$$[U_5,U_3]=(i/\sqrt{2})U_6$$
$$[U_3,U_6]=(i/\sqrt{2})U_5$$
$$[U_6,U_5]=(i/\sqrt{2})U_3$$
$$[U_4,U_3]=0$$
$$[U_4,U_7]=0$$
$$[U_4,U_8]=0$$
$$[U_3,U_8]=(i/\sqrt{2})2U_7$$
$$[U_8,U_7]=(i/\sqrt{2})2U_3$$
$$[U_7,U_3]=(i/\sqrt{2})2U_8$$
$$[U_4,U_5]=(i/\sqrt{2})\sqrt{3}U_2$$
$$[U_2,U_4]=(i/\sqrt{2})\sqrt{3}U_5$$
$$[U_5,U_2]=(i/\sqrt{2})(\sqrt{3}U_4-U_7)$$
$$[U_5,U_7]=(i/\sqrt{2})U_2$$
$$[U_7,U_2]=(i/\sqrt{2})U_5.$$

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Resonance Scattering of Phonons by Molecular Impurity Centers*

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The scattering of phonons at polyatomic (molecular) impurity centers cannot be handled by the regular Lifshitz method because of the additional degrees of freedom. A method is presented which makes it possible to eliminate the molecular coordinates by means of a molecular Green's function. This Green's function defines an effective disturbance in the lattice system with singular poles at the molecular frequencies. Thus the low rank t matrix of the scattering formalism, defining the scattering amplitude, has sharp resonances near the molecular frequencies. The abstract scattering formalism is applied to a simple example which exhibits the influence of librational modes of a molecule with strong internal bindings on phonon scattering. The t matrix for the chosen model is diagonalized by complete group theoretical reduction and reveals the structure of the molecular resonances explicitly. It is found that the resonance is very sharp if the molecular frequency is much smaller than the Debye frequency, and decreases for higher frequencies.

INTRODUCTION

RECENTLY, the problem of phonon resonance scattering at impurity centers has attracted much interest, mainly because these resonances give rise to indentations in the curves of thermal conductivity versus temperature. This was shown by Pohl[1] for the system KCl:KNO$_2$, and by Walker and Pohl[2] for systems like KCl:KI, KCl:NaCl, etc. In the first case we have a molecular impurity center, in the second a monatomic one, and both experiments can be explained rather well by a quasiphenomenological theory given by the author in a previous paper.[3] But as this theory still contains adjustable parameters, so it is desirable to investigate the underlying scattering process in full detail.

There is no difficulty in handling the monatomic impurities, because the number of degrees of freedom in the lattice is unchanged in this case and the application of the Lifshitz[4] method is straightforward. Very recent calculations by Krumhansl,[5] Klein,[6] and Takeno[7] have shown that there are, under certain conditions, resonances in the phonon scattering at monatomic centers due to the alterations in mass and force constants. These resonances can be said to be more or less "accidental"; they correspond to quasilocalized modes within the phonon bands which dissipate slowly into the surrounding lattice if the substitutional mass is very large,[8] or if the force constants are weakened drastically near the impurity center, e.g., for U centers or F centers.[5]

In contrast to that, there are, in general, more pronounced resonances in the case of molecular impurities. This problem, however, seems to be much more complicated because of the new degrees of freedom brought in by the molecular nuclei. The author[9] has shown how, in principle, the additional coordinates can be excluded by means of a molecular Green's function and the Lifshitz method is then easily applied to the remaining unchanged number of lattice coordinates. But there is now an additional effective disturbance which has poles at the molecular frequencies via the molecular Green's function. These poles will produce new sharp resonances if they lie within the phonon bands.

The abstract formalism for the general problem is outlined in Secs. I–III. In the remaining sections we will choose a particularly simple model of a molecule exhibit-

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ing the essential features, which we are able to calculate completely by group theoretical methods.

I. VIBRATIONS OF THE DISTURBED LATTICE

Let us introduce[10] a molecule of $s+1$ atoms into the lattice and replace one of the lattice atoms by the molecule. The three center-of-mass coordinates and the total mass of the molecule we add to the lattice system, thus making it a complete $3N$ system as in the ideal lattice. The remaining $3s$ reduced coordinates of the molecule are taken as the "molecular system." Then the time-independent equations of motion read,

$$[L+A(\omega^2)-\omega^2 I]\cdot z+B\cdot\zeta=0,\ (3N\text{ equations}),\qquad(1\text{a})$$

$$(\alpha-\omega^2 I)\cdot\zeta+\tilde{B}\cdot z=0,\ (3s\text{ equations}),\qquad(1\text{b})$$

where z is the set of mass-reduced Cartesian lattice coordinates, and ζ the set of molecular coordinates (center-of-mass excluded and mass-reduced). L is the ideal lattice matrix and $A(\omega^2)$ the deviation from it; both are $3N\times 3N$ matrices. B gives the interaction between the molecular and lattice coordinates ($3N\times 3s$ matrix) and α is the $3s\times 3s$ molecular matrix.

The fundamental system of equations (1a,b) can be reduced to $3N$ equations by means of a molecular Green's function, which is defined by the solution of the molecular eigenvalue equation,

$$\alpha\zeta(\kappa)=\omega_\kappa{}^2\zeta(\kappa),\qquad(2)$$

where $\zeta(\kappa)$ are $3s$-dimensional eigenvectors and $\omega_\kappa{}^2$ the respective eigenfrequencies. Physically, the Eqs. (2) represent the vibrations of the molecule if all lattice coordinates are fixed in their equilibrial position.

