which gives

$$Q=\frac{4u^2mN}{15\tau}(ql)^2f_0(\epsilon_0(T))$$

and, finally,

$$\alpha_{sl}=\frac{8mN}{15\rho v_l'\tau}(ql)^2f_0(\epsilon_0).$$

For the normal state,

$$\alpha_{nl}=\frac{4mN}{15\rho v_l'\tau}(ql)^2.$$

This attenuation agrees with Pippard's result for longitudinal waves for $ql<1$. Again the ratio is given by

$$\alpha_{sl}/\alpha_{nl}=2f_0(\epsilon_0).$$

Tsuneto has obtained the same result by using a matrix density formalism and assuming that the interaction between long-wavelength sound waves and electrons in a metal is mainly electromagnetic. A similar result was obtained by BCS for longitudinal waves for $ql>1$ by computing the net rate of absorption of energy in the superconducting state produced by direct absorption and induced emission of the imposed acoustic phonons. Since our result for the attenuation coefficient of longitudinal waves is similar to that obtained by Pippard, we may assume that the effect of the space charges may be neglected even in the normal state for $ql<1$. However, when $ql>1$, the above derivation which neglects space charges would not give the correct limit for α_n.

ACKNOWLEDGMENTS

The author wishes to express his gratitude to Professor Isadore Rudnick for many helpful discussions, and to Professor J. L. Olsen for his hospitality during an enjoyable stay at the Heliumlaboratorium of the Swiss Federal Institute.

PHYSICAL REVIEW VOLUME 131, NUMBER 4 15 AUGUST 1963

Phonon Scattering by Lattice Defects*

MILES V. KLEIN
Department of Physics, University of Illinois, Urbana, Illinois
(Received 18 March 1963)

The Green's-function matrix method first developed by I. M. Lifshitz is applied to the problem of the scattering of phonons by a localized perturbation in the lattice. The scattering can be described by a t matrix that is localized to the same extent as the perturbation and has similar symmetry properties. The t matrix can be written in terms of the perturbation matrix γ and the Green's-function matrix g, perhaps most easily in terms of the representation formed by the eigenvectors of the matrix $g\gamma,\gamma$; these vectors can often be found by symmetry considerations. Two cases are of particular interest: (1) a "singular" perturbation which leads to a t matrix independent of the strength of the perturbation, and (2) resonance scattering from a low-frequency virtual local mode. The latter case is discussed for the example of decreased central-force constants between ⟨100⟩ nearest neighbors and the impurity site. Some implications for thermal conductivity are mentioned.

I. INTRODUCTION

IN a series of papers that are as much as twenty years old, I. M. Lifshitz formally solved the dynamics of a crystal perturbed by a defect.[1–4] He assumed that the normal modes and frequencies were known for the unperturbed lattice, and by the use of the dynamic Green's-function matrix was able to reduce the number of degrees of freedom of the perturbed problem to a manageable size, essentially equal to the number of changes induced by the perturbation.

Subsequent work has been devoted mainly to one aspect of the perturbed problem, namely, the appearance of discrete frequencies belonging to lattice modes localized around the impurity.[5–7] The Green's-function matrix method may be readily applied to the electron impurity problem if Wannier functions are used, as shown by Koster and Slater.[8,9] In this case, the local modes correspond to bound electronic impurity states.

Lifshitz also discussed the problem of the remaining modes which still have running wave character.[3,4] As

* Work supported in part by the U. S. Atomic Energy Commission.

[1] I. M. Lifshitz, J. Phys. U.S.S.R. **7**, 211, 249 (1943); **8**, 89 (1944).

[2] I. M. Lifshitz, Zh. Eksperim. i Teor. Fiz. **17**, 1017 and 1076 (1947).

[3] I. M. Lifshitz, Zh. Eksperim. i Teor. Fiz. **18**, 293 (1948).

[4] I. M. Lifshitz, Suppl. Nuovo Cimento **3**, 716 (1956). This English review article contains more references than those given above.

[5] M. Lax, Phys. Rev. **94**, 1392 (1954).

[6] E. W. Montroll and R. B. Potts, Phys. Rev. **100**, 525 (1955).

[7] A. A. Maradudin, P. Mazur, E. W. Montroll, and G. H. Weiss, Rev. Mod. Phys. **30**, 175 (1959).

[8] G. J. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954).

[9] G. J. Koster, Phys. Rev. **95**, 1436 (1954).

one might expect, these solutions consist of an incident plane wave plus scattered waves. The scattering matrix can, in principle, be found exactly, without recourse to a perturbation series. Quite recently the scattering of lattice waves by isotopes has been treated in detail by Takeno.[10] His calculations of the cross-section yield resonance scattering, under appropriate circumstances, from virtual local modes associated with the impurity. The possibility of such modes had been pointed out by Brout and Visscher,[11] and the analogous virtual-bound electronic states had been discussed using the Koster-Slater formalism by Wolff.[12]

Our aim is to present the details of the general solution of the scattering problem and to discuss the scattering amplitude when the perturbation is large so that the Born approximation breaks down. Two cases of particular interest are "hard-core" scattering from a singular perturbation and resonance scattering from a virtual local lattice mode.

Phonon scattering by defects can be studied experimentally by measuring low-temperature thermal conductivity. A variety of data indicates that resonance scattering of phonons may have been observed experimentally[13–16]; in fact, the data motivated a search for a mechanism, which in turn led to the Green's-function method to be presented here.

A disadvantage of the use of Green's functions for three-dimensional problems is that they must be calculated numerically, even for the simplest cases. Such a calculation is necessary for quantitative work; nevertheless, quite a bit of information can be learned from qualitative arguments which have the advantage of not being restricted to a given model of the lattice. The latter course is taken here.

II. BACKGROUND

A. Perfect Lattice

The formal theory will be stated in quite general language. Consider a perfect crystal with N unit cells located at points given by the set $\{\mathbf{L}\}$ of primitive translation vectors. There are r atoms per unit cell located at $\mathbf{b}_m$, $m=1, 2, \cdots, r$ with respect to an origin in the cell. The equilibrium position of the mth atom in the $\mathbf{L}$th cell is $\mathbf{L}_m=\mathbf{L}+\mathbf{b}_m$. The displacement $\mathbf{u}_m(\mathbf{L})$ is defined in terms of the actual position of this atom $\mathbf{X}_m(\mathbf{L})$ by

$$u_m{}^a(L)=X_m{}^a(\mathbf{L})-L_m{}^a. \qquad a=1, 2, 3. \tag{1}$$

We shall find it convenient to drop the indices m, a and introduce a new index i (or j) running from 1 to $3r$ such that for the first atom in the cell, $i=1, 2, 3$ corresponds to $m=1$, $a=1, 2, 3$; for the second atom in the cell, $i=4, 5, 6$ corresponds to $m=2$, $a=1, 2, 3$; etc. This change will simplify the notation and make it superficially the same as for one atom per unit cell. In the new notation we have

$$L^i=L_m{}^a, \quad i=1, \cdots, 3r. \tag{2}$$

In the harmonic approximation, the Hamiltonian is

$$H_0=\tfrac{1}{2}\sum_{\mathbf{L},\mathbf{L}'}\sum_{ij} V^{ij}(\mathbf{L},\mathbf{L}')u^i(\mathbf{L})u^j(\mathbf{L}') +\tfrac{1}{2}\sum_{\mathbf{L},i} M_i[\dot{u}^i(\mathbf{L})]^2. \tag{3}$$

The mass of the mth atom in the cell is given by M_i. The spring constant or force constant coefficient matrix $V^{ij}(\mathbf{L},\mathbf{L}')$ is given in terms of the potential energy V of the lattice by

$$V^{ij}(\mathbf{L},\mathbf{L}')=(\partial^2 V/\partial u^i(\mathbf{L})\partial u^j(\mathbf{L}'))_{u=0}. \tag{4}$$

