as in the perfect crystal, plus a correction term due to a defect at $\ell = 0$. We shall now apply the mathematical methods derived previously to the problem of a simple defect at the origin.

B. Single Mass Defect

We consider a monatomic crystal with a single wrong mass M' at the origin. Then, from (2.4),

$$C_{\alpha\beta}(\ell\ell') = \epsilon M \omega^2 \delta_{\alpha\beta} \delta(\ell 0) \delta(\ell' 0), \quad (4.8)$$

where

$$\epsilon = \frac{M - M'}{M}. \quad (4.9)$$

Since localized and resonant modes will occur where

$$\text{Re}[1 - g(00, \omega) C(00)] = 0, \quad (4.10)$$

let us consider $g_{\alpha\beta}(00)$. From (1.20),

$$g_{\alpha\beta}(00) = \frac{1}{N} \sum_{j\bar{q}} \frac{\sigma_{\alpha}^{j+}(\bar{q}) \sigma_{\beta}^j(\bar{q})}{\omega^2 - \omega_j^2(\bar{q})} \left(\frac{1}{M_{\alpha} M_{\beta}} \right)^{1/2} \quad (4.11)$$

for a perfect lattice. In a cubic lattice, x, y, and z directions are all equivalent, and we expect $g_{xx} = g_{yy} = g_{zz}$.

The sums over wave vectors $\bar{q}$ in (4.11) may be separated into a sum of sums over a "star" of $\bar{q}$ values defined by operating on a particular $\bar{q}$ with the rotation elements of the perfect-crystal space group; $\omega_j(\bar{q})$ is then the same for all $\bar{q}$ in the star. If we perform a reflection in, for example, the x - z mirror plane, we turn σ_y into σ_{-y} . For any star,

$$\sum_{\bar{q}}^* \sigma_y^{j+}(\bar{q}) \sigma_z^j(\bar{q}) = \sum_{\bar{q}}^* \sigma_{-y}^{j+}(\bar{q}) \sigma_z^j(\bar{q}), \quad (4.12)$$

because for every $\sigma_y^j(\bar{q}_1)$, for $\bar{q}_1$ in the star, there will be a wave vector $\bar{q}_2$ in the star for which $\sigma_y^j(\bar{q}_1) = \sigma_{-y}^j(\bar{q}_2)$. However, since for every $\bar{q}$ in

the star, $\sigma_y^j(\bar{q}) = -\sigma_y^j(\bar{q})$, any star sum of the form (4.12) will vanish. Therefore, $g_{\alpha\beta}(\ell\ell)$ is diagonal on $\alpha\beta$ for perfect crystals of cubic symmetry.

1. Local Modes

From the normalization (1.6) and (3.13) for $\omega > \omega_m$, where there are no singularities,

$$g_{\alpha\beta}(00, \omega) = \frac{\delta_{\alpha\beta}}{M} \int \frac{\nu(\omega') d\omega'}{\omega^2 - \omega'^2}. \quad (4.13)$$

Then the local mode frequency ω_ℓ is given by the condition

$$1 - \epsilon\omega_\ell^2 \int \frac{\nu(\omega') d\omega'}{\omega_\ell^2 - \omega'^2} = 0. \quad (4.14)$$

It is natural to ask if we can get more information from the second, quantum-mechanical, Green's-function approach where, from Eq. (4.4),

$$G_{\alpha\beta}(00) = \sum_{\gamma} (1 - g_{00}C_{00})_{\alpha\gamma}^{-1} g_{\gamma\beta}(00) \quad (4.15)$$

$$= \delta_{\alpha\beta} \frac{g_{\alpha\alpha}(00)}{1 - M\epsilon\omega^2 g_{\alpha\alpha}(00)}. \quad (4.16)$$