Using the solutions of (2), the molecular Green's function can be written as

$$\gamma(\omega^2)=(\alpha-\omega^2 I)^{-1}=\sum_\kappa\frac{\zeta(\kappa)\zeta^\dagger(\kappa)}{\omega^2(\kappa)-\omega^2},\qquad(3)$$

and we can use this Green's function to rewrite Eq. (1b) as

$$\zeta=-\gamma(\omega^2)\tilde{B}\cdot z.\qquad(4)$$

Inserting this expression for ζ into (1a), we are left with a system of $3N$ equations and the molecular coordinates are excluded:

$$(L-\omega^2 I)\cdot z=-V\cdot z,\qquad(5)$$

where

$$V=A(\omega^2)-B\gamma(\omega^2)\tilde{B}.\qquad(6)$$

The effective disturbance V within the system of lattice coordinates contains, apart from the rather smooth function $A(\omega^2)$, an additional molecular term $-B\gamma(\omega^2)\tilde{B}$ which has poles at the molecular frequencies ω_κ. Thus V cannot be treated as a perturbation near the ω_κ frequencies, however small the coupling B may be.

To the system of Eqs. (5) we may now apply the method of Lifshitz. Let $\eta(\mathbf{k}\lambda)$ and $\omega^2(\mathbf{k}\lambda)$ be the solutions for the ideal lattice,

$$L\eta(\mathbf{k}\lambda)=\omega^2(\mathbf{k}\lambda)\eta(\mathbf{k}\lambda),\ \eta_{\mathbf{n}}{}^i(\mathbf{k}\lambda)=N^{-1/2}\epsilon^i(\mathbf{k}\lambda)e^{i\mathbf{k}\cdot\mathbf{n}},\qquad(7)$$

where $\mathbf{k}$ is the wave vector and λ the polarization of the phonon. Then the lattice Green's function reads

$$G(\omega^2)=(L-\omega^2 I)^{-1}=\sum_{\mathbf{k}\lambda}\frac{\eta(\mathbf{k}\lambda)\eta^\dagger(\mathbf{k}\lambda)}{\omega(\mathbf{k}\lambda)^2-\omega^2},\qquad(8)$$

and we can rewrite Eq. (5) as

$$z=-G(\omega^2)V(\omega^2)\cdot z.\qquad(9)$$

This seems to be a formal procedure, but it is in fact a great simplification. Namely, the disturbance V extends only to a small number of lattice points, say r, around the impurity center; therefore it can be written as

$$V=\begin{pmatrix}v&0\\0&0\end{pmatrix},\ v=a-b\gamma\tilde{b},\qquad(10)$$

where v is a $3r\times 3r$ matrix, and a and b the corresponding nonvanishing parts of A and B, respectively. Writing $G(\omega^2)$ in the form

$$G=\begin{pmatrix}g&q\\\tilde{q}^*&g'\end{pmatrix},\qquad(11)$$

where the $3r\times 3r$ matrix g corresponds to v, we see that the right-hand side of Eq. (9) contains only the coordinates of the r lattice points involved in the disturbance. Consequently, the system (9) consists in fact of only $3r$ independent equations, whereas the coordinates outside the disturbed region are given by the coordinates inside. Hence we can extract from the system (9) a determinental equation of rank $3r$:

$$D(\omega^2)=\operatorname{Det}[I+g(\omega^2)(a(\omega^2)-b\gamma(\omega^2)\tilde{b})]=0,\qquad(12)$$

and the $3N+3s$ roots of (12) are the eigen solutions of the fundamental equations of motion (1a,b). Considering for the moment only the factor $g(\omega^2)$, we see by looking at the definition (8) of the lattice Green's function that $g(\omega^2)$ jumps from $-\infty$ to $+\infty$ between two consecutive $\omega^2(\mathbf{k}\lambda)$ values. This means that there must be a solution of (12) between two neighboring $\omega(\mathbf{k}\lambda)$ values. Thus we have a spectrum of solutions in the same region and with the same density as in the ideal case. Eventually there are one or a few solutions outside the ideal bands; these are the true localized modes.

The factor $a(\omega^2)$ does not alter this picture, as $a(\omega^2)$ is not a strongly varying function of ω^2. But there are some new features if we take into account the factor $b\gamma(\omega^2)\tilde{b}$. This term has additional poles at the molecular frequencies $\omega_\kappa{}^2$, and gives rise to $3s$ new solutions distributed outside and inside the ideal bands. But the more important fact is that the Lifshitz solutions given by the matrix $g(\omega^2)a(\omega^2)$ are strongly disturbed in the neighborhood of those molecular frequencies $\omega_\kappa{}^2$ lying inside the bands; this has great influence on phonon

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[10] This section is a short review of the method given in Ref. 9.

scattering and produces resonances in the scattering amplitude.

II. THE SCATTERING FORMALISM

We have seen from the determinantal Eq. (12) that the spectrum of solutions for the disturbed lattice occupies the same regions as in the ideal lattice, apart from the singular solutions outside the bands which we shall not consider here. As the distribution is a very dense one, we ask for solutions of the form

$$z_{\mathbf{n}}^{i}(\mathbf{k}\lambda)=\eta_{\mathbf{n}}^{i}(\mathbf{k}\lambda)+w_{\mathbf{n}}^{i}(\mathbf{k}\lambda)\,, \tag{13}$$

the frequency of which lies very near to $\omega(\mathbf{k}\lambda)$. Then we may consider $\eta_{\mathbf{n}}^{i}(\mathbf{k}\lambda)$ as the incident phonon and $w_{\mathbf{n}}^{i}(\mathbf{k}\lambda)$ as the scattering amplitude. Far away from the scattering center we can write

$$\lim_{|\mathbf{n}|\to\infty} w_{\mathbf{n}}^{i}(\mathbf{k}\lambda)=N^{-1/2}\frac{\exp(i|\mathbf{k}|\,|\mathbf{n}|)}{|\mathbf{n}|}f_{\mathbf{k}\lambda}{}^{i}(\vartheta,\varphi)\,, \tag{14}$$

and define the differential cross section as

$$\sigma_{\mathbf{k}\lambda}{}^{i}(\vartheta,\varphi)=|f_{\mathbf{k}\lambda}{}^{i}(\vartheta,\varphi)|^{2}. \tag{15}$$

The scattering cross section thus being connected with the scattering amplitude, the task of our investigation is the calculation of $w_{\mathbf{n}}^{i}(\mathbf{k}\lambda)$.