The lattice vibration equations of motion can be obtained from Eq. (3). We assume a time dependence of the form $\exp(-i\omega t)$ and define

$$A^{ij}(\mathbf{L},\mathbf{L}')=(M_iM_j)^{-1/2}V^{ij}(\mathbf{L},\mathbf{L}'),$$

and

$$v^i(\mathbf{L})=(M_i)^{1/2}u^i(\mathbf{L}). \tag{5}$$

The equations of motion then give

$$\sum_{\mathbf{L}',j}(A^{ij}(\mathbf{L},\mathbf{L}')-\omega^2\delta^{ij}\delta(\mathbf{L},\mathbf{L}'))v^j(\mathbf{L}')=0 \tag{6}$$

or, in abbreviated matrix form,

$$(A-\omega^2 I)v=0. \tag{6'}$$

The normalized eigenvectors are running waves or phonons:

$$v(k\lambda) \quad \text{or} \quad v_{k\lambda}{}^i(\mathbf{L})=N^{-1/2}\mathcal{E}_{k\lambda}{}^i(e^{i\mathbf{k}\cdot\mathbf{L}}). \tag{7}$$

The wave vector $\mathbf{k}$ is "quasicontinuously" distributed throughout the first Brillouin zone, and the eigenvalues $\omega^2(k\lambda)$ form a quasicontinuous spectrum or band. The polarization index λ runs from 1 to $3r$. Some writers use $\mathbf{L}_m$ instead of $\mathbf{L}$ in the exponent; this changes the phase of the polarization vector $\mathcal{E}_{k\lambda}{}^i$.

B. Perturbed Lattice

Let us now put a defect into the lattice. This will change some of the masses to $M_i+\Delta M_i(\mathbf{L})$ and some of the spring constants to $V^{ij}(\mathbf{L},\mathbf{L}')+\Delta V^{ij}(\mathbf{L},\mathbf{L}')$. The equilibrium positions generally will be shifted somewhat from $\mathbf{L}_m$. The derivatives in the new potential matrix $V+\Delta V$ are to be evaluated at the new equilibrium positions, and $u^i(\mathbf{L})$ now refers to displacements from

[10] S. Takeno, Progr. Theoret. Phys. (Kyoto) **29**, 191 (1963).
[11] R. Brout and W. Visscher, Phys. Rev. Letters **9**, 54 (1962).
[12] P. A. Wolff, Phys. Rev. **124**, 1030 (1961).
[13] M. V. Klein, Phys. Rev. **122**, 1393 (1961).
[14] W. Gebhardt, J. Phys. Chem. Solids **23**, 1123 (1962).
[15] R. O. Pohl, Phys. Rev. Letters **8**, 481 (1962).
[16] C. T. Walker and R. O. Pohl, Phys. Rev. **131**, 34 (1963).

those positions. The equations of motion become

$$(A-\omega^2 I+\alpha\Gamma)v=0, \tag{8}$$

where

$$\alpha\Gamma^{ij}(\mathbf{L},\mathbf{L}')=(M_iM_j)^{-1/2}\Delta V^{ij}(\mathbf{L},\mathbf{L}') - (\Delta M_i/M_i)\omega^2\delta^{ij}\delta(\mathbf{L},\mathbf{L}'). \tag{9}$$

The strength of the perturbation is characterized by the dimensionless coupling constant α.

C. True Local Modes

To lay the foundation for the treatment of virtual local modes, we want to discuss briefly the case of true local modes, that is, modes with a frequency different from any in the quasicontinuous spectrum of the unperturbed lattice. We can define the Green's-function matrix by

$$G(\omega^2)=(A-\omega^2 I)^{-1}, \tag{10}$$

which is diagonal in the phonon representation

$$(k'\lambda'|\,G(\omega^2)\,|k\lambda)=\delta_{kk'}\delta_{\lambda\lambda'}(\omega_{k\lambda}{}^2-\omega^2)^{-1}. \tag{11}$$

Explicitly, we can write[17]

$$G=\sum_{k,\lambda} v(k\lambda)v(k\lambda)^\dagger(\omega_{k\lambda}{}^2-\omega^2)^{-1},$$

or

$$G^{ij}(\mathbf{L},\mathbf{L}')=\frac{1}{N}\sum_{k,\lambda}\frac{\exp[i\mathbf{k}\cdot(\mathbf{L}-\mathbf{L}')]\mathcal{E}_{k\lambda}{}^i\mathcal{E}_{k\lambda}{}^{j*}}{(\omega_{k\lambda}{}^2-\omega^2)}. \tag{12}$$

As the inverse of a symmetric matrix, $G(\omega^2)$ must also be symmetric. Multiplying Eq. (8) on the left by $G(\omega^2)$ gives

$$[1+\alpha G(\omega^2)\Gamma]v=0, \tag{13}$$

or

$$v=-\alpha G\Gamma v. \tag{13'}$$

This set of equations can be solved explicitly, in principle, if the defect is sufficiently localized; i.e., if Γ is nonzero only on a small set of indices. In this case, we can write, perhaps with some relabeling of rows and columns,

$$\Gamma=\begin{pmatrix}\gamma & 0\\ 0 & 0\end{pmatrix}, \tag{14}$$

where γ is a much smaller $n\times n$ symmetric matrix. Those points in the lattice and those components where Γ is nonzero we shall call the "space of γ". We now write G as a matrix of matrices,

$$G(\omega^2)=\begin{pmatrix}g(\omega^2) & \tilde{R}(\omega^2)\\ R(\omega^2) & B(\omega^2)\end{pmatrix}, \tag{15}$$

where the $n\times n$ matrix g is defined on the space of γ, R is a $(3rN-n)\times n$ matrix, and B is a symmetric $(3rN-n)\times(3rN-n)$ matrix. We also write for the $3rN$-dimensional column vector

$$v=\begin{pmatrix}v_l\\ v_r\end{pmatrix},$$

where v_l is n dimensional. We note that $\Gamma v=\gamma v_l$ and $G\Gamma v=G\gamma v_l=g\gamma v_l+R\gamma v_l$.

Thus, Eq. (13') becomes two equations:

$$v_l=-\alpha g(\omega^2)\gamma v_l, \tag{16}$$

an eigenvalue, eigenvector problem in the localized space of γ, and

$$v_r=-\alpha R(\omega^2)\gamma v_l, \tag{17}$$

which gives the "long-range" displacements in terms of the solutions of Eq. (16).

Solutions of Eq. (16) exist if and only if

$$\det|\,1+\alpha g(\omega^2)\gamma\,|=0. \tag{18}$$

If α is sufficiently small, there are no solutions of this equation because $g(\omega^2)$ is bounded as ω^2 approaches an edge of the quasicontinuous spectrum from outside. The modes are local for ω^2 outside the band in the sense that the vector v_r falls off rapidly with distance from the impurity. This can be seen by writing out Eq. (17) explicitly:

$$v^i(\mathbf{L})=(-)\frac{1}{N}\sum_{\mathbf{L}',\mathbf{L}''}\sum_{r,s}\sum_{k,\lambda}\frac{\exp[i\mathbf{k}\cdot(\mathbf{L}-\mathbf{L}')]\mathcal{E}_{k\lambda}{}^i\mathcal{E}_{k\lambda}{}^{r*}\Gamma^{rs}(\mathbf{L}',\mathbf{L}'')v^s(\mathbf{L}'')}{\omega_{k\lambda}{}^2-\omega^2}. \tag{17'}$$

If the defect is localized near the origin, the sum (or integral) over k will yield a decreasing contribution as $|L|$ increases, because of the rapid oscillations of the exponential.

Such local modes can be shown to result from a sufficiently large decrease in mass $\Delta M/M<0$ or from a sufficiently large increase in force constant.

[17] An asterisk denotes the complex conjugate; a dagger, the Hermitian conjugate; and a wavy line, the transpose.

III. SCATTERING AND THE T MATRIX

A. Formal Solution of the Scattering Problem

If ω^2 is in the band, the singularity in Eq. (17') at $\omega_{k\lambda}{}^2=\omega^2$ will pick out plane waves of this frequency at large distances $|\mathbf{L}|$. Exactly how this is done will depend upon how we decide to integrate near the singularity. The problem is best formulated using the language of scattering.