We shall be interested in the imaginary part of $G(00)$, and we replace ω by $\omega + i\gamma$ and let γ tend to zero. Near the resonance, where the denominator of (4.16) will be zero, we may expand

$$G_{\alpha\alpha}(00, \omega) = \frac{-g_{\alpha\alpha}(00, \omega_\ell)}{(\omega - \omega_\ell) \left[\frac{d}{d\omega} M\epsilon\omega^2 g_{\alpha\alpha}(00, \omega) \right]_{\omega=\omega_\ell}}, \quad (4.17)$$

and from Eq. (3.8),

$$\text{Im}G_{\alpha\alpha}(00, \omega) = \pi\delta(\omega - \omega_\ell) \frac{g_{\alpha\alpha}(00, \omega_\ell)}{\left[\frac{d}{d\omega} M\epsilon\omega^2 g_{\alpha\alpha}(00, \omega) \right]_{\omega=\omega_\ell}}. \quad (4.18)$$

The denominator may be immediately differentiated and the expression simplified with (4.14). Then we have, for the frequency Fourier transform of the thermally averaged correlation function for mean-square displacement of the defect,

$$J(\omega) = \hbar \frac{\delta(\omega - \omega_\ell)(e^{-\beta\hbar\omega} - 1)^{-1}}{(M\epsilon\omega_\ell)^2 \frac{d}{d\omega} \omega^2 g(\omega) \Big|_{\omega=\omega_\ell}} \quad (4.19)$$

If we add together the contributions from $\pm\omega$, the thermal factors

$$(e^{-\beta\hbar\omega} - 1)^{-1} - (e^{\beta\hbar\omega} - 1)^{-1} = -\coth \frac{1}{2}\beta\hbar\omega \quad (4.20)$$

give the usual harmonic-oscillator result.

The actual normal-mode coordinates may be obtained directly from the Green's function for the conjugate operators. From Eq. (3.48),

$$\int \frac{i}{\hbar} \ll P_\alpha(\ell, t); u_\beta(\ell', 0) \gg e^{i\omega t} dt = M'_\alpha(\ell) \omega G_{\alpha\beta}(\ell, \ell', \omega). \quad (4.21)$$

The spectral function comparable to J in this case contains the thermal factor

$$(e^{-\beta\hbar\omega} - 1)^{-1} + (e^{\beta\hbar\omega} - 1)^{-1} = -1, \quad (4.22)$$

i.e., there is no temperature dependence, and the square of the localized normal-mode amplitude at the defect is given by

$$M'|\chi(0)|^2 = \frac{1 - \epsilon}{M\epsilon^2\omega_\ell \frac{d}{d\omega} \omega^2 g(\omega) \Big|_{\omega=\omega_\ell}} \quad (4.23)$$

The quantum-mechanical Green's functions have not only given us the resonant frequency but also the strength of local-mode vibrations at the defect. To determine the space localization of the local mode, we might calculate

$$G(0, \ell) = \frac{g(0, \ell)}{1 - \epsilon M \omega^2 g(0, 0)}, \quad (4.24)$$

for which the simplifying symmetry feature of $G(0, 0)$ will not apply.

The $\bar{q}$ -space Fourier transform of $G_{\alpha\beta}(\ell\ell')$ is perhaps more interesting since neutron-scattering experiments measure the transform of the correlation function

$$\sum_{\ell\ell'} e^{i\bar{q}\cdot[\bar{R}(\ell')-\bar{R}(\ell)]} \langle u_{\alpha}(\ell, t) u_{\beta}(\ell', 0) \rangle_T, \quad (4.25)$$

which is related to

$$\text{Im} \sum_{\ell\ell'} G_{\alpha\beta}(\ell\ell', \omega) e^{i\bar{q}\cdot[\bar{R}(\ell')-\bar{R}(\ell)]}. \quad (4.26)$$

For our example of a defect at the origin, (4.26) equals

$$\text{Im} \sum_{\ell\ell'} [g(\ell\ell') + g(\ell 0) X(00) g(0\ell')] e^{i\bar{q}\cdot[\bar{R}(\ell')-\bar{R}(\ell)]}. \quad (4.27)$$

But

$$M \sum_{\ell} g(\ell 0) e^{-i\bar{q}\cdot\bar{R}(\ell)} = \sum_j \frac{\sigma_{\alpha}^{j+}(\bar{q}) \sigma_{\beta}^j(\bar{q})}{\omega^2 - \omega_j^2(\bar{q})}, \quad (4.28)$$

of which the imaginary part is proportional to $\delta[\omega \pm \omega_j(\bar{q})]$. For a localized mode, $\omega > \omega_m$, and g itself gives no contribution to the sum. The contribution from the defect term is then equal to

$$\frac{\pi \delta(\omega - \omega_{\ell}) \omega^2}{\frac{d}{d\omega} M^2 \omega^2 g(00, \omega)} \bigg|_{\omega=\omega_{\ell}} \left[\sum_j \frac{\sigma_{\alpha}^{j+}(\bar{q}) \sigma_{\beta}^j(\bar{q})}{\omega^2 - \omega_j^2(\bar{q})} \right]^2. \quad (4.29)$$

This Fourier transform will give information about the strength of a local mode and about its spatial extent.