The spectrum of both the ideal and the disturbed solutions is discrete but very dense. It is convenient, therefore, to go to the continuum by replacing summations in $\mathbf{k}$ space by integrations

$$N^{-1}\sum_{\mathbf{k}\lambda}\cdots=\left(\frac{a}{2\pi}\right)^{3}\sum_{\lambda}\int\cdots d^{3}k. \tag{16}$$

But then the Green's function $G(\omega^2)$ is no longer defined, being an improper integral. We redefine it according to standard scattering theory as

$$G_{(+)}(\omega^{2})=(L-I(\omega^{2}+i\epsilon))^{-1}=\sum_{\mathbf{k}\lambda}\frac{\eta(\mathbf{k}\lambda)\eta^{+}(\mathbf{k}\lambda)}{\omega^{2}(\mathbf{k}\lambda)-(\omega^{2}+i\epsilon)}\,, \tag{17}$$

which is the Green's function for the "outgoing" wave solution. (ϵ is an infinitesimal positive number.) By means of this Green's function we can write down the Lippman-Schwinger equation,

$$z^{(+)}(\mathbf{k}\lambda)=\eta(\mathbf{k}\lambda)-G_{(+)}(\omega^{2})V(\omega^{2})z^{(+)}(\mathbf{k}\lambda). \tag{18}$$

This is the fundamental integral equation of scattering theory. The $+$ sign indicates the outgoing wave solution. (The corresponding equation for the incoming wave solution is of no physical significance, although it is important in the more advanced scattering formalism; but we will not need it in our formulation.)

Instead of using directly the Lippman-Schwinger equation we establish a T matrix formulation,

$$z^{(+)}(\mathbf{k}\lambda)=\eta(\mathbf{k}\lambda)-G_{(+)}(\omega^{2})T_{(+)}(\omega^{2})\eta(\mathbf{k}\lambda)\,, \tag{19}$$

which yields for the scattering amplitude:

$$w^{(+)}(\mathbf{k}\lambda)=-G_{(+)}(\omega^{2})T_{(+)}(\omega^{2})\eta(\mathbf{k}\lambda). \tag{20}$$

We get the properties of the T matrix by iterating Eq. (18). Doing this we have the following series:

$$T_{(+)}=V-VG_{(+)}V+VG_{(+)}VG_{(+)}V\mp\cdots. \tag{21}$$

The first term represents the Born approximation. But we have to take the higher terms also, because V cannot be assumed to be small, thinking only of the molecular poles contained in it. It is easily seen, however, that we can write the series in the simple form

$$T_{(+)}=V(I+G_{(+)}V)^{-1}. \tag{22}$$

Remembering now that the disturbance V is essentially a $3r\times3r$ matrix [Eq. (10)] extending over a small region around the scattering center only, it is elementary to verify that the T matrix also can be written in the form

$$T_{(+)}=\begin{pmatrix} t & 0\\ 0 & 0\end{pmatrix}, \tag{23}$$

where

$$t=v(I+g_{(+)}v)^{-1} \tag{24}$$

is a $3r\times3r$ matrix in v space.

III. RESONANCES IN THE SCATTERING AMPLITUDE

According to (20) and (17) the scattering amplitude can be written down in the form

$$w^{(+)}(\mathbf{k}\lambda)=-\sum_{\mathbf{k}'\lambda'}\frac{1}{\omega(\mathbf{k}'\lambda')^{2}-(\omega(\mathbf{k}\lambda)^{2}+i\epsilon)}\times\eta(\mathbf{k}'\lambda')\langle\eta(\mathbf{k}'\lambda')|t|\eta(\mathbf{k}\lambda)\rangle, \tag{25}$$

which means that we have to calculate the scalar product $\langle\eta'|t|\eta\rangle$, where only the components $\eta_{\mathbf{n}}^{i}$ in t space are involved. The resonances of the scattering amplitude are given by the resonances in the t matrix.

Because of the low rank $3r$, it is, in general, very easy to diagonalize the denominator of the t matrix by symmetry considerations. Let us assume that we know the eigensolutions of the matrix $g_{(+)}v$:

$$g_{(+)}v\cdot e(j)=\mu_{j}e(j)\,, \tag{26}$$

then we can write the t matrix in the form

$$t=v\sum_{j}\frac{e(j)e(j)^{+}}{1+\mu_{j}}. \tag{27}$$

Very often the symmetry of v is contained in the higher symmetry of $g_{(+)}$, and in this special case v has the same eigenvectors as $g_{(+)}v$,

$$v\cdot e(j)=v_{j}e(j)\,, \tag{28}$$

so that the t matrix takes the form

$$t=\sum_{j}\frac{v_{j}}{1+\mu_{j}}e(j)e(j)^{+}. \tag{27a}$$

The expressions (27) or (27a) show that there is a resonance in the scattering amplitude if the real part of one of the denominators $1+\mu_j$ becomes zero. Hence, the resonance condition is

$$1+\mathrm{Re}\mu_j(\omega^2)=0, \tag{29}$$

yielding a special resonance frequency $\omega^2=\omega_j^2$. Supposing the resonance to be sufficiently strong, the jth term in the t matrix exceeds all other terms in the neighborhood of $\omega^2=\omega_j^2$:

$$t\approx v(\omega_j^2)\frac{e(j)e(j)^+}{(\omega^2-\omega_j^2)R_j+iI_j}, \text{ for } \omega^2\approx\omega_j^2, \tag{30}$$

where we have expanded the denominator around $\omega^2=\omega_j^2$,

$$R_j=\frac{d}{d\omega^2}\mathrm{Re}\mu_j(\omega^2)\,|_{\omega=\omega_j},\; I_j=\mathrm{Im}\mu_j(\omega_j^2). \tag{31}$$

As the denominator of (30) enters with its absolute square into the expression for the scattering cross section [Eq. (15)], the half-width of the resonance is given by

$$(\omega_H{}^{(j)2}-\omega_j^2)/\omega_j^2=I_j/\omega_j^2R_j, \tag{32}$$

and there is a sharp resonance if this expression is much smaller than unity.

The formalism developed so far is not restricted to any special form of the disturbance v. It is quite similar to the abstract formalism used by Klein[6] as a basis for the calculation of scattering resonances if there is a monatomic defect in the lattice. Klein has discussed the formalism in great detail and we refer to his work.