We look for a solution to Eq. (8) of the form

$$v=v(k_0\lambda_0)+w, \tag{19}$$

where $v(k_0\lambda_0)$ is the plane wave of Eq. (7) for phonon mode $k_0\lambda_0$. Equation (8) yields

$$(\omega_{k_0\lambda_0}{}^2-\omega^2)v(k_0\lambda_0)+\gamma\Gamma v(k_0\lambda_0) +(A-\omega^2 I+\gamma\Gamma)w=0. \tag{20}$$

We now set

$$\omega^2=\omega_{k_0\lambda_0}{}^2+i\epsilon\equiv\omega_0{}^{2+}, \tag{21}$$

where ϵ is an infinitesimally small positive number. The matrix $A-\omega^{2+}I$ now becomes Hermitian and has a unique inverse

$$G^+=G(\omega_0{}^{2+})=(A-\omega_0{}^{2+}I)^{-1}. \tag{10'}$$

We can multiply Eq. (20) on the left by G^+ to obtain

$$(I+\gamma G^+\Gamma)w=-\alpha G^+\Gamma v(k_0\lambda_0). \tag{22}$$

The first-order perturbation result is obtained by neglecting the second term on the left in Eq. (22):

$$w\approx-\alpha G^+\Gamma v(k_0\lambda_0). \tag{23}$$

The T matrix is defined so that the correct solution takes the form

$$w=-G^+T^+v(k_0\lambda_0). \tag{24}$$

This will be true if T satisfies the matrix equation

$$T^+=\alpha\Gamma-\alpha\Gamma G^+T^+=\alpha\Gamma-\alpha T^+G^+\Gamma. \tag{24'}$$

The solution is

$$T^+=(I+\alpha\Gamma G^+)^{-1}\alpha\Gamma=\alpha\Gamma(I+\alpha G^+\Gamma)^{-1},$$

or

$$T^+=\alpha\Gamma+\alpha^2\Gamma G^+\Gamma+\alpha^3\Gamma G^+\Gamma G^+\Gamma+\cdots. \tag{25}$$

The last form is the perturbation expansion of the solution, which converges well for small α.

The choice (21) for ω^2 and, hence, for the way of handling the singularities in G guarantees that we have chosen the outgoing asymptotic scattering solution.[3,4,9] The proof of this statement begins by writing Eq. (24) explicitly:

$$w^i(\mathbf{L})=(-)\frac{1}{N}\sum_{\mathbf{L}',\mathbf{L}''}\sum_{r,s}\sum_{k,\lambda}\frac{\exp[i\mathbf{k}\cdot(\mathbf{L}-\mathbf{L}')]\mathcal{E}_{k\lambda}{}^i\mathcal{E}_{k\lambda}{}^{r*}}{(\omega_{k\lambda}{}^2-\omega_0{}^2-i\epsilon)} \times T^{rs}(\mathbf{L}',\mathbf{L}'')^+v_{k_0\lambda_0}{}^s(\mathbf{L}'').$$

A stationary-phase argument can be used to show that the integral picks out those values of k which make the denominator small. Such values of k correspond to outgoing waves. A similar result can be obtained from a time-dependent calculation. If the perturbation was "turned on" in the distant past when the solution was $v(t)=v(k_0\lambda_0)e^{-i\omega_0 t}$, the solution in the present becomes $[v(k_0\lambda_0)+w]e^{-i\omega_0 t}$ with w given by Eq. (24).

The Green's-function matrix $G(\omega^{2+})$ is complex. We can use the relation

$$\frac{1}{x-i\epsilon}=P\frac{1}{x}+\pi i\delta(x), \tag{26}$$

where $P(1/x)$ denotes the principle value of $1/x$, and $\delta(x)$ is the Dirac δ function, to obtain

$$G^+=G_R(\omega^2)+iG_I(\omega^2), \tag{27}$$

where

$$G_R(\omega^2)=P\sum_{k\lambda}v(k\lambda)v^\dagger(k\lambda)(\omega_{k\lambda}{}^2-\omega^2)^{-1}, \tag{27'}$$

and

$$G_I(\omega^2)=\pi\sum_{k\lambda}v(k\lambda)v^\dagger(k\lambda)\delta(\omega_{k\lambda}{}^2-\omega^2). \tag{27''}$$

For large $|\mathbf{L}-\mathbf{L}'|$ one can again apply a stationary-phase argument to show that G_R and G_I are comparable. In fact, in the limit of large distances we have $G_R\rightarrow iG_I$. In this case, only a few phonon states are picked out in both expressions, namely, those where $\omega_{k\lambda}{}^2=\omega^2$. At short range we have $|G_R|\gg|G_I$ provided ω^2 is far from its value at the edge of Brillouin zone (i.e., roughly for $\omega^2/\omega_D{}^2\ll1$, ω_D=Debye frequency). Under these conditions the exponential will not oscillate very rapidly and will allow a relatively large number of phonon states to contribute to G_R, whereas the delta function severely limits the number of states that can contribute to G_I.

B. Connection with Thermal Conductivity

As usually treated,[18,19] the calculation of the thermal conductivity involves a Boltzmann equation for the occupation numbers N_k of the form

$$(-)\left(\frac{\partial N_k}{\partial t}\right)_{\text{drift}}=\left(\frac{\partial N_k}{\partial t}\right)_{\text{coll}}. \tag{28}$$

The collision processes occurring on the right side of Eq. (28) will be of at least two types: (1) inelastic or three-phonon processes characteristic of the defect-free anharmonic crystal; and (2) elastic scattering by a random distribution of n impurities. It is usually assumed that there is no interference between the two processes so that the collision terms add. A case where this assumption apparently does not hold has been discussed by Carruthers[20] and by Abeles, Beers, Cody, and Dismukes.[21] In this paper we assume no interference.

The elastic-collision term as calculated by perturbation theory takes the form

$$\left(\frac{\partial N_k}{\partial t}\right)_{\text{el. coll}}=\int K(k,k')(N_{k'}-N_k)d^3k', \tag{29}$$

[18] P. G. Klemens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 1.
[19] P. Carruthers, Rev. Mod. Phys. **33**, 92 (1961).
[20] P. Carruthers, Phys. Rev. **126**, 1448 (1962).
[21] B. Abeles, D. S. Beers, G. D. Cody, and J. P. Dismukes, Phys. Rev. **125**, 44 (1962).

where the kernel K is proportional to $nN^{-1}|\Gamma_{kk'}|^2 \times\delta(\omega_k-\omega_{k'})$. The impurity concentration is given by nN^{-1}, and $\Gamma_{kk'}$ is the matrix element of Γ for a single impurity between two phonon states. When the defect-phonon interaction is strong, but the concentration of the randomly distributed defects is small, one must replace $\Gamma_{kk'}$ in the above expressions by the corresponding matrix elements $T_{kk'}{}^+$ of $T(\omega_0{}^{2+})$, where $\omega_0=\omega_k=\omega_{k'}$. This statement has been proven (i.e., the T-matrix Boltzmann equation was derived from first principles starting with the equation of motion for the density matrix) for electrical conductivity with elastic scattering of electrons by Luttinger and Kohn.[22] They treated the electric field as causing a small perturbation of the electron-plus-scatterer system. For the thermal conductivity the corresponding temperature gradient cannot be introduced into the Hamiltonian, and it is probably better to start with a correlation-function expression.[23] We have not carried out the derivation but feel quite confident that it would give the above result. This confidence is based on the mathematical similarity between a drifting electron gas producing an electrical current limited by elastic scattering from defects and a drifting phonon gas producing a thermal current limited by elastic scattering from defects.

We shall, therefore, use T instead of Γ in the calculation of thermal conductivity. Interesting possibilities arise when the two are quite different; that is, when perturbation theory breaks down. We now examine some of these possibilities.

