PHYSICAL REVIEW B VOLUME 8, NUMBER 10 15 NOVEMBER 1973

Dynamics of Crystals with Molecular Impurity Centers. II. Resonance Scattering of Lattice Waves*†

Hans R. Fankhauser
Advanced Studies Center, Battelle Institute, CH-1227 Carouge-Geneva, Switzerland ‡
Department of Physics, Michigan State University, East Lansing, Michigan 48823

(Received 26 October 1972; revised manuscript received 25 June 1973)

We consider a monatomic host lattice containing molecular impurity centers and find that even in the harmonic approximation impurity modes can interact. This leads to an interference term in the scattering cross section for lattice waves which may be of the same order as the direct terms. From a knowledge of the nonvanishing elements of the scattering matrix, one can obtain all information on the possible scattering mechanisms and acoustical activity (depolarization) of the modes involved. A model calculation reveals the contribution to the forward-scattering cross section of the term due to the interference between a librational mode and the motion of the center of mass. We also study the case where the symmetry at the defect site is reduced. We conclude with a discussion of what we might expect in a more realistic situation and point out that from corresponding experimental data it should be possible to obtain information about the extent to which a molecular defect of lower symmetry affects the dynamics of the host lattice.

I. INTRODUCTION

A study of the dynamics of a molecule in a host crystal based on group-theoretical methods was presented in a previous paper[1] (I). As an example of the practical value of symmetry arguments it was demonstrated that an analysis of the dependence of the infrared absorption on polarization relative to the crystallographic axes already leads to specific information on the orientation of a polyatomic molecule imbedded in a cubic crystal. As a second example we shall now study the scattering of lattice waves by a stereoscopic defect molecule in a simple cubic crystal in some detail.

In the harmonic approximation[2] it is possible to transform the dynamical variables of the system into a form in which there is no energy exchange between the new variables. The description defined this way in terms of normal modes or phonons is equivalent to a quantum mechanical discussion. Point defects, i.e., local changes of force constants or mass differences at a point compared to the ideal lattice, introduce either reasonances in the quasicontinuous spectrum of lattice vibrations or localized vibrations above the ideal band(s).

The scattering of lattice waves by point defects is understood rather well.[3-11] The reason for the considerable interest in this subject is due to the experimental verification of resonances in the scattering cross section from thermal-conductivity measurements at low temperatures.[12]

In Sec. II we refer to the extension of the Green's-function formalism of Lifshitz[3] to molecular impurities with additional degrees of freedom by Wagner[13,14] and we give an expression for the differential scattering cross section for lattice waves. The scattering cross section contains two terms, the direct one and an interference term, which may be of the same order of magnitude and contribute appreciably to the scattering cross section. This is a manifestation of the interaction of impurity modes which we do not find in the case of point defects. [We shall denote by *impurity* (or *defect*) *modes* those excitations of the molecular impurity center which are "normal modes" in the defect space (but not, however, exact eigenstates of the perturbed crystal); they are labeled by rows of a certain irreducible representation of the appropriate point group.] In Sec. III we consider the simple model of a spherical defect molecule and calculate the different contributions to the scattering cross section. In Sec. IV we replace the sphere by a rigid spheroid. This particular defect results in a lower symmetry at the defect site. We find that the number of nonvanishing matrix elements has increased, but there are no new scattering mechanisms. Of course, the degenerate modes may be partially split depending on the orientation of the spheroid with respect to the crystallographic axes. We conclude in Sec. V with a summary of our results, discuss a more realistic situation, and indicate the possibility of obtaining information about the extent to which a molecular defect of lower symmetry than the host crystal affects the dynamics of the latter from corresponding experimental data.

II. SCATTERING OF LATTICE WAVES

The Green's-function formalism introduced by Lifshitz[3] for the calculation of lattice vibrations in impure crystals is restricted to perturbed lattices with an unchanged number of particles (monatomic impurity centers), i.e., to cases where there are neither new degrees of freedom nor a change in symmetry at this particular lattice site. Wagner[13,14] extended this method to molecular impurity centers, and for details we refer to his work.

We are interested in the scattering of lattice waves by molecular impurity centers and consider the following system. A molecule replaces a regular lattice atom at a site, which we choose as origin of our coordinate system. We assume that the disturbance extends only to a small number r of lattice sites around the origin and treat the dynamical problem in the *harmonic approximation.*

The theory of the scattering of lattice waves by imperfections was first worked out rigorously by Lifshitz.[15] This theory has subsequently been developed further by Callaway,[4,8,16] Klein,[5,11] Krumhansl,[6] Takeno,[7] and Ludwig.[9]

We can write down a formally exact solution for the scattered wave in terms of the so-called scattering matrix t, which in turn is defined as the solution of the equation

$$\begin{aligned} t &= v - vgt = v - tgv \\ &= v(I+gv)^{-1}. \end{aligned} \tag{1}$$

Here $g(\omega^2)$ denotes the Green's function of the unperturbed lattice and

$$v = d(\omega^2) - b\gamma(\omega^2)\tilde{b}, \tag{2}$$

in analogy to the case of a point defect, is called the effective perturbation. It contains, apart from the rather smooth function $d(\omega^2)$ which characterizes the perturbation of the lattice by the molecule (difference in mass of the molecule and the replaced lattice atom, changes in the force constants involved), the additional molecular term $b\gamma(\omega^2)\tilde{b}$ which has poles [in the Green's function of the molecule $\gamma(\omega^2)$] at the eigenfrequencies of the molecule $\omega(\kappa)$. Thus v cannot be treated as a perturbation near these frequencies however small the coupling b ($\tilde{b}$ being the transpose of b) may be. Molecular frequencies lying within the band(s) of the unperturbed crystal exercise a great influence on the scattering of lattice waves and give rise to resonances in the scattering amplitudes.