Considering our special form of the disturbance [Eq. (10)], we realize that some of the μ_j's (at least one) must contain the poles of the molecular Green's function γ; these vary over a wide range and are very likely to give a solution of the resonance condition (29). On the other hand, there may be some of the μ_j's which do not contain the molecular poles; for them there may also exist a solution of the resonance condition (29), but these resonances are of the monatomic defect type.

To calculate the structure and spectral position of the resonances explicitly, we have to establish a specific model for both the lattice and the molecular defect. The calculation of the decisive eigenvalues μ_j is then often greatly simplified by symmetry considerations.

IV. A SIMPLE MODEL

To demonstrate the principal new features of the scattering at molecular impurities we choose a particular model of the utmost simplicity, which, however, exhibits just the important features. We know that the internal binding in the molecule is often much stronger than the lattice binding and it is practically unchanged when the molecule is brought into the lattice. For example, this is true for the NO_2^- molecule in an alkali halide crystal.

If we assume such strong internal binding, we can distinguish three types of motion for the atoms of the molecule:

(a) The internal vibrations, which are practically the same as for the free molecule. Their frequencies lie far above the phonon bands, so that they are not likely to be excited by phonon scattering.
(b) The translational vibrations of the whole molecule; these are the same as if the molecule was a single mass, and this case has been treated already.[5–7]
(c) The rotational vibrations of the whole molecule, for which the molecule acts as a rigid body with three moments of inertia.

It is clear that we are principally interested in the third type of motion with its new degrees of freedom and we establish, therefore, a model which allows us to exclude the first two types. We take the molecule to be a rigid body, and for simplicity we take it even as a rigid sphere of one single moment of inertia Θ. The total mass of the sphere we postulate to be just the mass of the lattice atom which is replaced by the molecule, and we postulate also that the translational interaction with the surrounding lattice be undisturbed.

The host lattice we assume to be monatomic (with mass M) and cubic, and the rigid sphere may be coupled to the six nearest lattice atoms by tangential springs with constants f. Then the three remaining molecular coordinates[11] are degenerate and conveniently taken as the rotations φ_x, φ_y, φ_z around the three axes, and the molecular Green's function simply reads

$$\gamma(\omega^2)=\frac{1}{\omega_\kappa{}^2-\omega^2}I \text{ (3 dimensional)}, \tag{33}$$

where

$$\omega_\kappa{}^2=\frac{4f}{(\Theta/a^2)} \text{ (a=lattice spacing)}. \tag{34}$$

There are 12 lattice coordinates involved in the disturbance, namely, those to which the molecular sphere is coupled by tangential springs

$$x\equiv\{y_1,z_1,z_2,x_2,x_3,y_3,y_4,z_4,z_5,x_5,x_6,y_6\}, \tag{35}$$

whence the v and t space is 12 dimensional. The coordinates are shown in Fig. 1. The matrices a, $b\gamma\tilde{b}$, and $g_{(+)}$ are defined by their Hermite forms in the space x:

$$\langle x|a|x\rangle=(f/M)\{y_1^2+z_1^2+z_2^2+x_2^2+\cdots+y_6^2\}, \tag{36a}$$

$$\langle x|b\gamma\tilde{b}|x\rangle=\frac{f}{4M}\frac{\omega_\kappa{}^2}{\omega_\kappa{}^2-\omega^2}\{(y_1+x_2+y_4+x_5)^2 + (z_2+y_3+z_5+y_6)^2+(x_3+z_1+x_6+z_4)^2\}, \tag{36b}$$

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[11] It should be remembered that the three translational coordinates of the molecule belong to the "lattice system" according to our convention.

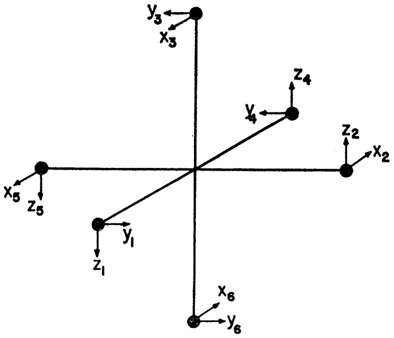

FIG. 1. The tangential nearest-neighbor coordinates involved in the disturbance.

$$\langle x|g_{(+)}|x\rangle=\tfrac{1}{2}(A\text{-}C)\{(y_1+y_4)^2+(z_1+z_4)^2+\cdots\}+\tfrac{1}{2}(A+C)\{(y_1-y_4)^2+(z_1-z_4)^2+\cdots\}-2B\{(y_1-y_4)(y_3-y_6)+(z_1-z_4)(z_2-z_4)+(x_2-x_5)(x_3-x_6)\}. \quad (36c)$$

For the last expression we have taken into account that the reciprocal lattice is also cubic. Moreover, we have used the approximation

$$\omega(\mathbf{k}\lambda)^2\equiv\omega(\mathbf{k})^2, \quad (37)$$

which allows the summation over the different polarizations λ. This is, in fact, not necessary for the following calculation. A more accurate form for $g_{(+)}$ would contain a few more constants, but would be diagonalized by the same symmetry coordinates as (36a,b,c). The constants A, B, and C in (36c) are given by

$$A=N^{-1}\sum_{\mathbf{k}'}\frac{1}{\omega(\mathbf{k}')^2-(\omega(\mathbf{k})^2+i\epsilon)}, \quad (38a)$$

$$B=N^{-1}\sum_{\mathbf{k}'}\frac{\exp[ia(k_x'+k_y')]}{\omega(\mathbf{k}')^2-(\omega(\mathbf{k})^2+i\epsilon)}, \quad (38b)$$

$$C=N^{-1}\sum_{\mathbf{k}'}\frac{\exp(2iak_x')}{\omega(\mathbf{k}')^2-(\omega(\mathbf{k})^2+i\epsilon)}. \quad (38c)$$