C. Nonperturbative Behavior of T

We first note from Eq. (24′) or (25) that T is localized to the space of γ. We can, therefore, write

$$T=\begin{pmatrix} t & 0 \\ 0 & 0 \end{pmatrix}, \tag{30}$$

where

$$t=\alpha\gamma(1+\alpha g^+\gamma)^{-1}, \tag{31}$$

and where the Green's-function matrix in the space of γ can be written $g^+=g_R(\omega_0{}^2)+ig_I(\omega_0{}^2)$. It is convenient to work with the eigenvectors $e(j)$ and the eigenvalues μ_j of the matrix $g^+\gamma=g(\omega_0{}^{2+})\gamma$:

$$g^+\gamma e(j)=\mu_j e(j). \tag{32}$$

Corresponding to the two parts of g, there will be two parts of $\mu=\mathrm{Re}\mu+i\,\mathrm{Im}\mu$:

$$\begin{aligned}[\mathrm{Re}g]\gamma e(j)&=[\mathrm{Re}\mu]e(j),\\ [\mathrm{Im}g]\gamma e(j)&=[\mathrm{Im}\mu]e(j).\end{aligned} \tag{32′}$$

As we shall see, the eigenvectors can often be determined by symmetry considerations and can be assumed to form a complete orthogonal set in the space of γ. If this is true, we can then express t as follows:

$$t=\alpha\sum_{i=1}^{n}\gamma\frac{e(i)\tilde{e}(i)}{1+\mu_i\alpha}. \tag{33}$$

If the eigenvalues $\mu_i(\omega^2+i\epsilon)$ satisfy $|\mu_i\alpha|\gg1$ for all i, we have the strong coupling limit and can write

$$t\approx\sum_{i=1}^{n}\frac{\gamma e(i)\tilde{e}(i)}{\mu_i}, \tag{34}$$

a result independent of the coupling constant. The t matrix remains finite even for a "singular" perturbation $\alpha\gamma$. This result is well known in scattering theory.

A resonance in the scattered amplitude will occur at a frequency $\omega^2=\omega_l{}^2$ satisfying

$$1+\alpha\,\mathrm{Re}\mu_l(\omega_l{}^2)=0. \tag{35}$$

Near such a resonance we can write

$$1+\alpha\mu_l(\omega^{2+})\approx\alpha(\omega^2-\omega_l{}^2)\frac{d}{d\omega^2}[\mathrm{Re}\mu_l(\omega^2)]_{\omega^2=\omega_l{}^2}+i\alpha\,\mathrm{Im}\mu_l(\omega_l{}^2). \tag{35′}$$

Near a large enough resonance only the lth term in Eq. (33) is important. In such a case we have

$$t\approx\frac{\gamma e(l)\tilde{e}(l)}{(\omega^2-\omega_l{}^2)R_l{}'(\omega_l{}^2)+iI_l(\omega_l{}^2)}, \tag{36}$$

where

$$R_l{}'(\omega_l{}^2)=\frac{d}{d\omega^2}[\mathrm{Re}\mu_l(\omega^2)]_{\omega_l{}^2}, \tag{37}$$

and

$$I_l(\omega_l{}^2)=\mathrm{Im}[\mu_l(\omega_l{}^2)]. \tag{38}$$

The resonant peak in the intensity $|t|^2$ is down to half-maximum when $\Delta\omega^2=\omega^2-\omega_l{}^2=\pm S\omega_l{}^2$, where

$$S=\frac{I_l(\omega_l{}^2)}{\omega_l{}^2R_l{}'(\omega_l{}^2)}. \tag{39}$$

From this result and Eqs. (32′) we see that the peak is narrow when, roughly speaking, the imaginary part of the localized Green's function is much smaller than the real part. As pointed out in connection with Eq. (27), this should be the case for $\omega_l{}^2\ll\omega_D{}^2$; i.e., for long-wavelength acoustical modes.

Equation (35) is equivalent to

$$\det|1+\alpha\,\mathrm{Re}g(\omega_l{}^2)\gamma|=0. \tag{40}$$

This condition is as close to Eq. (18), the condition for a real local mode, as one can get with ω^2 in the quasi-continuous spectrum. We are, therefore, justified in referring to Eqs. (35) and (40) as the condition for the existence of a *virtual* local mode. The smaller the frequency of this mode, the narrower the resonance peak, and the more "real" the virtual mode becomes.

[22] J. M. Luttinger and W. Kohn, Phys. Rev. **109**, 1892 (1958).
[23] H. Mori, J. Phys. Soc. Japan **11**, 1029 (1956); R. Kubo, *ibid.* **12**, 570 (1957).

III. SOME EXAMPLES OF VIRTUAL LOCAL MODES AND RESONANCE SCATTERING FROM THEM

A. Heavy "Isotopic" Impurity

Suppose the mth atom in the unit cell at the origin has a different mass $M_m'>M_m$, but there are no changes in force constant. Then, in our original notation, the space of γ is the 3×3 space where $\mathbf{L}=\mathbf{L}'=0$, $m=m'$, and

$$\gamma=-\frac{M_m'-M_m}{M_m}\omega^2\delta^{ab},\quad a,b=1,2,3. \tag{41}$$

If the mth atom is at a site of cubic symmetry, the reduced Green's-function matrix is also diagonal:

$$g^{ab}(\omega^{2+})=(3N)^{-1}\sum_{k\lambda}\delta^{ab}(\omega_{k\lambda}{}^2-\omega^2-i\epsilon)^{-1}. \tag{42}$$

Equation (40) becomes

$$1-\left(\frac{M'-M}{M}\right)\omega^2\frac{1}{3N}P\sum_{k\lambda}\frac{1}{\omega_{k\lambda}{}^2-\omega^2}=0. \tag{42'}$$

For small ω^2, we can write

$$(3N)^{-1}P\sum_{k\lambda}(\omega_{k\lambda}{}^2-\omega^2)^{-1}\approx(3N)^{-1}\sum_{k\lambda}\omega_{k\lambda}{}^{-2}=Q\omega_D{}^{-2},$$

where Q is a constant of the order of, but less than, unity. We then have

$$1=Q(M'-M)\omega^2/M\omega_D{}^2. \tag{42''}$$

Thus, for a low-frequency mode for which $(\omega/\omega_D)^2\ll1$, we must have $(M'-M)/M\approx M'/M\gg1$. Such an "isotope" is not likely to be found in nature.

The possibility of a virtual local mode for a heavy isotope was pointed out by Brout and Visscher in connection with the Mössbauer effect.[11] Takeno has recently calculated the resonance scattering cross section numerically for a simple model of the lattice.[10] The reader is referred to his paper for a more precise estimate than that of Eq. (42''). He points out that there is a solution of Eq. (42') in the band for a light isotope in addition to that for a true local mode outside the band. The frequencies of these two modes approach each other as $\Delta m/m$ increases from negative values towards zero. They meet at the band edge for a critical value of $\Delta m/m$. Just before this happens the width of the virtual level is quite narrow because of the small density of phonon states available for decay. Resonance scattering from such a level would probably be masked by strong three-phonon processes at these frequencies.

B. Substitutional Impurity Bound with Weaker Force Constants to Nearest Neighbors

The true local modes resulting from an increase in force constants have been discussed by Takeno[24] and by Lengeler and Ludwig.[25] These authors chose to deal with a monatomic simple-cubic lattice with central- and noncentral-force constants between nearest neighbors only. The substitutional impurity was bound with different force constants to its neighbors. Some aspects of the related virtual normal mode problem have been discussed by Visscher,[26] again as they pertain to the Mössbauer effect.

Since we do not intend here to obtain exact numerical results, we shall not use a particular model for the unperturbed lattice, except that it be a monatomic Bravais lattice with cubic symmetry. The results can be easily generalized to simple diatomic lattices such as the NaCl structure. Calculations for other than cubic symmetry could be carried out in a similar manner. We insert a substitutional impurity at a site of octahedral symmetry. Its mass is assumed to be unchanged (it would have to change by a large amount to affect the conclusions to be reached), but the central-force constant to its six octahedral nearest neighbors is changed by an amount $\alpha M\omega_m{}^2$, where ω_m is maximum frequency of the unperturbed lattice and where α is negative and dimensionless.