Because of the low rank $3r$ (the number of degrees of freedom in the crystal affected by the introduction of the defect is $3r$), it is in general easy to diagonalize the denominator as well as the numerator of the t matrix [Eq. (1)] by symmetry considerations. The eigenvectors are given by the invariant subspaces (composing the defect space) of the corresponding proper or improper subgroups of the symmetry group of the host crystal consistent with the compatibility conditions (Paper I and Appendix). With this information we can write down the solutions immediately,

$$gve(\nu) = u(\nu)e(\nu)$$

and

$$ve(\nu) = v(\nu)e(\nu)\,.$$

Here $e(\nu)$ is a column vector and ν labels the row of the irreducible representation according to which the eigenvectors transform. Thus we can write the t matrix in the form

$$t = \sum_\nu \frac{v(\nu)}{1+u(\nu)}\, e(\nu)\tilde{e}(\nu) = \sum_\nu t(\nu)T(\nu)\,, \tag{3}$$

where we sum over all defect modes ν. The factors

$$t(\nu) = \frac{v(\nu)}{1+u(\nu)} \tag{4}$$

depend mainly on the Green's functions which characterize the dynamics of the system of the host lattice and the molecular impurity center. The matrices $T(\nu) = e(\nu)\tilde{e}(\nu)$ reflect essentially the symmetry of the system. They are given by the outer product of the invariant carrier (sub)spaces of the rows of the irreducible representations of the symmetry group of the defect which are compatible with the corresponding invariant subspaces of the symmetry group of the unperturbed crystal.

As in the quantum mechanical theory of scattering, the differential scattering cross section and the scattering amplitude are related[8] by

$$\sigma(\vec{k}\lambda,\, \vec{k}'\lambda') = |f(\vec{k}\lambda,\, \vec{k}'\lambda')|^2\,. \tag{5}$$

However, the proof of an optical theorem does not carry over directly to phonon scattering[11] because when changes in mass are involved, there is also a change in the "effective metric tensor." We use a relation between the scattering matrix and the scattering amplitude which was derived by Ludwig[9] from an asymptotic expression for the scattered wave. If we make the *acoustic approximation*

$$\omega(\vec{k}\lambda) = c(\lambda)\,|\vec{k}|\,, \tag{6}$$

$c(\lambda)$ being the group velocity in the λ branch, then in our notation and introducing the symbol $|\vec{k}\lambda\rangle$ to label a plane-wave state, the scattering amplitude has the form

$$f(\vec{k}\lambda,\, \vec{k}'\lambda') = \frac{a^3}{4\pi c^2(\lambda)}\,\langle \vec{k}'\lambda'|t|\vec{k}\lambda\rangle\,,$$

where a denotes the lattice parameter. Hence the differential scattering cross section [Eq. (5)] is given by

$$\begin{aligned} \sigma(\vec{k}\lambda,\, \vec{k}'\lambda') = \frac{a^6}{16\pi^2 c^4(\lambda)} \sum_{\mu\nu} t^*(\mu)t(\nu) \\ \times\langle\vec{k}'\lambda'|T(\mu)|\vec{k}\lambda\rangle^*\langle\vec{k}'\lambda'|T(\nu)|\vec{k}\lambda\rangle \end{aligned} \tag{7}$$

using the decomposition (3). Terms which contribute with $\mu=\nu$ we call *direct terms*, and those which contribute with $\mu\neq\nu$ we call *interference terms*, for they are due to the interaction of the different impurity modes labelled by μ and ν, respectively. It should be emphasized that this interaction of impurity modes is in clear distinction from the situation in a molecular crystal where the normal modes themselves are plane waves partly translational, partly rotational in character.[17]

From this expression we see that resonances in the t matrix also introduce resonances in the scattering cross section. The conditions for such resonances to occur were discussed by Klein[5] and also by Wagner.[14] It was found that modes for which the eigenvalues of the dynamical problem contain the poles of the molecular Green's function are likely to satisfy the resonance condition

$$1+\mathrm{Re}\,u(\nu,\omega^2)=0, \tag{8}$$

i.e., the real part of one of the denominators of Eq. (4) be zero.

We realize that the scattering of lattice waves by an impurity is much more complicated than the scattering of plane waves by a static potential in quantum theory. The equation $\omega^2(\vec{k}\lambda)=\omega^2$, which determines the stationary points, can have solutions in several branches of the function $\omega^2(\vec{k}\lambda)$. This has the consequence that although the incoming wave is in a definite branch of $\omega^2(\vec{k}\lambda)$, there can be several scattered waves propagating in different directions with the same frequency but with different group velocities and polarizations.