2. Band Resonant Modes

To find the behavior of band modes at the defect we apply a similar sort of technique. For $\omega < \omega_m$, the sum over j and $\bar{q}$ in (4.11) may be converted to a principal-part integral plus an imaginary part,

$$g(00, \omega) = \frac{1}{M} \int \frac{\nu(\omega') d\omega'}{\omega^2 - \omega'^2} - \frac{i\pi\nu(\omega)}{2\omega M}. \quad (4.30)$$

If $g \equiv g_1 + ig_2$, then rationalizing the denominator (realizing that C is real), we find

$$\text{Im}G(00) = \text{Im} \frac{g}{1 - gC} = \frac{g_2}{(1 - Cg_1)^2 + (Cg_2)^2} \quad (4.31)$$

$$= \frac{\pi\nu(\omega)}{2M\omega \left[\left(1 - \epsilon\omega^2 \int \frac{\nu(\omega') d\omega'}{\omega^2 - \omega'^2} \right)^2 + \left(\frac{1}{2}\pi\nu(\omega) \epsilon\omega \right)^2 \right]} \quad (4.32)$$

Using formula (4.21) for H gives a similar expression without the $(M\omega)^{-1}$. This gives the square of the normalized-mode coordinates at

Fig. 2. Reciprocal of the Denominator of (4.32) for a Debye Spectrum and Various Single Mass Defects (showing resonances for heavy defects and band attenuation for light defects)

the defect site. The denominator of (4.32) is plotted in Fig. 2 for a Debye model. The resonance occurs when the first term in the brackets vanishes; a peak appears in $\text{Im}G(00)$ with a width roughly proportional to the perfect crystal density of states to which the resonance can decay. Therefore $\text{Im}G(00)$ looks like the perfect density of states [i.e., the imaginary part of $g(00)$] with a resonant enhancement.

Figures 2 through 5 have been calculated for a Debye density of states, $\nu(\omega) \sim \omega^2$, $0 \leq \omega \leq \omega_m$. Curve 1 of Fig. 3 shows the frequency of a localized mode plotted as

$(\omega_\ell/\omega_m - 1)$ against the mass-change parameter $\epsilon = 1 - M'/M$. Curve 2 of Fig. 3 shows the mean-square displacement of the defect atom multiplied by its mass. This quantity is given by (4.23) and measures the fraction of the total-crystal mean-square amplitude at frequency ω_ℓ , which is on the defect atom only. Clearly, as the defect atom becomes lighter and the local-mode frequency higher, the local mode becomes more localized. Because of the singularity in the Debye spectrum at $\omega = \omega_m$, a local mode appears for all $\epsilon > 0$. For a more realistic density of states, $\sim(\omega_m - \omega)^{1/2}$ near ω_m , the local mode will not appear until a certain critical value of ϵ is reached.

Fig. 3. Local-mode Frequency and Mean-square Displacement for a Single Light Mass Defect and a Debye Spectrum

Fig. 4. Temperature Dependence of the Mean-square Displacement for an Atom (in a perfect crystal) and for a light and a heavy defect atom)

Fig. 5. Temperature Dependence of the Kinetic Energy of a Defect Atom

Figure 2 plots the reciprocal of the denominator in brackets in (4.32) at band-mode frequencies for various mass defects. Heavy defects, $\epsilon < 0$, show a resonance that is lower in frequency and sharper for heavier defects, as would be expected. Light mass defects show an attenuation in the band-mode region.