The perturbation matrix Γ of Eq. (9) becomes

$$\Gamma^{ij}(\mathbf{L},\mathbf{L}')=\omega_m{}^2\sum_{\mathbf{n}}(\delta_{Ln}-\delta_{L0})(\delta_{L'n}-\delta_{L'0})n^in^j, \tag{43}$$

where the $\mathbf{n}$ are unit vectors to the nearest neighbors:

$$\mathbf{n}=\pm\hat{\imath}_1,\quad\pm\hat{\imath}_2,\quad\pm\hat{\imath}_3,$$

$\hat{\imath}_1$, $\hat{\imath}_2$, $\hat{\imath}_3$ being unit vectors along cube axes. The sum is over all six values of $\mathbf{n}$. Let a be the nearest neighbor spacing.

There are only six degrees of freedom for this problem represented by the relative displacements along the six bond directions:

$$x(\mathbf{n})=[\mathbf{v}(\mathbf{n})-\mathbf{v}(0)]\cdot\mathbf{n}. \tag{44}$$

We can normalize the $x(\mathbf{n})$ and use them as a basis for the space of γ. From Eq. (43) we see that γ is already orthogonal:

$$(\mathbf{n}'|\gamma|\mathbf{n})=\omega_m{}^2\delta_{nn'}. \tag{45}$$

This result is more general than the specific model of octahedral neighbors.

Since γ and g both have octahedral symmetry, the eigenvectors of the matrix γg form irreducible representations of the group O_h.[27] Those in each different irreducible representation will generally have a different eigenvalue μ. The reduction of the representation (44) begins by a splitting into states that are even and odd

[24] S. Takeno, Progr. Theoret. Phys. (Kyoto) **28**, 33 (1962).

[25] B. Lengeler and W. Ludwig, Z. Physik **171**, 273 (1963).

[26] W. M. Visscher, Phys. Rev. **129**, 28 (1963).

[27] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon Press, Inc., New York; and Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), p. 314 ff.

TABLE I. Character table for the irreducible representations of the group O. The last two rows give the characters of the even and odd representations in Eqs. (47′) and (47″).

	E	$8C_3$	$3C_2$	$6C_2$	$6C_4$	
A_1	1	1	1	1	1	
A_2	1	1	1	−1	−1	
E	2	−1	2	0	0	
F_2	3	0	−1	1	−1	
F_1	3	0	−1	−1	1	
Even	3	0	3	1	1	$=E+A_1$
Odd	3	0	−1	−1	1	$=F_1$

under the inversion $\mathbf{n}\rightarrow-\mathbf{n}$:

$$x(\pm\hat{\imath})=2^{-1/2}[\pm O(\hat{\imath})+E(\hat{\imath})], \tag{46}$$

where

$$E(\hat{\imath})=2^{-1/2}[x(\hat{\imath})-x(-\hat{\imath})],$$

and

$$O(\hat{\imath})=2^{-1/2}[x(\hat{\imath})+x(-\hat{\imath})].$$

Equation (45) becomes

$$\begin{aligned}(O_{i'}|\gamma|O_i)&=\omega_m^2\delta_{ii'},\\ (E_{i'}|\gamma|E_i)&=\omega_m^2\delta_{ii'},\\ (O_{i'}|\gamma|E_i)&=0.\end{aligned} \tag{47}$$

The remaining reduction can be accomplished via the character table for the group O shown in Table I.

The odd representation is already reduced and will give a triply degenerate eigenvalue belonging to the eigenvectors $O(1)$, $O(2)$, $O(3)$. The even representation reduces to a totally symmetric "breathing" mode in representation A_1 with eigenvector

$$e(A_1)=3^{-1/2}[E(1)+E(2)+E(3)]$$

and two doubly degenerate modes orthogonal to it in representation E having eigenvectors that can be taken to be

$$e_1(E)=6^{-1/2}[2E(1)-E(2)-E(3)],$$

and

$$e_2(E)=2^{-1/2}[E(2)-E(3)].$$

The matrix elements of g between the displacements of Eq. (44) are

$$(n'|g|n)=\sum_{k\lambda}(n'|N|n)(\omega_{k\lambda}^2-\omega^2-i\epsilon)^{-1}, \tag{48}$$

where the numerator is given by

$$\begin{aligned}(n'|N|n)=\{&[\cos(\mathbf{k}\cdot\mathbf{n}a)-1][\cos(\mathbf{k}\cdot\mathbf{n}'a)-1]\\ &+\sin(\mathbf{k}\cdot\mathbf{n}a)\sin(\mathbf{k}\cdot\mathbf{n}'a)\}\\ &\times(\boldsymbol{\mathcal{E}}_{k\lambda}\cdot\mathbf{n})(\boldsymbol{\mathcal{E}}_{k\lambda}\cdot\mathbf{n}').\end{aligned} \tag{49}$$

After the splitting of Eq. (46) the numerator becomes

$$\begin{aligned}(E_{i'}|N|E_i)&=2\sin(k_ia)\sin(k_{i'}a)\mathcal{E}_{k\lambda}{}^i\mathcal{E}_{k\lambda}{}^{i'},\\ (O_{i'}|N|O_i)&=2[\cos(k_ia)-1]\\ &\quad\times[\cos(k_{i'}a)-1]\mathcal{E}_{k\lambda}{}^i\mathcal{E}_{k\lambda}{}^{i'}.\end{aligned} \tag{50}$$

From symmetry considerations we can write

$$\omega_m^2(O_{i'}|g|O_i)=\delta_{ii'}\mu(F_1), \tag{51}$$

where $\mu(F_1)$ is the threefold degenerate eigenvalue belonging to representation F_1. It is given by

$$\mu(F_1,\omega^2)=2\omega_m^2N^{-1}\sum_{k\lambda}[\cos(k_1a)-1]^2(\mathcal{E}_{k\lambda}{}^1)^2\times(\omega_{k\lambda}^2-\omega^2-i\epsilon)^{-1}. \tag{52}$$

For the even mode in representation A_1, we have

$$\sum_i\omega_m^2(E_{i'}|g|E_i)e_i(A_1)=\mu(A_1)e_{i'}(A), \tag{53}$$

where $e_i(A_1)=1/\sqrt{3}$, $i=1, 2, 3$.

This gives

$$\begin{aligned}\mu(A_1,\omega^2)=\omega_m^2\sum_i(E_{i'}|g|E_i)&=(2\omega_m^2/3N)\cdot\sum_{k\lambda}\frac{[\sin(k_1a)\mathcal{E}_{k\lambda}{}^1+\sin(k_2a)\mathcal{E}_{k\lambda}{}^2+\sin(k_3a)\mathcal{E}_{k\lambda}{}^3]^2}{\omega_{k\lambda}^2-\omega^2-i\epsilon}\\ &=\frac{2\omega_m^2}{N}\sum_{k\lambda}\frac{(1-\cos^2k_1a)(\mathcal{E}_{k\lambda}{}^1)^2+2\sin(k_1a)\sin(k_2a)\mathcal{E}_{k\lambda}{}^1\mathcal{E}_{k\lambda}{}^2}{\omega_{k\lambda}^2-\omega^2-i\epsilon}.\end{aligned} \tag{54}$$

From a similar equation for mode E we get

$$\begin{aligned}\mu(E,\omega^2)&=\frac{\omega_m^2}{N}\sum_{k\lambda}\frac{[\sin(k_1a)\mathcal{E}_{k\lambda}{}^1-\sin(k_2a)\mathcal{E}_{k\lambda}{}^2]^2}{\omega_{k\lambda}^2-\omega^2-i\epsilon}\\ &=\frac{2\omega_m^2}{N}\sum_{k\lambda}\frac{(1-\cos^2k_1a)(\mathcal{E}_{k\lambda}{}^1)^2-\sin(k_1a)\sin(k_2a)\mathcal{E}_{k\lambda}{}^1\mathcal{E}_{k\lambda}{}^2}{\omega_{k\lambda}^2-\omega^2-i\epsilon}.\end{aligned} \tag{55}$$

The second term in Eqs. (54), (55) will probably be much smaller than the first term. It will be zero under the assumption that $\omega_{k\lambda}$ is independent of λ, for then

$$\sum_{\lambda} \mathcal{E}_{k\lambda}{}^{i}\mathcal{E}_{k\lambda}{}^{j}=\delta^{ij}.$$

It is also zero for a simple cubic lattice with nearest neighbor forces[28]; the Green's-function matrix is diagonal in i and j in such a model. For other models G^{ij} will not be diagonal, but we expect the nondiagonal terms to be much smaller than the diagonal terms. This statement holds, for example, for the numerical values of the static Green's function [i.e., $G(\omega^2=0)$] calculated by Flinn and Maradudin for a fcc lattice with central forces to nearest neighbors.[29] Thus, for rough estimates we may set

$$\mu(A_1)\approx\mu(E)\approx 2\omega_m{}^2N^{-1}\sum_{k\lambda}(1-\cos^2k_1a)(\mathcal{E}_{k\lambda}{}^1)^2 \times(\omega_{k\lambda}{}^2-\omega^2-i\epsilon)^{-1}.$$

A similar case, that of changed force constant to $\langle 111\rangle$ nearest neighbors is discussed in the Appendix.