Even though it is not likely that a resonance in the interference term [Eq. (7)] would be as pronounced as one in a direct term, there still exists the possibility that the two terms might be of equal importance since the cross term does not enter through a perturbation calculation. A pair of modes, which transform according to rows of different irreducible representations, with eigenfrequencies in the same range and matrix elements between appropriate states different from zero may contribute appreciably to the scattering cross section. This possibility exists for instance in the combination of an in-band librational mode and the motion of the center of mass of the molecular defect, and we shall come back to this situation later on.

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.

III. SPHERICAL MOLECULES

We know that the internal binding in a molecule is often much stronger than the binding to the host lattice and it is practically unchanged when the molecule is brought into the lattice.

If we assume such strong internal binding, we can distinguish three types of motion for the molecular defect.

(a) One type of motion is *internal vibrations*, which are practically the same as for the free molecule. Some of their frequencies may lie far above the phonon band(s) and are not likely to be excited by phonon scattering. On the other hand, there also might be low-frequency modes below the maximum frequency of the host lattice. Such modes usually are associated with the stretching motion involving heavy atoms or bending modes. Bending vibrations have substantially lower frequencies than stretching modes of the same bonds (approximately $\frac{1}{3}$ or even less[18]). The reason for this is that bending motions primarily change angles in the configuration of the participating points which do not call for the same kind of restoring force (electrostatic repulsion) as in the case of stretching modes where the bond length changes.

(b) Another type of motion is *translational vibrations* of the whole molecule, which are essentially the same as if the molecule was a single mass. The dynamical behavior of point defects is quite well understood.[9,19–21] Also, the scattering problem for this case has been treated already[3–11,15,16,19,20] and we can take over the relevant results from there.

(c) The third type is *rotational vibrations* (quasirotations, librations) of the whole molecule, for which the molecule acts as a rigid body with three moments of inertia. The coupling of this type of motion to the host lattice will normally be weak and the associated frequency is likely to be found within the phonon band(s).

In many practical examples the frequencies associated with motions of type (a) lie above the frequencies propagated by the host crystal and will not affect the scattering cross section. Therefore we shall restrict our attention to the latter two types [types (b) and (c)]. Wagner,[14] in his analysis, left out the motion of the center of mass. This we shall not do here for the following reasons: First, modes associated with this motion are most likely to be inband modes. It is well known[2,9,19,20] that a heavier isotopic mass or the weakening of the force constants around a point defect give rise to resonance (pseudolocalized) modes. Then to be consistent with our model, where the center of mass of the molecular defect belongs to the lattice system, and with the assumption that the defect molecule be only weakly bound to the host crystal, we have to expect that the force constants describing the links between the molecular center of mass and the neighboring atoms are weaker than in the ideal lattice. Second, as already mentioned in the discussion of the differential cross section, Eq. (7), this mode might not only contribute directly to the scattering cross section but also appreciably through the interference term.

Let us now consider a rather simple model. As host lattice we choose a monatomic (mass M) lattice of simple cubic structure with radial force constants α and tangential force constants β. We restrict the interaction among the lattice points to nearest neighbors only. This crystal is elastically stable as long as[22] $0<2\beta<\alpha$ and the highest frequency propagated is

$$\omega_{\max}^2=4(\alpha+2\beta)/M=\omega_D^2,$$

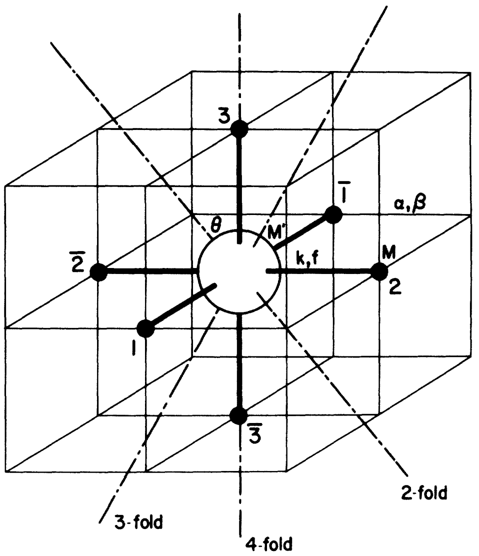

FIG. 1. The molecular defect is represented by a uniform rigid sphere with moment of inertia θ and mass M' different from the mass M of the atom replaced by the molecule. The sphere is coupled to the six nearest lattice atoms by radial springs as well as tangential springs. The axes indicated in the figure correspond to the three orientations with respect to the crystallographic axes of a nonspherical defect molecule as considered in Sec. IV.

which defines the Debye frequency ω_D. We represent the molecular defect by a rigid sphere of a single moment of inertia θ and mass M' which may be different from that of the atom replaced by the molecule. The sphere is coupled to the six nearest lattice atoms by radial springs with constants k and tangential springs with constants f (Fig. 1). Then the three remaining molecular coordinates are degenerate and conveniently taken as rotations around the three cubic axes. It is easy enough to see that this model allows motions of type (b) as well as of type (c).