A thermally averaged mean-square displacement may be found from

$$\text{Im} \int G(00, \omega) \frac{d\omega}{e^{\beta\hbar\omega} - 1} \quad (4.33)$$

and is plotted in Fig. 4. The zero-point motion is given by the $T = 0$ limit; at higher T , the mean-square amplitudes are linear in T , the classical behavior. As $T \rightarrow \infty$, the three solid curves all tend to the classical limit.

In the high-temperature limit, the mean thermal energy of a defect atom $M'\langle\dot{u}^2(0)\rangle_T$ is equal to that of a perfect atom. Figure 5 shows the energy ratios.

The quantities we have been discussing are directly related to observable physical quantities. If the defect carries a charge in an otherwise uncharged and nonpolarizable perfect crystal, then the electrical susceptibility at low frequency is given by $G(00)$ and the optical absorption coefficient by $\text{Im}\omega G(00)$. The density of states for silicon is given in Fig. 6. Figure 7 shows the predicted optical-absorption coefficient for $10^{19}/\text{cm}^3$ concentration of the following defects: solid curve, boron, an average of two curves for ^{10}B and ^{11}B weighted according to their natural abundance; broken curve, phosphorus; dotted curve, antimony.

Fig. 6. Unperturbed Density of Phonon States in a Perfect Silicon Crystal (calculated from a shell model by F. A. Johnson)

Fig. 7. Calculated Infrared Absorption Spectrum for Defects in Silicon. Solid curve: Boron, an average of curves for ^{10}B and ^{11}B , weighted according to their natural abundance. Dotted curve: Antimony. Broken curve: Phosphorus. All concentrations are 10^{19} defects/ cm^3 .

The comparison with experiments is quite good for local-mode frequencies of boron and carbon defects in silicon. A no-parameter mass-defect-only theory predicts frequencies that are consistently 7 or 8% high for two isotopes of boron and three of carbon. The mass-defect-only theory has neglected the softening of the crystal due to defects, and a force-constant change could easily account for the discrepancy. Local-mode absorption intensities are not so well predicted by the simple theory, presumably because of the polarizability of the host and defect atoms. The absorption lines due to in-band resonances are definitely seen experimentally. The line shapes predicted by the simple theory, however, are not very satisfactory. Generally, the mass-defect model alone is too simple to give detailed agreement with experiment. Force constants to first- and sometimes second-nearest neighbors must be changed to fit experiments.

V. PHYSICALLY MORE REALISTIC MODELS

A. Force-constant Changes and Higher-defect Concentrations

In the previous sections we discussed the changes in normal modes and in observable quantities in a harmonic crystal due to single defects; we concentrated on the simple-point mass defect. Three extensions of this basic theory are described below:

1. The mass defect alone is almost always too simple a model of an imperfect crystal, and for good agreement with optical experiments, force-constant changes to nearest neighbors or farther must be considered. The defect now appears mathematically as a "molecule" with normal modes, which may be classified by group theoretical techniques and which couple to the rest of the crystal. The principal theoretical ideas of this problem have already been discussed.

2. The model of a single defect in the crystal is not realistic, although for a finite defect concentration $\lesssim 3\%$, multiplying the defect part of Green's function G by the number of defects gives an adequate theory which is linear in the concentration. Such a theory then considers all multiple phonon-scattering events from individual defects, but neglects all interference scattering from different defects. Extensions to higher concentrations of defects, resulting in a shift and additional width to local- and resonance-mode peaks, are listed in the references for phonon, electron, and magnon systems.

3. The remainder of this section will be devoted to anharmonic effects, due to terms in the Hamiltonian to third and fourth powers of the atomic displacements. To accommodate these terms, we shall revise somewhat the harmonic problem for the imperfect crystal. Let matrix $\phi' \equiv \phi$; then,

$$H = \sum_{\alpha l} \frac{p_{\alpha}^2(l)}{2M_{\alpha}(l)} + \sum_{ll'\alpha\beta} \phi_{\alpha\beta}(ll') u_{\alpha}(l) u_{\beta}(l'). \quad (5.1)$$

The solutions of the dynamical matrix are eigenvalues $M_{\alpha}\omega^2(f)$, where f replaces j and q of the perfect case, and in terms of annihilation $[a(f)]$ and creation $[a^{\dagger}(f)]$ operators,

$$H = \sum_f \frac{1}{2} \hbar \omega(f) [a^{\dagger}(f) a(f) + a(f) a^{\dagger}(f)]. \quad (5.2)$$