C. Some Properties of the Eigenvalues of $g\gamma$

We consider $\mathrm{Re}\mu(\omega^2)$ for both positive and negative ω^2. The latter case is useful for consideration of the stability of the perturbed lattice. We see directly from Eqs. (52), (53), (55) that μ is positive for $\omega^2\leq 0$, and it decreases monotonically to zero as $\omega^2\rightarrow-\infty$. In addition it is clear that μ is negative for $\omega^2>\omega_m{}^2$, the maximum lattice frequency, and its magnitude decreases monotonically to zero as $\omega^2\rightarrow+\infty$.

It is also true that

$$(d/d\omega^2)[\mathrm{Re}\mu(\omega^{2+})]_0>0.$$

To prove the statement, first convert the sum over k to an integral

$$N^{-1}\sum_{\lambda k}=a^3(8\pi^3)^{-1}\sum_{\lambda}\int\int\int d^3k.$$

Now divide d^3k into a piece $d^2S_\lambda(\omega^2)$ of the constant frequency surface for polarization λ times dk_n, the change of k in the direction normal to the surface. The latter can be expressed as $dk_n=d\omega^2/|d\omega_{k\lambda}{}^2/d\mathbf{k}|$. We now carry out the integral over the constant frequency surface. For example, Eq. (52) gives

$$\int\int d^2S_\lambda(\omega^2)(\cos k_1a-1)^2(\mathcal{E}_{k\lambda}{}^1)^2|d\omega_{k\lambda}{}^2/d\mathbf{k}|^{-1} =\rho_\lambda(\omega^2)\langle(\cos k_1a-1)^2(\mathcal{E}_{k\lambda}{}^1)^2\rangle_{\omega^2,\lambda}, \quad (52')$$

where we have used the mean-value theorem to express the integral in terms of the value of the integrand at some point on the surface. The function

$$\rho_\lambda(\omega^2)=\int\int d^2S_\lambda(\omega^2)|d\omega_{k\lambda}{}^2/d\mathbf{k}|^{-1} \quad (56)$$

is the density of states for branch λ. For small ω^2, ρ_λ is of order ω. We can, therefore, express $\mathrm{Re}\mu$ as an integral of the form

$$\mathrm{Re}\mu(\omega_0^2)=P\int_0^{\omega_m{}^2}f(\omega^2)(\omega^2-\omega_0{}^2)^{-1}d\omega^2, \quad (57)$$

where $f(\omega^2)$ is positive and of order ω^3 for even modes and of order ω^5 for odd modes.

Thus, we can write

$$(d/d\omega_0^2)\,\mathrm{Re}\mu(\omega_0^2)=-\int_0^{\omega_m{}^2}f(\omega^2)\frac{\partial}{\partial\omega^2}P\frac{1}{\omega^2-\omega_0{}^2}d\omega^2 =\int_0^{\omega_m{}^2}\left[\frac{d}{d\omega^2}f(\omega^2)\right]P\frac{1}{\omega^2-\omega_0{}^2}d\omega^2. \quad (58)$$

We have made use of the fact that $f(0)=f(\omega_m{}^2)=0$. This gives the desired result,

$$(d/d\omega^2)\,\mathrm{Re}\mu(\omega^2)_0=\int_0^{\omega_m{}^2}[(d/d\omega^2)f(\omega^2)]\omega^{-2}d\omega^2>0. \quad (59)$$

A general feature that holds for all perturbations is the inequality,

$$1+\alpha\mu(0)>0. \quad (60)$$

This follows from the requirement that the perturbed potential energy matrix at $\omega^2=0$, $A+\Gamma$, must be positive definite. Thus, for any nonzero vector $U=\begin{pmatrix}u\\v\end{pmatrix}$, with u in the space of γ, and v in the orthogonal space, we must have

$$0<(U,(A+\Gamma)U)=(U,A(1+G\Gamma)U). \quad (61)$$

We write the G matrix by Eq. (15) as

$$G=\begin{pmatrix}g & \tilde{R}\\ R & B\end{pmatrix}, \quad (15)$$

where g is in the space of γ. Similarly, we write

$$A=\begin{pmatrix}a & \tilde{H}\\ H & C\end{pmatrix},$$

where a is in the space of γ. The condition $I=AG$ gives

$$\begin{aligned} ag+\tilde{H}R&=1,\\ Hg+CR&=0,\\ a\tilde{R}+\tilde{H}B&=0,\\ H\tilde{R}+CB&=1. \end{aligned} \quad (62)$$

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

[29] P. A. Flinn and A. A. Maradudin, Ann. Phys. (N. Y.) **18**, 81 (1962).

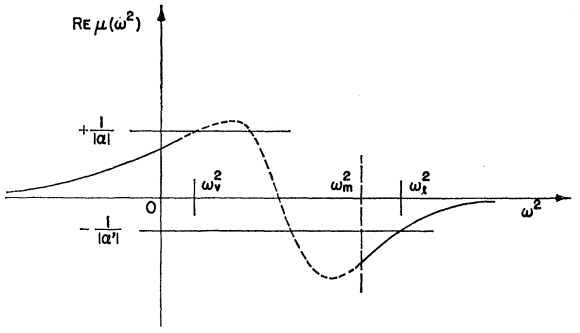

FIG. 1. Qualitative behavior of the real part of μ, the eigenvalue of $g\gamma$ as a function of ω^2. The solid line represents proven functional behavior as discussed in the text; the dashed line represents a reasonable way of connecting the solid curves. Irregularities should appear wherever the density of states $\rho(\omega^2)$ has a discontinuous change of slope (but not at the origin). These are not shown.

Let u be an eigenvector of $g\gamma$ with eigenvalue μ and let

$$v=-C^{-1}Hu, \tag{63}$$

so that

$$AU=\begin{pmatrix} a & \tilde{H} \\ H & C \end{pmatrix}\begin{pmatrix} u \\ v \end{pmatrix}=\begin{pmatrix} au+\tilde{H}v \\ Hu+Cv \end{pmatrix}=\begin{pmatrix} au-\tilde{H}C^{-1}Hu \\ 0 \end{pmatrix}.$$

This gives

$$0<(U,A(1+G\Gamma)U)=(u,(a-\tilde{H}C^{-1}H)(1+\alpha\mu)u)$$
$$=(1+\alpha\mu)(u,(a-\tilde{H}C^{-1}H)u). \tag{64}$$

From the second of Eqs. (62) we have $R=-C^{-1}Hg$, or with the first of Eqs. (62), $ag-\tilde{H}C^{-1}Hg=1$. This gives us a relation for the matrix in Eq. (64): $a-\tilde{H}C^{-1}H=g^{-1}$. This is positive definite because G and g are. Thus, we have

$$0<(1+\alpha\mu)(u,gu) \quad \text{or} \quad 1+\alpha\mu(0)>0.$$

This inequality coupled with the monotonic decrease of $\mu(\omega^2)$ for $\omega^2<0$ guarantees that there are no local-mode solutions having an imaginary frequency. This is another way of stating that the perturbed lattice is stable against small displacements from equilibrium.