V. GROUP THEORETICAL REDUCTION

The Hermite forms (36a,b,c) are invariant under any operation of the octahedral group O_h, which means that $\langle x|t|x\rangle$ is also invariant:

$$O_h\langle x|t|x\rangle=\langle x|t|x\rangle. \quad (39)$$

Hence we can diagonalize the matrices a, $b\gamma\tilde{b}$, $g_{(+)}$, and t by complete reduction of the representation Γ of O_h given by the set of coordinates $x\equiv\{y_1,z_1,\cdots\}$. This 12-dimensional representation can be separated into two 6-dimensional ones by noting that

$$O_h=O\times i, \quad (40)$$

where i is the inversion group consisting only of two elements and with two (one-dimensional) irreducible representations: a totally symmetric, and an antisymmetric one. Thus the set x is divided into two subsets x_g and x_u belonging to the two representations of i:

$$x_g\equiv\{(y_1+y_4),(z_1+z_4),(z_2+z_5),(x_2+x_5),(x_3+x_6),(y_3+y_6)\}, \quad (41a)$$

$$x_u\equiv\{(y_1-y_4),(z_1-z_4),(z_2-z_5),(x_2-x_5),(x_3-x_6),(y_3-y_6)\}. \quad (41b)$$

Each subset has 6 coordinates, and both sets are orthogonal to one another. It is easily verified that both x_g and x_u transform within themselves under the operations of O, which we can write in a shorthand notation as

$$O\cdot x_g=x_g,\ O\cdot x_u=x_u. \quad (42a,b)$$

Therefore, each subset constitutes a 6-dimensional representation of O, say Γ_g and Γ_u. The Hermite forms $\langle x|a|x\rangle$, etc., are easily transcribed into the coordinates of (41a,b), and it is seen that they do not have any mixed terms between x_g and x_u.

Table I gives the character table of the group O and the characters of the representations Γ_g and Γ_u. From this data we are able to determine the numbers $n^{(\nu)}$, how often an irreducible representation $\Gamma^{(\nu)}$ is contained in Γ_g or Γ_u, using the formula

TABLE I. Character table of the irreducible representations of O and of the representations Γ_g and Γ_u.

O	E	$8C_3$	$3C_4^2$	$6C_4$	$6C_2$	$n_g^{(\nu)}$	$n_u^{(\nu)}$
A_1	1	1	1	1	1	0	0
A_2	1	1	1	−1	−1	0	0
E	2	−1	2	0	0	0	0
F_1	3	0	−1	1	−1	1	1
F_2	3	0	−1	−1	1	1	1
Γ_g	6	0	−2	0	0		
Γ_u	6	0	−2	0	0		

$$n^{(\nu)}=\frac{1}{g}\sum_R\chi^{(\nu)}(R)^*\chi(R), \quad (43)$$

where $\chi(R)$ are the characters of Γ_g or Γ_u, respectively, $\chi^{(\nu)}(R)$ the character of the irreducible representation $\Gamma^{(\nu)}$, g the order of the group ($g=24$), and the sum extends over all group operations R. From Table I we see that the threefold degenerate representations F_1 and F_2 are both contained once in either Γ_g and Γ_u:

$$\Gamma_g=F_{1g}+F_{2g},\ \Gamma_u=F_{1u}+F_{2u}, \quad (44a,b)$$

and the total representation Γ of the set x splits into

$$\Gamma=F_{1g}+F_{2g}+F_{1u}+F_{2u}. \quad (45)$$

The typical symmetry vectors are shown in Fig. 2 and all the 12 symmetry vectors are given in Table II. These are just the 12 eigenvectors of Eq. (26). They are also the eigenvectors of Eq. (28), as the matrices $g_{(+)}v$ and v

have the same symmetry in our special model. We find the eigenvalues μ_j and v_j of (26) and (28), respectively, by transforming the Hermite forms (36a,b,c) to the symmetry coordinates defined by the eigenvectors $e_i^{(\nu)}(j)$ of Table II[12]:

$$s^{(\nu)}(j)=\sum_i x_i e_i^{(\nu)}(j),\ (\nu=1,2,3)\,, \tag{46}$$

where $x_i=y_1,z_1$, etc. We get

$$\langle x|a|x\rangle=(f/M)\{s^{(1)}(1g)^2+s^{(2)}(1g)^2+\cdots+s^{(3)}(2u)^2\}\,, \tag{47a}$$

$$\langle x|b\gamma\tilde{b}|x\rangle=\frac{f}{16M}\frac{\omega_\kappa^2}{(\omega_\kappa^2-\omega^2)}\{s^{(1)}(1g)^2+s^{(2)}(1g)^2+s^{(3)}(1g)^2\}\,, \tag{47b}$$

$$\begin{aligned}\langle x|g_{(+)}|x\rangle=&(A-C)\{s^{(1)}(1g)^2+\cdots+s^{(1)}(2g)^2+\cdots\}\\&+(A+C+B)\{s^{(1)}(1u)^2+s^{(2)}(1u)^2+s^{(3)}(1u)^2\}\\&+(A+C-B)\{s^{(1)}(2u)^2+s^{(2)}(2u)^2+s^{(3)}(2u)^2\}\,,\end{aligned} \tag{47c}$$

from which we have for the four different eigenvalues μ_j

$$\mu_{1g}=\frac{f}{M}(A-C)\left[1-\frac{\omega_\kappa^2}{16(\omega_\kappa^2-\omega^2)}\right], \tag{48a}$$

$$\mu_{2g}=(f/M)(A-C)\,, \tag{48b}$$

$$\mu_{1u}=(f/M)(A+C+B)\,, \tag{48c}$$

$$\mu_{2u}=(f/M)(A+C-B)\,, \tag{48d}$$

each of which is triply degenerate. Further on we get from (47)

$$v_{1g}=\frac{f}{M}\left[1-\frac{\omega_\kappa^2}{16(\omega_\kappa^2-\omega^2)}\right], \qquad v_{2g}=v_{1u}=v_{2u}=f/M\,. \tag{49a–d}$$

TABLE II. The 12 symmetry vectors of the t matrix (N-normalization constant).