For this model, the molecular Green's function is given by

$$\gamma(\omega^2)=\frac{1}{\omega^2(\kappa)-\omega^2}\,I \text{ (three dimensional)},$$

where

$$\omega^2(\kappa)=\frac{4f}{\theta/a^2}\,.$$

There are 21 lattice coordinates involved in the disturbance, namely, those to which the spherical molecule is coupled complemented by the three coordinates of the center of mass. Our dynamical problem as well as the matrix t are defined in this 21-dimensional defect space (matrix v). However, group theory provides a powerful tool for reducing the calculational effort, and we do not have to work in this high-dimensional space. From the information given in Table I (Appendix) we see that the most that we must do is to solve a 3×3 secular determinant for the modes transforming according to the irreducible representation F_{1u}. It is also easy to see that only modes transforming either according to the irreducible representation F_{1g} or according to F_{1u} can induce dynamical effects in this model where we have replaced the molecular defect by a rigid sphere. The former yield the librational motion and the latter are connected with the motion of the center of mass. The symmetry of the other modes is such that they provide no coupling which could lead to a net force or torque.

TABLE I. Invariant subspaces of the full cubic group O_h.

O_h	m_v^μ	m_r^μ	m_T^μ	Invariant subspaces																				
				$\bar{3}$			$\bar{2}$			$\bar{1}$			0			1			2			3		
A_{1g}	1	0	1	{0	0	x_1	0	x_1	0	x_1	0	0	0	0	0	$\bar{x}_1$	0	0	0	$\bar{x}_1$	0	0	0	$\bar{x}_1$}
E_g^1	1	0	1	{0	0	$2\bar{x}_1$	0	x_1	0	x_1	0	0												
E_g^2	1	0	1	{0	0	0	0	$\bar{x}_1$	0	x_1	0	0												
F_{1g}^1	0	1	1	{0	$\bar{z}_2$	0	0	0	z_2	0	0	0												
F_{1g}^2	0	1	1	{$\bar{z}_1$	0	0	0	0	0	0	0	z_1												
F_{1g}^3	0	1	1	{0	0	0	$\bar{y}_1$	0	0	0	y_1	0												
F_{2g}^1	1	0	1	{0	z_2	0	0	0	z_2	0	0	0												
F_{2g}^2	1	0	1	{z_1	0	0	0	0	0	0	0	z_1												
F_{2g}^3	1	0	1	{0	0	0	y_1	0	0	0	y_1	0												
F_{1u}^1	2	0	3	{x_2	0	0	x_2	0	0	x_1	0	0	x_0	0	0	x_1	0	0	x_2	0	0	x_2	0	0}
F_{1u}^2	2	0	3	{0	y_1	0	0	y_2	0	0	y_1	0	0	y_0	0									
F_{1u}^3	2	0	3	{0	0	z_3	0	0	z_1	0	0	z_1	0	0	z_0									
F_{2u}^1	1	0	1	{$\bar{x}_2$	0	0	x_2	0	0	0	0	0	0	0	0									
F_{2u}^2	1	0	1	{0	$\bar{y}_1$	0	0	0	0	0	y_1	0	0	0	0									
F_{2u}^3	1	0	1	{0	0	0	0	0	$\bar{z}_1$	0	0	z_1	0	0	0									

In order to determine the individual contributions to the scattering cross section [Eq. (7)] we need, besides the ratios $v(\nu)/[1+u(\nu)]$, the matrix elements of the form $\langle \vec{k}'\lambda' | T(\nu) | \vec{k}\lambda \rangle$. From the invariant subspaces given in Table I (Appendix) it is not difficult to construct the matrices $T(\nu)$ (the vectors spanning the stable subspaces have to be normalized first) and to determine the nonvanishing matrix elements for each row of the different irreducible representations. From the matrix elements which are different from zero we get all the information about the possible scattering processes. The results may be summarized as follows:

A_{1g}: This mode scatters *longitudinally polarized* phonons. It is *acoustically active* in the sense that the scattered phonons may be either longitudinally or transversely polarized.

E_g: This mode also scatters *longitudinally polarized* phonons only and is again *acoustically active.*

F_{1g}: This mode scatters *transversely polarized* phonons only and the *acoustical activity* is restricted to transversely polarized final states, such that propagation and polarization vectors of initial and final states span the same plane.

F_{2g}: Also this mode scatters *transversely polarized* phonons only and has the same restricted *acoustical activity* as F_{1g}.

F_{1u}: This mode scatters *any* incident phonon regardless of the polarization but does *not change* the polarization.

F_{2u}: This mode scatters *transversely polarized* phonons only and *maintains* the polarization.

The mode which transforms according to the irreducible representation F_{1g} is associated with the additional degrees of freedom introduced by the molecular defect (librational motion) and the mode transforming according to F_{1u} corresponds to the motion of the center of mass of the molecule. From the results above it becomes clear that, for example, the combination of the two modes mentioned above can give rise to a *nonvanishing interference term* in Eq. (7) which enhances the scattering cross section for lattice waves.