The displacement in any normal mode, from Eq. (1.11), is

$$Q(f) = \sum_{\ell\alpha} \chi_{\alpha}(f, \ell) u_{\alpha}(\ell). \quad (5.3)$$

As usual, the displacement may be normalized and written

$$Q(f) = \left(\frac{\hbar}{2\omega(f)} \right)^{1/2} [a(f) + a^{\dagger}(f)], \quad (5.4)$$

and the thermally averaged energy is given by the number $n(f)$ of modes of type f ,

$$\langle H \rangle = \sum_f \hbar \omega(f) [\langle n(f) \rangle + \frac{1}{2}]. \quad (5.5)$$

B. Anharmonic Effects

The potential energy of the system is expanded in powers of atomic displacements $\bar{u}$ from equilibrium positions. By the definition of equilibrium, terms to first power in $\bar{u}$ vanish. The harmonic approximation consists of keeping only terms to second power in $\bar{u}$; but interatomic potentials are not parabolic, and third, fourth, and higher derivatives of the potential exist. Contributions to the energy in the n th power of the displacement are of the order of the n th power of the ratio of the atomic displacement to the interatomic spacing and we shall keep only third- and fourth-order anharmonic terms,

$$\phi_{\alpha\beta\gamma}(\ell\ell'\ell'') u_{\alpha}(\ell) u_{\beta}(\ell') u_{\gamma}(\ell'') \quad (5.6a)$$

and

$$\phi_{\alpha\beta\gamma\delta}(\ell\ell'\ell''\ell''') u_{\alpha}(\ell) u_{\beta}(\ell') u_{\gamma}(\ell'') u_{\delta}(\ell'''). \quad (5.6b)$$

These terms may be transformed to normal coordinates of the harmonic problem

$$B(f_1 f_2 f_3) Q(f_1) Q(f_2) Q(f_3) \quad (5.7a)$$

and

$$C(f_1 f_2 f_3 f_4) Q(f_1) Q(f_2) Q(f_3) Q(f_4). \quad (5.7b)$$

More physics may be introduced into the transformed Hamiltonian by redefining B and C . The two defect modes (local and band modes) will be

treated on a slightly different basis, and we introduce the annihilation and creation operators b and $b^\dagger$ to represent $a(f_\ell)$ and $a^\dagger(f_\ell)$, respectively, where f_ℓ refers to a local mode. An atomic displacement $\underline{u}$ varies as $(\hbar/2M\omega\zeta)^{1/2}$, where ζ is the number of atoms covered by the mode at frequency ω . For a well-localized mode, $\zeta \approx 1$ and $\underline{u}(0) \sim (\hbar/2M'\omega_\ell)^{1/2}$. For a band mode, $\zeta = N$. We are not so much interested in the actual $\underline{u}(\ell)$, but in relative displacements; we would like to subtract out any $\underline{k} = 0$ motion (uniform translation of all atoms) so that $\underline{u}(\underline{k} = 0) = 0$. Since $\underline{u}(\ell) \sim e^{i\underline{k} \cdot \underline{R}(\ell)}$ in the perfect crystal, near $\underline{k} = 0$ the relative $\underline{u}(\ell) \sim \underline{k} \cdot \underline{R}(\ell)$. For the imperfect crystal, $\underline{k}$ is not a meaningful quantity for normal modes, and we replace $\underline{k} \cdot \underline{R}(\ell)$ by ω/ω_m . Then for band modes,

$$\underline{u} \sim \frac{\omega}{\omega_m} \left(\frac{\hbar}{2MN\omega} \right)^{1/2} \quad (5.8)$$

The qualitative validity of the dependences inserted above may be judged from Figs. 2 and 3. Curve 2 of Fig. 3 shows increasing localization of a local mode for small $\epsilon - 1$, and χ is then $\sim M'^{-1/2}$. Figure 2 shows that our replacement of the perturbed displacements with perfect crystal displacement is reasonable near $\omega = 0$. The validity breaks down near a resonance, however. With B and C redefined, anharmonic terms for band modes will have the form

$$B \prod_{i=1}^3 \left(\frac{\hbar\omega(f_i)}{2MN\omega_m^2} \right)^{1/2} [a(f_i) + a^\dagger(f_i)]; \quad (5.9a)$$

and

$$C \prod_{i=1}^4 \left(\frac{\hbar\omega(f_i)}{2MN\omega_m^2} \right)^{1/2} [a(f_i) + a^\dagger(f_i)]. \quad (5.9b)$$

The remainder of our discussion will be concerned with the effects of anharmonicity on localized modes, where these effects are most striking.