		y_1	z_1	z_2	x_2	x_3	y_3	y_4	z_4	z_5	x_5	y_6	y_6	N
	$e^{(1)}$	0	0	1	0	0	1	0	0	1	0	0	1	$\frac{1}{2}$
F_{1g}	$e^{(2)}$	0	1	0	0	1	0	0	1	0	0	1	0	$\frac{1}{2}$
	$e^{(3)}$	1	0	0	1	0	0	1	0	0	1	0	0	$\frac{1}{2}$
	$e^{(1)}$	0	0	1	0	0	−1	0	0	1	0	0	−1	$\frac{1}{2}$
F_{2g}	$e^{(2)}$	0	1	0	0	−1	0	0	1	0	0	−1	0	$\frac{1}{2}$
	$e^{(3)}$	1	0	0	−1	0	0	1	0	0	−1	0	0	$\frac{1}{2}$
	$e^{(1)}$	0	0	0	1	−1	0	0	0	0	−1	1	0	$\frac{1}{2}$
F_{1u}	$e^{(2)}$	1	0	0	0	0	−1	−1	0	0	0	0	1	$\frac{1}{2}$
	$e^{(3)}$	0	1	−1	0	0	0	0	−1	1	0	0	0	$\frac{1}{2}$
	$e^{(1)}$	0	0	0	1	1	0	0	0	0	−1	−1	0	$\frac{1}{2}$
F_{2u}	$e^{(2)}$	1	0	0	0	0	1	−1	0	0	0	0	−1	$\frac{1}{2}$
	$e^{(3)}$	0	1	1	0	0	0	0	−1	−1	0	0	0	$\frac{1}{2}$

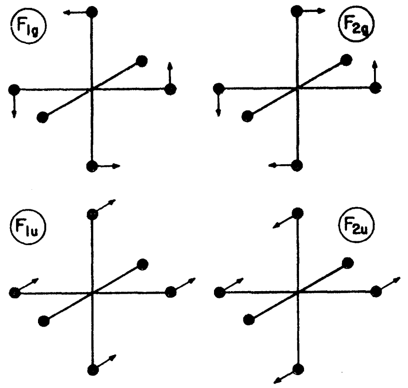

FIG. 2. The typical symmetry vectors of the t matrix.

Thus the group theoretical analysis has given us the complete solution of the originally rather awkward eigenvalue problems (26) and (28) of 12 dimensions.

VI. THE MOLECULAR RESONANCE

The most interesting eigenvalue of (48) is μ_{1g}, because it contains the "molecular resonance," whereas the other eigenvalues give the more or less accidental resonances. Let us focus therefore our attention on μ_{1g}. We make the following approximations,

$$\omega(\mathbf{k}\lambda)\equiv\omega(\mathbf{k}) \tag{50}$$

and

$$\omega(\mathbf{k})\equiv c|\mathbf{k}|\ \text{(acoustic approximation)}. \tag{51}$$

Using these approximations it is straightforward to replace the first Brillouin zone by a sphere of equal volume in k space, by means of which the limiting wave vector k_D is given by

$$k_D=\omega_D/c=(\pi/a)(6/\pi)^{1/3}\approx(5/4)(\pi/a)\,, \tag{52}$$

where ω_D is the Debye frequency, and a the lattice spacing. Thus the average sound velocity c is given by the Debye frequency as

$$c=(\pi/6)^{1/3}(a/\pi)\omega_D\approx\tfrac{1}{4}a\omega_D\,. \tag{53}$$

The function (A-C), given by (38a) and (38c), is then easily calculated, if we replace the summation by an integration according to (16) and use the well-known relations

$$\frac{1}{x-i\epsilon}=P\frac{1}{x}+i\pi\delta(x)\,, \tag{54a}$$

$$\delta(\omega'^2-\omega^2)=\frac{\delta(\omega'-\omega)+\delta(\omega'+\omega)}{2\omega'}\,, \tag{54b}$$

$$\delta(ck)=\frac{\delta(k)}{c}\,. \tag{54c}$$

Then we get after some elementary reduction

$$(A-C)=\tfrac{1}{4}(a/\pi c)^2[S(z)+iS'(z)]\,, \tag{55}$$

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[12] The symmetry coordinates can be read off directly from Table II by multiplying the coordinates of the first row with the components of the respective eigenvector below.

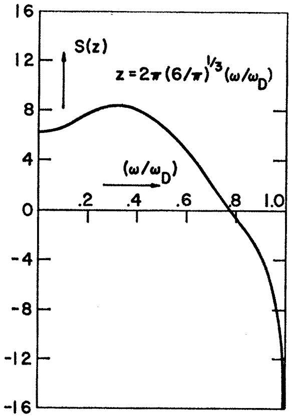

FIG. 3. The function $S(z)$.

where $S(z)$ represents the principal value integral

$$S(z)=P\int_0^{z_0}\frac{z'}{z'^2-z'}[z'-\sin z']dz',\qquad (z_0=2ak_D,\ z=2ak).\qquad (56)$$

This integral is transcribed into terms of integral sines and cosines which are tabulated in standard literature.

$$S(z)=z_0+\frac{z}{2}\ln\left(\frac{z_0-z}{z_0+z}\right)-\tfrac{1}{2}\{\cos z[Si(z_0-z)+Si(z_0+z)]+\sin z[Ci(z_0-z)-Ci(z_0+z)]\}.\qquad (56a)$$

Figure 3 shows the behavior of the function $S(z)$. The integral $S'(z)$ is simply given by

$$S'(z)=(\pi/2)(z-\sin z).\qquad (57)$$

Introducing the expression (55) into (48a), the resonance condition (29) for $j=1g$ reads

$$1+\frac{1}{4}\frac{f}{M}\left(\frac{a}{\pi c}\right)^2 S(z)\left[1-\frac{\omega_\kappa^2}{16(\omega_\kappa^2-\omega^2)}\right]=0,\qquad (58)$$

or

$$\omega_\kappa^2-\omega_{1g}^2=\tfrac{1}{16}\omega_\kappa^2\left(1+\frac{1}{KS(z_{1g})}\right)^{-1},\qquad (59)$$

where

$$K=\tfrac{1}{4}\frac{f}{M}\left(\frac{a}{\pi c}\right)^2=\tfrac{1}{4}\left(\frac{6}{\pi}\right)^{2/3}\frac{f}{M}\left(\frac{1}{\omega_D^2}\right).\qquad (60)$$