To proceed with the calculations we consider the following particular situation which corresponds essentially to that of an isotopic mass defect. We take the defect molecule to have a mass M' different from that of the lattice atom that it replaces, but assume that the force constants involved do not change ($\alpha = k$, $\beta = f$). These assumptions are reasonable and do not oversimplify in the sense that besides the mode transforming according to the irreducible representation F_{1g}, which is associated with one of the internal degrees of freedom of the molecule, there is still one other mode (F_{1u}) contributing to the scattering cross section. They also allow us to demonstrate the presence of the interference term in the cross section. We solve the dynamical problem associated with the motion of the center of mass (defined in the three-dimensional invariant subspace of F_{1u}) using the values for the Green's functions as tabulated by Oitmaa[23] and obtain the eigenvalues $v(F_{1u})$ and $u(F_{1u})$. Owing to the fact that the coordinates associated with the librational motion of the molecule are degenerate (with one single moment of inertia only), the invariant subspace of F_{1g} splits into one-dimensional components and the eigenvalues $v(F_{1g})$ and $u(F_{1g})$ can be read off immediately.

We recall that a consequence of the Debye approximation [Eq. (6)] is that[9] $|\vec{k}'| = |\vec{k}|$, i.e., we are dealing with elastic scattering.

As our main interest is to show the existence of the interference term it is sufficient to limit our considerations to the forward scattering cross section. The assumptions we have made so far and the structure of the matrix elements different from zero as discussed above (F_{1g} scatters transversely polarized phonons only and propagation direction and polarization are confined to a plane; F_{1u} does not change the polarization) allow us to write Eq. (7) as

$$\sigma(\vec{k}\lambda,\ \text{forward}) = \frac{a^6}{16\pi^2 c^4(\lambda)} \sum_{\mu\nu} \sum_{\lambda'} t^*(\mu) t(\nu) \langle \vec{k}\lambda' | T(\mu) | \vec{k}\lambda \rangle^* \langle \vec{k}\lambda' | T(\nu) | \vec{k}\lambda \rangle$$

or in the more transparent form,

$$\sigma(\vec{k}\lambda,\ \text{forward}) = \frac{a^6}{16\pi^2 c^4(\lambda)} \sum_{\lambda'} \Big(\sum_{\mu} |t(\mu)|^2 |\langle \vec{k}\lambda' | T(\mu) | \vec{k}\lambda \rangle|^2$$
$$2\,\mathrm{Re} \sum_{\mu<\nu} t^*(\mu) t(\nu) \langle \vec{k}\lambda' | T(\mu) | \vec{k}\lambda \rangle^* \langle \vec{k}\lambda' | T(\nu) | \vec{k}\lambda \rangle \Big),$$

where in our case $\mu, \nu = F_{1g}, F_{1u}$. The first term represents the direct contributions to the scattering cross section of one of the modes and the second term arises from the interaction between the different modes.

The resulting individual contributions and the total forward scattering cross section for three different choices of $\omega(\kappa)$ are shown in Figs. 2–4. The difference in mass was chosen to be $\epsilon = (M' - M)/M = 3.0$ and the moment of inertia of the spherical de-

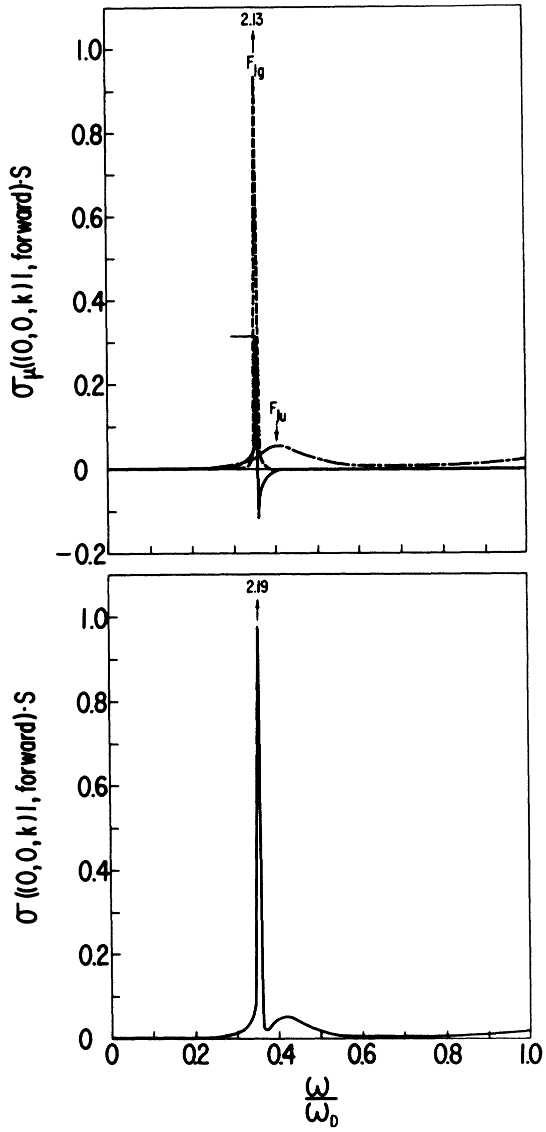

FIG. 2. (a) The individual contributions to the forward scattering cross section $\sigma_{F_{1g}}$: - - -, $\sigma_{F_{1u}}$: — — —, and $\sigma_{F_{1g}F_{1u}}$: ———, respectively, as a function of the normalized lattice wave frequency for $\omega(\kappa)/\omega_D = 0.36$. The horizontal bar marks the height of the latter term. (b) The sum of the contributions above.

fect molecule was taken as $\theta = M'(\frac{1}{4}a)^2$. The scaling parameter S in the figure is $S = 16\pi^2 c^4(t)/a^6\omega_D^4$.