The condition (60) implies that the "strong coupling limit" discussed in Sec. IIIC cannot exist for a decrease in force constant where $\alpha<0$. It can occur, however, for large positive α. This corresponds to hard-core scattering; i.e., scattering from a very stiff substitutional impurity.

The qualitative behavior of $\mathrm{Re}\mu(\omega^2)$ is shown in Fig. 1. The resonance condition $\mathrm{Re}\mu(\omega^2)=-1/\alpha$ gives a virtual mode at ω_v^2 for negative α. Real local modes are found at $\omega_l^2>\omega_m^2$ for positive α.

D. The Scattering Amplitude

For our simple example of changed force constants γ is diagonal in the eigenvectors of $g\gamma$. This allows us to express t near a resonance in mode l approximately by Eq. (36) as

$$t\approx\frac{\omega_m^2 e(l)\tilde{e}(l)}{(\omega^2-\omega_l^2)R_l'(\omega_l^2)+iI_l(\omega_l^2)},$$

or for the matrix element

$$(k'\lambda'|t|k\lambda)=\frac{\omega_m^2[\tilde{v}(k'\lambda')e(l)][\tilde{e}(l)v(k\lambda)]}{(\omega^2-\omega_l^2)R_l'(\omega_l^2)+iI_l(\omega_l^2)}. \tag{65}$$

The contribution to the Born approximation result $(k'\lambda'|\gamma|k\lambda)$ from mode l is the numerator of Eq. (65) times α. Thus, the resonance represents an increase of the scattering probability by the factor

$$\alpha^{-2}\{[(\omega^2-\omega_l^2)R_l'(\omega_l^2)]^2+I_l(\omega_l^2)^2\}^{-1}. \tag{66}$$

We can get some very rough estimates of the imaginary part of $\mu(\omega^2)$ as follows. For an odd mode, we get from Eqs. (52), (52′), and (56),

$$\mathrm{Im}\mu=2\pi\omega_m^2N^{-1}\sum_{k\lambda}(\cos k_1a-1)^2(\mathcal{E}_{k\lambda}{}^1)^2\delta(\omega_{k\lambda}{}^2-\omega^2)$$
$$=2\pi\omega_m^2a^3(8\pi^3)^{-1}\sum_{\lambda}\rho_\lambda(\omega^2)\langle(\cos k_1a-1)^2(\mathcal{E}_{k\lambda}{}^1)^2\rangle_{\omega^2,\lambda}.$$

For low frequencies we expand the cosine and further suppose that the polarization vectors point along the cube axes and that the Debye approximation holds with a single sound velocity c. Thus, we can write

$$\rho(\omega^2)=2\pi\omega/c^3,$$
$$\omega_m=\omega_D,$$

and

$$\langle(\cos k_1a-1)^2(\mathcal{E}_{k\lambda}{}^1)^2\rangle_{\omega^2,\lambda}=\tfrac{1}{4}\langle k_1{}^4a^4\rangle_{k^2=\omega^2/c^2}=\omega^4a^4c^{-4}/20,$$

where we have estimated the angular average for the case of isotropy,

$$\langle k_1{}^4/k^4\rangle=\langle\cos^4\theta\rangle=\tfrac{1}{5}.$$

This gives

$$\mathrm{Im}\mu=2\pi\omega_D{}^2a^3(8\pi^3)^{-1}2\pi\omega c^{-7}\omega^4a^4.$$

The Debye frequency is defined by

$$\tfrac{1}{3}=a^3(8\pi^3)^{-1}\int_0^{\omega_D{}^2}\rho(\omega^2)d\omega^2,$$

or

$$1=\omega_D{}^3a^3/(2\pi^2c^3). \tag{67}$$

Our estimate then becomes

$$\mathrm{Im}\mu=8.4(\omega/\omega_D)^5. \tag{68}$$

For the even mode the imaginary part of μ can be written from Eq. (53):

$$\mathrm{Im}\mu(\omega^2)=2\pi\omega_D{}^2/(3N)\sum_{k\lambda}(\sin k_1a\mathcal{E}_{k\lambda}{}^1+\sin k_2a\mathcal{E}_{k\lambda}{}^2$$
$$+\sin k_3a\mathcal{E}_{k\lambda}{}^3)^2\delta(\omega_{k\lambda}{}^2-\omega^2),$$
$$=2\pi\omega_D{}^2a^3/(24\pi^3)\sum_{\lambda}\rho_\lambda(\omega^2)\langle\sin k_1a\mathcal{E}_{k\lambda}{}^1$$
$$+\sin k_2a\mathcal{E}_{k\lambda}{}^2+\sin k_3a\mathcal{E}_{k\lambda}{}^3)^2\rangle_{\omega^2,\lambda}.$$

Under the same assumptions used in the previous case this becomes

$$\langle(\sin k_1 a \mathcal{E}_{k\lambda}{}^1+\sin k_2 a \mathcal{E}_{k\lambda}{}^2+\sin k_3 a \mathcal{E}_{k\lambda}{}^3)^2\rangle \approx \tfrac{2}{3}k^2a^2 = 2\omega^2a^2/c.$$

Then we have

$$\mathrm{Im}\mu \approx \tfrac{2}{3}\pi\omega_D{}^2a^3(8\pi^3)^{-1}2\pi\omega c^{-3}2\omega^2a^2 = 15.2(\omega/\omega_D)^3. \quad (69)$$

The real part of the denominator is not easy to estimate, even roughly, without a realistic model of the unperturbed lattice. We can use Eq. (58) and note that

$$f(\omega^2)=\pi^{-1}\,\mathrm{Im}\mu(\omega^2)=O(\omega/\omega_D)^3 \quad \text{or} \quad O(\omega/\omega_D)^5 \quad (70)$$

for even and odd modes, respectively. Very rough estimates indicate that for $(\omega/\omega_D)^2 \ll 1$, $\omega_D{}^2 d[\mathrm{Re}\mu(\omega^2)/d\omega^2]$ is less than but of the order of unity for both even and odd modes.

The numerator of Eq. (65) is $\omega_m{}^2$ times the numerator of Eq. (48), which is given by Eq. (50). At low frequencies the contribution of the odd modes is of order $\omega_D{}^2(\omega/\omega_D)^4$, and that of the even modes of order $\omega_D{}^2(\omega/\omega_D)^2$. The latter modes in Born approximation give Rayleigh scattering with a scattering probability proportional to ω^4. We see from the above considerations that the matrix element, Eq. (65), is about the same size for both even and odd modes near resonance. In fact, we can write

$$(k'\lambda'|t|k\lambda) \sim \frac{\omega_D{}^2(\omega/\omega_D)^n}{s(\omega^2-\omega_l{}^2)\omega_D{}^{-2}+s'i(\omega_l/\omega_D)^{n+1}}, \quad (71)$$

where s, $s'=O(1)$, and $n=2$ for even modes and $n=4$ for odd modes. At resonance the square of the matrix element is given by $|t|^2 \sim \omega_D{}^5\omega_l{}^{-1}$, in contrast with the Rayleigh result, $|t|^2 \sim \alpha^2\omega_l{}^4$. The resonance peak is $(\omega_D/\omega)^5$ times higher than the Rayleigh scattering expression.

The width of the resonance will be about $\Delta\omega^2/\omega_l{}^2 \sim (\omega_l/\omega_D)^{n-1}$ and, hence, is narrower by a factor of $(\omega_l/\omega_D)^2$ for the odd modes. The value of $|t|^2$ integrated over the resonance will be smaller by the same factor. Even for the odd mode, the integrated scattering should be much larger than Rayleigh scattering.

V. DISCUSSION

A. Future Needs

We have made a general formulation of phonon scattering by an impurity in terms of the dynamic Greens-function matrix of the unperturbed lattice. Clearly, one of the first tasks to be done is to compute some numerical values of $G(\omega^2+i\epsilon)$ for simple models of monatomic and diatomic lattices. Then one can fill in the details of a plot such as Fig. 1 of the eigenvalue of $g\gamma$ as a function of ω^2, given a particular model of the perturbation γ.