1. Local Modes Only

The Hamiltonian for a local mode by itself takes the form

$$H = \frac{1}{2} \hbar \omega_\ell (bb^\dagger + b^\dagger b) + B \left(\frac{\hbar}{2M'\omega_\ell} \right)^{3/2} (b + b^\dagger)^3 + C \left(\frac{\hbar}{2M'\omega_\ell} \right)^2 (b + b^\dagger)^4. \quad (5.10)$$

The local-mode normal coordinates for the completely localized mode are simply the x, y, and z components of displacement. For an extended local

mode, the solution is more complicated, but the modes will always reflect the point symmetry of the crystal around the defect.

The force constants A , B , and C will have the symmetry of the crystal, and spectroscopic observations of local modes are very useful in determining the position of the defect in a complicated crystal. We shall specifically consider tetrahedral (T_d) symmetry, that of a boron defect in silicon or a hydrogen ion (H^-) on the fluorine site in CaF_2 ; or cubic (O_h) symmetry, that of an H^- ion in $NaCl$ or on the calcium or interstitial site in CaF_2 . In cubic symmetry, for example, all directions are equivalent, $A_{xx} = A_{yy} = A_{zz}$, and terms in $(b_x + b_x^+)^2$, $(b_y + b_y^+)^2$, and $(b_z + b_z^+)^2$ are all equal; terms in $b_x b_y^+$, $b_y b_z^+$, etc., are zero.

For third-order terms in the Hamiltonian, a cubic symmetry results in $B = 0$, since B must be of odd symmetry in at least one coordinate. There are therefore no cubic anharmonic terms in cubic symmetry. In tetrahedral symmetry, only one cubic term is allowed:

$$B \left(\frac{\hbar}{2M'\omega_\ell} \right)^{3/2} (b_x + b_x^+)(b_y + b_y^+)(b_z + b_z^+). \quad (5.11)$$

For both symmetries,

$$\phi_{xxxx} = \phi_{yyyy} = \phi_{zzzz}$$

and

$$\phi_{xxyy} = \phi_{yyzz} = \phi_{zzxx},$$

and two quartic terms are allowed:

$$C_1 \sum_x \left(\frac{\hbar}{2M'\omega} \right)^2 (b_x + b_x^+)^4; \quad (5.13a)$$

and

$$C_2 \sum_{xy} \left(\frac{\hbar}{2M'\omega} \right)^2 (b_x + b_x^+)^2 (b_y + b_y^+)^2. \quad (5.13b)$$

Generally, for these two symmetries the anharmonic terms change a spherically symmetric oscillator into one with symmetry given by the form of the Hamiltonian

$$H \sim Ar^2 + Bxyz + C_1 \sum_x x^4 + C_2 \sum_{xy} x^2 y^2. \quad (5.14)$$

The n th harmonic of the harmonic oscillator is of energy $\hbar \omega_{\ell}(n + \frac{1}{2})$; the energy levels are equally spaced. Harmonic-oscillator wave functions $\psi_n^{(0)}(\underline{r})$ are normal functions for which

$$\int \psi_n^{(0)}(\underline{r}) \underline{r} \psi_m^{(0)}(\underline{r}) d\underline{r} = 0$$

for $|m - n| \neq 1$. The dipole operator of electromagnetic radiation can therefore induce only $|m - n| = 1$ transitions, and only radiation of energy $\hbar \omega_{\ell}$ can be absorbed. Terms in B and C, treated as perturbations, lift the degeneracy of the energy levels, and matrix elements of $\underline{r}$ between perturbed-wave functions for a number of $|m - n| \neq 1$ are no longer symmetry-forbidden. Such a perturbed energy-level diagram for anharmonic terms of tetrahedral symmetry is shown in Fig. 8, and transitions observed in experiments on H^- in CaF_2 are indicated. Since a similar analysis for anharmonic terms of cubic symmetry ($n = 0 \rightarrow 2$ forbidden) agrees much less with experimental observations, it may be concluded that an H^- defect sits on a fluorine site.