We see not only that the interference term can be of the same order of magnitude as the direct terms and contribute appreciably to the scattering cross section, but also that the position of the maximum of the weaker resonance (F_{1u}) can be shifted (Fig. 2). This could mean a change in the infrared properties, for as we know, infrared-active modes transform according to the irreducible representation F_{1u}. Magnitude and shape of the interference term depend very much on the relative position of the resonances due to the modes F_{1g} and F_{1u} and also on their dependence on ω. It is clear that the contribution of this term to the scattering cross section diminishes the further apart the two resonances appear.

We know from the case of point defects[24] that resonances are not exact eigenstates of the perturbed crystal. They occur at frequencies at which localized modes would tend to appear, but because the density of in-band modes is finite at these fre-

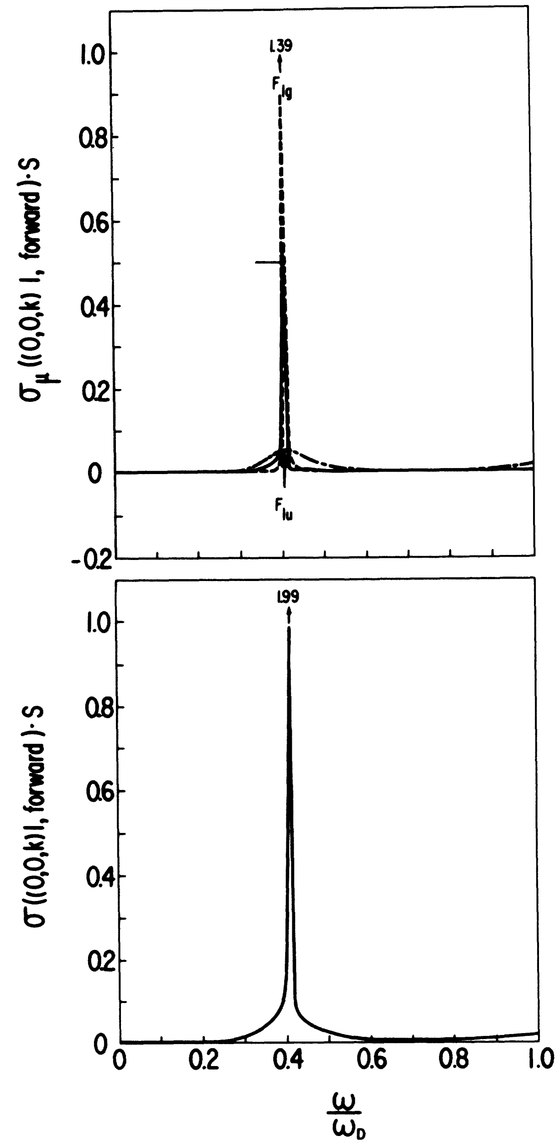

FIG. 3. (a) The individual contributions to the forward scattering cross section $\sigma_{F_{1g}}$: ----, $\sigma_{F_{1u}}$: — — —, and $\sigma_{F_{1g}F_{1u}}$: ———, respectively, as a function of the normalized lattice wave frequency for $\omega(\kappa)/\omega_D = 0.41$. The horizontal bar marks the height of the latter term. (b) The sum of the contributions above.