From Fig. 3 it is seen that $-10<S(z)<+10$ except for frequencies near the Debye frequency ($\omega>0.98\omega_D$), but in this region the Debye approximation (51) is very poor and $S(z)$ is no longer given by the integral (56). Therefore we exclude this region from our consideration. $S(z)$ is zero at $\omega_s=0.775\omega_D$, positive below this ω value, and negative above. This means in view of (59) that ω_{1g} lies below ω_κ for $\omega_\kappa<\omega_s$, and above for $\omega_\kappa>\omega_s$; for $\omega_\kappa=\omega_s$ we have just $\omega_{1g}=\omega_\kappa$. If we extrapolate this behavior up to the boundary of the phonon band, there will be no longer a solution of (58) inside the phonon band and therefore no scattering resonance as ω approaches the upper boundary. For $\omega_\kappa<\omega_s$ there will always be a resonance. By means of (48a), (49a), and (55) the diagonal element of the t matrix can be calculated:

$$|t_{1g}|^2=\left[\left(\frac{f}{M}\right)^2\cdot K^{-2}\right]\frac{\left[1-\dfrac{\omega_\kappa^2}{16(\omega_\kappa^2-\omega^2)}\right]}{\left[K^{-1}+S(z)\left[1-\dfrac{\omega_\kappa^2}{16(\omega_\kappa^2-\omega^2)}\right]\right]^2+S'(z)^2\left[1-\dfrac{\omega_\kappa^2}{16(\omega_\kappa^2-\omega^2)}\right]^2}.\qquad (61)$$

In the particularly interesting case, where the tangential spring connection between the molecule and the lattice is weak, the constant K is much smaller than unity:

$$K\ll 1 \text{ for } (f/M)\ll\omega_D^2.\qquad (62)$$

Therefore, $(KS)^{-1}\gg 1$, and (59) can be written approximately

$$\omega_\kappa^2-\omega_{1g}^2=\tfrac{1}{16}\omega_\kappa^2 KS(z_{1g})\ll\omega_\kappa^2 \text{ for } (f/M)\ll\omega_D^2.\qquad (59a)$$

In this case, the resonance frequency ω_{1g} lies only slightly below the molecular frequency ω_κ, and in the neighborhood of the resonance $|t_{1g}|^2$ can be written [Eq. (30)] as

$$|t_{1g}|^2_{\omega^2\approx\omega_{1g}^2}=\left[\tfrac{1}{16}\left(\frac{f}{M}\omega_\kappa^2\right)\right]^2\times\frac{1}{(\omega_{1g}^2-\omega^2)^2+[(\omega_\kappa^2/16)KS'(z_{1g})]^2},\qquad (61a)$$

for $\omega_\kappa^2\ll\omega_D^2$. The resonance is very sharp; using (32) and (57) we have

$$(\omega_H^{(1g)2}-\omega_{1g}^2)/\omega_{1g}^2=\frac{K}{16}S'(z_{1g})<\frac{\pi^2}{16}\left(\frac{6}{\pi}\right)^{1/3}K\ll 1,\qquad (63)$$

for $\omega_\kappa^2\ll\omega_D^2$. For higher molecular frequencies ω_κ the resonance gradually becomes broader and decreases.

It is now elementary to calculate also the scattering cross section, using the approximations (50) and (51). For a transverse incident phonon in the z direction

$$\mathbf{k}=k(0,0,1),\quad \epsilon_{\mathbf{k}\lambda}=(1,0,0),\qquad (64)$$

one gets after some algebra for the scattering at the modes F_{1g}

$$\sigma_{1g}{}^i(\mathbf{k},\text{transv.})=24\pi^5\left(\frac{6}{\pi}\right)^{2/3}a^2\frac{\omega^4|t_{1g}|^2}{\omega_D^8},\ \text{for } \omega\ll\omega_D,\qquad (65)$$

and this cross section is the domainant term in the neighborhood of the resonance of $|t_{1g}|^2$. It is seen that the Rayleigh scattering ($\sim\omega^4$) is modified by the functional form of $|t_{1g}|^2$. It is to be noted that for higher frequencies the Rayleigh term ($\sim\omega^4$) has to be changed into a smoother function of ω, but the proportionality to $|t_{1g}|^2$ naturally is unchanged.

For longitudinal phonons the partial scattering amplitude, belonging to the eigenvectors F_{1g} of the t matrix disappears.

The functional behavior of $|t_{1g}|^2$ without restriction to small frequencies is demonstrated in Fig. 4 for two different molecular frequencies ω_κ. For $\omega_\kappa^2=0.2\omega_D^2$ and $(f/M)=\frac{1}{4}\omega_\kappa^2$ [Fig. 4a] we have a very sharp resonance peak slightly below ω_κ. There is still another peak at the end of the spectrum which is due to the functional behavior of $S(z)$, however, as the acoustical approximation (51) breaks down near the Debye frequency, $S(z)$ is, in fact, not given by (56) in this region. Therefore, the form or even the existence of the second peak is somewhat questionable. Moreover, it is not unique to molecular defects and we need not consider it here, the more so as it is of no physical significance.

If the molecular frequency lies in the upper part of the spectrum, the resonance decreases more and more, as seen from Fig. 4(b) [$\omega_\kappa^2=0.8\omega_D^2$, $(f/M)=\frac{1}{4}\omega_\kappa^2$].

VII. SUMMARY AND DISCUSSION

In this paper we have formulated a theory on the scattering of phonons by molecular imperfections. By means of a molecular Green's function γ a new effective disturbance $-B\gamma\tilde{B}$ is introduced in the lattice system, whereas the molecular coordinates are removed. Thus, standard scattering theory is applicable in the lattice system. But the t matrix contains the molecular Green's function γ with its singular poles at the molecular frequencies which give rise to sharp molecular resonances in the scattering cross section. These resonances are revealed by diagonalizing the t matrix, or at least the denominator of the t matrix; in most practical cases this can be achieved by symmetry considerations.