One should then investigate the effect of a nonlocal change in force constant around a point defect in the lattice. In many cases, this can be calculated in terms of the anharmonic coupling constants and the static strain field around the defect.[19,30] It is important to investigate whether or not the long-range changes in the force constant qualitatively affect the results presented in this paper.

B. Implications for Thermal Conductivity

The theory of Sec. II formally solves the problem of elastic scattering from a defect that has only changes in mass and changes in force constants. At present, it cannot handle the introduction of new degrees of freedom by, say, a molecular impurity. It can handle the removal of degrees of freedom as for a vacancy. Here the perturbed force constants must be such that all bonds to the vacancy site be broken. In a realistic model one would expect rearrangement of the near neighbors so that there would be at least changed force constants between nearest neighbors of the vacancy site that are nearest neighbors of each other. One could make a first approximation to the virtual local modes by neglecting this latter effect altogether.

If one can further restrict the broken bonds to be central bonds to nearest neighbors, the eigenvectors for the modes are given in the discussion following Eq. (47) for the case of $\langle 100\rangle$ neighbors and in the Appendix for $\langle 111\rangle$ neighbors. In both cases, the t-matrix element near a resonance in the lth mode is given by Eq. (65). Knowing $e(l)$ we can calculate the numerator of the right side exactly in this model; this is not useful unless the Green's functions needed to compute the denominator are known. We must be content at present with the estimate (71). The effect of this resonance on the reciprocal relaxation time can be obtained from the usual expression[18] for isotope scattering by replacing $(\Delta m/m)^2\omega^4$ by the square of the absolute value of (71). This gives the estimate

$$\tau_{\mathrm{res}}{}^{-1} \approx \frac{a^3 n\omega_D{}^2(\omega/\omega_D)^{2n}}{4\pi c^3 N[s^2(\omega^2-\omega_l{}^2)^2\omega_D{}^{-4}+s'^2(\omega_l/\omega_D)^{2n+2}]}, \quad (72)$$

where a^3 is the atomic volume, c the velocity of sound, and n/N the fractional concentration of defects.

It is fitting to inquire whether a resonance such as Eq. (72) has already been observed experimentally. Pohl[15] used a similar expression to fit his data on nitrate-doped KCl. One suspects, however, that in this case any virtual local modes would come from internal degrees of freedom of the molecule. Such low-lying energy levels might be quantum mechanical in nature (an example is the inversion in NH_3), and would not be included in the classical formalism presented here. The "dip-" or "high-"temperature resonant-like behavior found by Walker and Pohl[16] for monatomic impurities such as I^- and Na^+ in KCl occurred at the same temperature in all cases. The position of resonance in the theory given here is quite sensitive to small

[30] H. Bross, Physica Status Solidi **2**, 481 (1962).

details of the perturbation, and it is hard to imagine how such a theory could predict resonances at the same place for dissimilar impurities. An interesting suggestion has been recently made by Wagner[31] to explain the results of Walker and Pohl; he discusses a three-phonon scattering process in which a running-wave phonon is inelastically scattered from a true local mode.

Gebhardt[14] found a very large low-temperature thermal resistivity in KBr that was x-rayed at low temperatures and thus contained negative ion vacancies together with the anticenter, presumably an interstitial halide ion. When the anticenter was an interstitial H^- ion, the resistivity was an order of magnitude less. The simplest explanation is that the anomalously high resistivity was due to the interstitial halide ion. If this be true, there could be no resonant scattering from virtual modes because the expected changes in force constant should be large and positive. This brings up the possibility of hard-core scattering and the approximation of Eq. (34). The μ_l in the denominator would have a strong enough frequency dependence to give an anomalous (i.e., non-Rayleigh) frequency dependence to the relaxation time. Another possibility is that the negative ion vacancy has one or more low-frequency virtual modes that are somehow quenched by the nearby presence of an interstitial H^- ion but not by a nearby halide ion.

ACKNOWLEDGMENTS

This work was started while the author was at the Max Planck Institut für Metallforschung in Stuttgart, Germany. Thanks are expressed to Professor Alfred Seeger for his hospitality and to the U. S. National Science Foundation for a Postdoctoral Fellowship. The author also gratefully acknowledges helpful discussions with Leo Kadanoff.

APPENDIX: EIGENVECTORS OF $g\gamma$ FOR CHANGED CENTRAL FORCE CONSTANTS TO ⟨110⟩ NEAREST NEIGHBORS

We begin by the parity splitting of Eq. (46), where now $\hat{\imath}$ refers to any of the 12 ⟨110⟩ directions. The character table for the even and odd modes is shown in Table II. We need only six directions after the above splitting, which we take to be (110), ($\bar{1}10$), (101), ($10\bar{1}$), (011), and ($0\bar{1}1$). The eigenvectors are found to be

TABLE II. Character table for the reducible representations formed by even and odd combinations of displacements along the 12 ⟨110⟩ directions in the group O.

	E	$8C_3$	$3C_2$	$6C_2$	$6C_4$
Even	6	0	2	2	$0=F_2+E+A_1$
Odd	6	0	−2	0	$0=F_1+F_2$

Even F_2: $2^{-\frac{1}{2}}[E(110)-E(\bar{1}10)]$,
$2^{-\frac{1}{2}}[E(011)-E(0\bar{1}1)]$,
$2^{-\frac{1}{2}}[E(101)-E(10\bar{1})]$.

Even A_1: $6^{-\frac{1}{2}}[E(110)+E(101)+E(011)+E(\bar{1}10)+E(10\bar{1})+E(0\bar{1}1)]$.

Even E: $3^{-\frac{1}{2}}[E(110)+E(\bar{1}10)]-12^{-\frac{1}{2}}[E(011)+E(0\bar{1}1)+E(101)+E(10\bar{1})]$,
$\frac{1}{2}[E(011)+E(0\bar{1}1)-E(101)-E(10\bar{1})]$.

Odd F_2: $\frac{1}{2}[O(011)+O(0\bar{1}1)-O(101)+O(10\bar{1})]$,
$\frac{1}{2}[-O(011)+O(0\bar{1}1)+O(110)+O(\bar{1}10)]$,
$\frac{1}{2}[-O(110)+O(\bar{1}10)+O(101)+O(10\bar{1})]$.

Odd F_1: $\frac{1}{2}[O(011)+O(0\bar{1}1)+O(101)-O(10\bar{1})]$,
$\frac{1}{2}[O(011)-O(0\bar{1}1)+O(110)+O(\bar{1}10)]$,
$\frac{1}{2}[O(110)-O(\bar{1}10)+O(101)+O(10\bar{1})]$.

The eigenvectors $e(\hat{\imath})$ are the coefficients of $E(\hat{\imath})$ or $O(\hat{\imath})$ in the above expressions. The eigenvalues μ of $g\gamma$ can be obtained from Eqs. (47), (48), and a slight generalization of Eq. (50) in terms of the $e(\hat{\imath})$. The expressions to use are

Even Modes:

$$\mu(\omega^2-i\epsilon)=2\omega_m{}^2N^{-1}\sum_{k\lambda}\Big[\sum_i \sin(\mathbf{k}\cdot a\hat{\imath})(\boldsymbol{\varepsilon}_{k\lambda}\cdot\hat{\imath})e(\hat{\imath})\Big]^2 \times(\omega_{k\lambda}{}^2-\omega^2-i\epsilon)^{-1}. \quad \text{(A1)}$$

Odd Modes:

$$\mu(\omega^2-i\epsilon)=2\omega_m{}^2N^{-1}\sum_{k\lambda}\Big\{\sum_i \big[\cos(\mathbf{k}\cdot a\hat{\imath})-1\big](\boldsymbol{\varepsilon}_{k\lambda}\cdot\hat{\imath})e(\hat{\imath})\Big\}^2 \times(\omega_{k\lambda}{}^2-\omega^2-i\epsilon)^{-1}. \quad \text{(A2)}$$

Again, a represents the nearest neighbor separation.

[31] Max Wagner, Phys. Rev. **131**, 47 (1963).