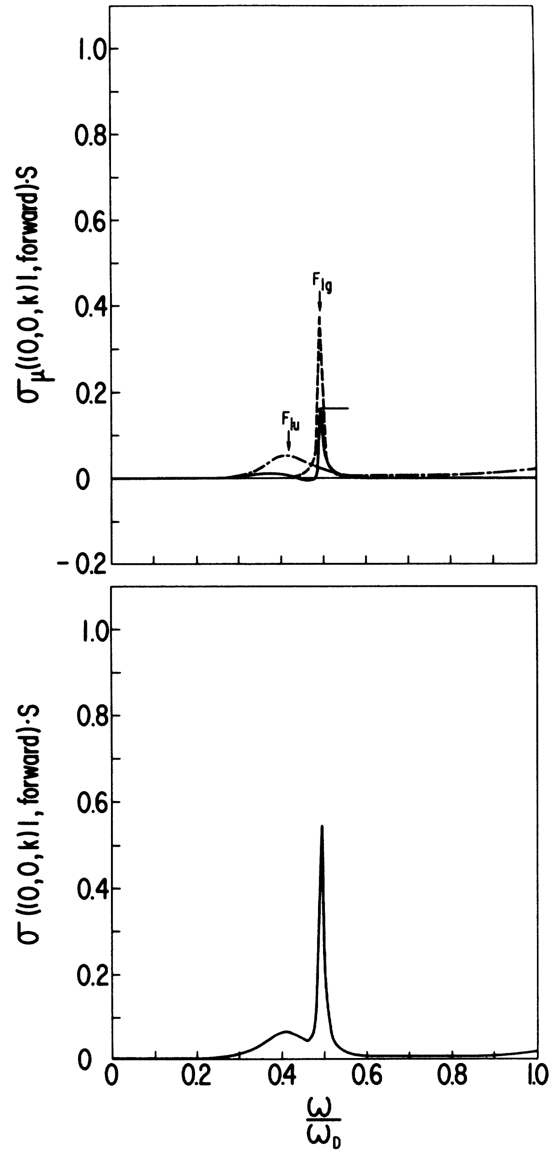

FIG. 4. (a) The individual contributions to the forward scattering cross section $\sigma_{F_{1g}}$: ----, $\sigma_{F_{1u}}$: —·—, and $\sigma_{F_{1g}F_{1u}}$: ————, respectively, as a function of the normalized lattice wave frequency for $\omega(\kappa)/\omega_D = 0.50$. The horizontal bar marks the height of the latter term. (b) The sum of the contributions above.

quencies, they can decay into the quasicontinuum of wavelike modes and acquire a width, or lifetime. We note that the resonance character of the contribution from the librational motion is much more pronounced than that of the contribution due to the motion of the center of mass (F_{1u}). This is even more true if the resonance appears in a region where the density of states of the ideal crystal is low, reflecting the increasing lifetime of the F_{1g} mode with decreasing density of states of the host crystal. This property is known[24] in the case of a point defect, and it was to be expected to find it also in the case of a molecular defect. The fact that the librational mode introduces a stronger resonance than the translational motion of the center of mass can be understood as follows. In the first instance the mode has a different character (rotational) from the wavelike modes of the host crystal, whereas in the second case the motion of the center of mass is of the same translational type as the eigenstates of the host crystal. This situation has a parallel in the case of molecular crystals with impurities. The detailed Green's-function analysis of Dettmann and Ludwig[25] showed that there can be localized librational modes within the quasicontinuum of translational states. Hence by this analogy, in the case of the resonances due to the librational modes we are dealing with *truly localized modes* rather than with pseudolocalized modes as occurs for the motion of the center of mass.

IV. SPHEROIDAL MOLECULES

We now replace in our model the rigid sphere by a rigid spheroid with two equal moments of inertia (different from the third one). As we are mostly interested in the dynamical behavior of the librational modes in this case, we assume the coupling to the lattice to be the same as in the spherical case. Introducing this particular defect into the host lattice results in a lower symmetry at the defect site depending upon the orientation of the molecule with respect to the crystallographic axes. We shall consider the following three situations (Fig. 1). The defect molecule is oriented along one of the axes of the cube. In this case the symmetry of the dynamical problem is D_{4h}. If the molecular defect is oriented along a body diagonal, then we are dealing with the symmetry group D_{3d}. The appropriate symmetry group for the molecule with its third axis parallel to one of the face diagonals is D_{2h}.

We are primarily interested in seeing if there are any new scattering mechanisms (different initial and final states) associated with the librational motion which are introduced by the nonspherical defect molecule. This is conveniently done by looking at the elements of the scattering matrix. The necessary information for constructing the corresponding $T(\nu)$ matrices is contained in Tables II–VII (see Appendix). In all three cases the analysis shows that the number of matrix elements different from zero increases considerably, but there is the same feature as for the spherical defect, namely, that only transversely polarized phonons are scattered into transversely polarized final states. However, phonons propagating parallel to the distinguished orientation of the molecule are

TABLE II. Invariant subspaces of the subgroup D_{4h}.

D_{4h}	m_v^μ	m_r^μ	m_T^μ	Invariant subspaces $\bar{3}$	$\bar{2}$	$\bar{1}$	0	1	2	3
A_{1g}	2	0	2	$\{0 \quad 0 \quad z_3$	$0 \quad x_1 \quad 0$	$x_1 \quad 0 \quad 0$	$0 \quad 0 \quad 0$	$\bar{x}_1 \quad 0 \quad 0$	$0 \quad \bar{x}_1 \quad 0$	$0 \quad 0 \quad \bar{z}_3\}$
A_{2g}	0	1	1	$\{0 \quad 0 \quad 0$	$\bar{y}_1 \quad 0 \quad 0$	$0 \quad y_1 \quad 0$				
B_{1g}	1	0	1	$\{0 \quad 0 \quad 0$	$0 \quad \bar{x}_1 \quad 0$	$x_1 \quad 0 \quad 0$				
B_{2g}	1	0	1	$\{0 \quad 0 \quad 0$	$y_1 \quad 0 \quad 0$	$0 \quad y_1 \quad 0$				
E_g^1	1	1	2	$\{x_3 \quad 0 \quad 0$	$0 \quad 0 \quad 0$	$0 \quad 0 \quad z_1$				
E_g^2	1	1	2	$\{0 \quad y_3 \quad 0$	$0 \quad 0 \quad z_2$	$0 \quad 0 \quad 0$				
A_{2u}	2	0	3	$\{0 \quad 0 \quad z_3$	$0 \quad 0 \quad z_1$	$0 \quad 0 \quad z_1$	$0 \quad 0 \quad z_0$	$0 \quad 0 \quad z_1$	$0 \quad 0 \quad z_1$	$0 \quad 0 \quad z_3\}$
B_{2u}	1	0	1	$\{0 \quad 0 \quad 0$	$0 \quad 0 \quad \bar{z}_1$	$0 \quad 0 \quad z_1$	$0 \quad 0 \quad 0$			
E_u^1	3	0	4	$\{x_3 \quad 0 \quad 0$	$x_2 \quad 0 \quad 0$	$x_1 \quad 0 \quad 0$	$x_0 \quad 0 \quad 0$			
E_u^2	3	0	4	$\{0 \quad y_3 \quad 0$	$0 \quad y_2 \quad 0$	$0 \quad y_1 \quad 0$	$0 \quad y_0 \quad 0$			