Further on we have applied the abstract formalism to a particular, simple example consisting of a rigid sphere (molecule) embedded in a monatomic cubic crystal and interacting with the lattice via tangential springs to the 6 nearest neighbors. For this system the t matrix is diagonalized by complete group-theoretical reduction, and there is only one (threefold degenerate) eigenvalue t_{1g} of t, which contains the molecular resonance. The type of motion for t_{1g} is given by the symmetry vectors of the representation F_{1g} of O_h, and shown in Fig. 2. The functional behavior of $|t_{1g}|^2$ versus frequency is drawn in Fig. 4 and exhibits a peak near the molecular frequency ω_κ. This peak is very sharp and high if ω_κ lies well below the Debye frequency ω_D, whereas it gradually decreases if ω_κ approaches ω_D.

This simple model of a molecular impurity, though rather unrealistic, provides a good description of the scattering at the real molecule if its three moments of inertia do not differ strongly. This is plausible as the axial directions of all the molecular impurities in the crystal are equally distributed on the equivalent symmetry directions of the lattice and therefore, the molecule approaches in a statistical sense the features of a sphere. A well-known example of such a behavior is the system KCl:KNO$_2$; here the thermal conductivity, as measured by Pohl,[1] exhibits an indentation at about 10°K which indicates one single resonance in phonon scattering although there are three different moments of inertia for the molecule NO_2^-.

An application of the abstract formalism of Secs. I–III to more realistic models is without difficulty, although the practical calculation may be awkward. But for molecules with a small number of atoms the group theoretical reduction always leads to a great simplifica-

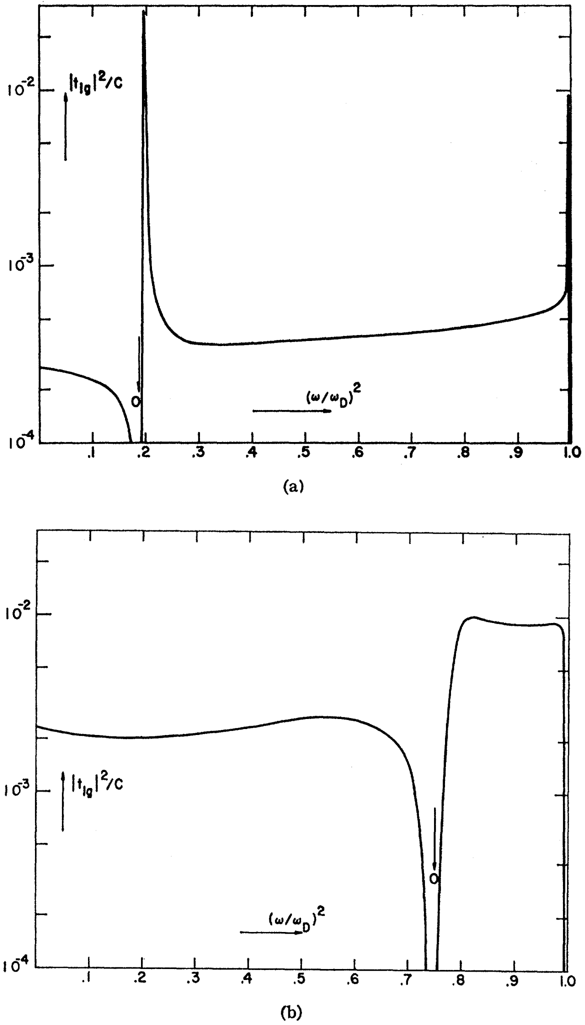

FIG. 4(a). The resonance behavior of $|t_{1g}|^2$ for $\omega_\kappa^2=0.2\omega_D^2$, $(f/M)=\omega_\kappa^2/4$. 4(b). The resonance behavior of $|t_{1g}|^2$ for $\omega_\kappa^2=0.8\omega_D^2$, $(f/M)=\omega_\kappa^2/4$. $C=16(\pi/6)^{4/3}\omega_D^4$.

tion, if not to the complete diagonalization of the t matrix, provided that the molecule and the surrounding lattice have some symmetry elements in common.

In our simple rigid model we have neglected the internal vibrations by assuming that their frequencies lie high above the phonon band. This is, of course, not true for all kinds of polyatomic defects and there may be "internal" frequencies lying within the phonon band; then there are also scattering resonances for this type of molecular motion. Yet in most practical cases the librational frequencies lie below the other molecular frequencies and have therefore the predominant scattering resonance.

The rotational binding forces of a molecule in the lattice are normally very weak; therefore, the librational amplitudes are very large, and exceed sometimes the region where the harmonic approximation is valid. This is a serious limitation, since in such a case the fundamental equations are no longer linear. However, the result will not change in principle: there will be a scattering resonance, but the resonance frequency will now depend on the amplitude of the incoming wave, i.e., on temperature. Thus the scattering cross section will also depend on temperature. The resonance frequency will decrease to zero with increasing amplitude and start increasing again when the amplitude exceeds the critical value where the libration is transferred into free rotation; but this process has not yet been tested by experiment.

It is to be emphasized that the theory given in this paper is purely classical. Naturally it has to be supplemented by a quantum-mechanical treatment, but this reveals no new features except for one effect which cannot be described classically. In general, the molecule in the lattice has several different equilibrium positions and is able to flip from one potential well to the other by tunneling. As the potential wells are cyclically closed, each eigenstate of the single well splits up into a "band" of energy values. The molecule may be able to make transitions between two states within one band, caused by phonon scattering. Thus, there exists the possibility of new scattering resonances at very low frequencies, but they have not yet been found experimentally. For example, in the case of the system $KCl:KNO_2$ there is no evidence as yet that there is another resonant indentation in the curves of thermal conductivity at extremely low temperatures.[13] However, there is evidence for the aforementioned "band" due to the tunneling; it was found by Pohl and Narayanamurti by optical excitation of the internal molecular vibrations.[14]

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[13] R. O. Pohl (private communication). Measurements at extremely low temperatures are in preparation at Cornell University.

[14] R. O. Pohl (private communication).