Fig. 8. Schematic Representation of Lower Vibrational Energy Levels of H^- in CaF_2 at 20°K. Observed transitions are indicated by vertical lines. Energies of other levels have been calculated.

2. Mixing of Local Mode and Band Mode

The annihilation-creation operator formalism is very useful in classifying the types of effects that may occur. Above we have considered an anharmonic perturbation term entirely in local-mode operators. Other terms in the Hamiltonian involve local and band modes.

a. Side Bands

Band-mode side bands appear on the local mode through terms such as

$$B \left(\frac{\hbar}{2M'\omega_{\ell}} \right) \left(\frac{\hbar \omega(f)}{2MN\omega_m^2} \right)^{1/2} \left\{ (bb^+ + b^+b) [a(f) + a^+(f)] \right\}. \quad (5.15)$$

Then if vibrations are excited by light, a local mode plus or minus a band mode may be created. The matrix element with the creation of a band mode varies as $(n_f + 1)^{1/2}$ (anti-Stokes line), and with the destruction of a band mode varies as $n_f^{1/2}$ (Stokes line). The intensity of both processes is temperature-dependent; the Stokes line disappears at $T = 0$. The intensity

of the side bands at ω (from ω_ℓ) relative to the local mode line is [with energy denominator $\omega(f)$]

$$\sum_f B^2 \frac{\hbar [n(\omega) + 1] \delta[\omega - \omega(f)]}{2M'^2 M \omega_\ell^2 \omega_m^2 N \omega(f)} \quad (5.16)$$

b. Line Width

In the harmonic approximation, the local mode of an isolated defect has no width. Two anharmonic effects may contribute a width. Terms of the form $bb^+ a(f) a^+(f')$, where $\omega(f') = \omega(f)$, represent an elastic scattering of band modes. The total state of band and local modes then has a finite lifetime, and the local mode has a width. Alternatively, the local mode itself may decay into two band modes, $ba^+(f_1) a^+(f_2)$, or three band modes, $ba^+(f_1) a^+(f_2) a^+(f_3)$.

c. Frequency Shift

The thermal average over band modes

$$(b^+b + bb^+) \langle a(f)^+ a(f) + a(f) a(f)^+ \rangle \quad (5.17)$$

results in a temperature-dependent shift of the local-mode frequency since the local-mode fundamental energy is given by

$$E = \frac{1}{2} \hbar \omega_\ell (b_x^+ b_x + b_x b_x^+). \quad (5.18)$$

The experimental shift and width of the second harmonic of the local mode due to H^- in CaF_2 is shown in Fig. 9 as a function of temperature.

d. Uniaxial Stress

The application of a uniaxial stress will remove the degeneracy of a local mode associated with the symmetry of a defect site. A stress in the $[110]$ direction will remove all the degeneracy due to the tetrahedral environment of H^- in CaF_2 . A stress in the $[111]$ direction will result in a doublet and a singlet line (see Fig. 10a). An applied static-electric field will likewise remove a certain inversion symmetry of the H^- site (see Fig. 10b).

Fig. 9. Variation with Temperature of Peak Position and Width of Second-harmonic Vibrational Line of H^- in CaF_2 . Side bands have not been included.

Fig. 10. Splitting of Fundamental Vibrational Line of H^- in CaF_2 at $20^\circ K$ (a) By uniaxial compressional stress (b) By an electric field along the $[111]$ direction. In both cases, the high-energy line is observed with light with the electric vector $\vec{E}$ parallel to $[111]$ and the low-energy line with $\vec{E}$ perpendicular to $[111]$. Continuous lines are drawn through the experimental points.

Furthermore, an applied stress will make optically active certain anharmonic ($|m - n| > 1$) transitions. For example, an applied stress in the $[111]$ direction will mix some Γ_5 into the Γ_1 and Γ_3 modes of the $n = 2$ level (Fig. 8). Transitions from $n = 0$ to these two states may then be seen in the optical-absorption spectrum.

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