not affected by the libration mode which is associated with the other moment of inertia. (A_{2g} in case of D_{4h}, A_{2g} in case of D_{3d}, and B_{1g} in case of D_{2h}, respectively. In the latter case we assumed the spheroidal defect to be oriented along the [110] direction.) Of course, degenerate modes may be partially split depending on the orientation of the spheroid.

V. SUMMARY AND DISCUSSION

Using the results in a previous paper (I) we have analyzed the scattering of lattice waves by a stereoscopic defect molecule in a simple cubic crystal. Assuming that the internal binding in a molecule is much stronger than the binding to the host lattice, we considered the simple model of a rigid sphere coupled to a simple cubic lattice with tangential as well as radial springs. The nonvanishing matrix elements in the expression for the differential scattering cross section provide information on the possible scattering mechanisms and we found that all the even modes are acoustically active and that some of the modes interact with longitudinally or with transversely polarized phonons only.

In a model calculation using the Green's functions given by Oitmaa[23] we determined the individual contributions to the scattering cross section and found an interference term, representing the interaction of the librational motion and the motion of the center of mass. This is in contrast to the case of point defects where in the harmonic approximation defect modes do not interact. This has the following consequence. It is conjectured that this interaction in reality would be *temperature dependent* and that only an anharmonic treatment could reveal all the requisite details. The possibility that owing to the presence of the interference term the position of the weaker resonance (i.e., F_{1u}, according to which the infrared active modes transform) may be shifted is of practical importance as it is a common

TABLE III. Invariant subspaces of the subgroup D_{3d}.

D_{3d}	m_v^μ	m_r^μ	m_T^μ	Invariant subspaces $\bar{3}$	$\bar{2}$	$\bar{1}$	0	1	2	3
A_{1g}	2	0	2	$\{y_1 \quad y_1 \quad x_1$	$y_1 \quad x_1 \quad y_1$	$x_1 \quad y_1 \quad y_1$	$0 \quad 0 \quad 0$	$\bar{x}_1 \quad \bar{y}_1 \quad \bar{y}_1$	$\bar{y}_1 \quad \bar{x}_1 \quad \bar{y}_1$	$\bar{y}_1 \quad \bar{y}_1 \quad \bar{x}_1\}$
A_{2g}	0	1	1	$\{\bar{y}_1 \quad y_1 \quad 0$	$y_1 \quad 0 \quad \bar{y}_1$	$0 \quad \bar{y}_1 \quad y_1$				
E_g^1	2	1	3	$\{x_3^+ \quad x_3^+ \quad 2\bar{x}_1$	$y_1 \quad x_1 \quad z_1$	$x_1 \quad y_1 \quad z_1$				
E_g^2	2	1	3	$\{\bar{x}_3^- \quad x_3^- \quad 0$	$\bar{y}_1 \quad \bar{x}_1 \quad \bar{z}_1$	$x_1 \quad y_1 \quad z_1$				
A_{1u}	1	0	1	$\{\bar{y}_1 \quad y_1 \quad 0$	$y_1 \quad 0 \quad \bar{y}_1$	$0 \quad \bar{y}_1 \quad y_1$	$0 \quad 0 \quad 0$	$0 \quad \bar{y}_1 \quad y_1$	$y_1 \quad 0 \quad \bar{y}_1$	$\bar{y}_1 \quad y_1 \quad 0\}$
A_{2u}	2	0	3	$\{y_1 \quad y_1 \quad x_1$	$y_1 \quad x_1 \quad y_1$	$x_1 \quad y_1 \quad y_1$	$x_0 \quad x_0 \quad x_0$			
E_u^1	3	0	4	$\{x_3^+ \quad x_3^+ \quad 2\bar{x}_1$	$y_1 \quad x_1 \quad z_1$	$x_1 \quad y_1 \quad z_1$	$x_0 \quad x_0 \quad 2\bar{x}_0$			
E_u^2	3	0	4	$\{\bar{x}_3^- \quad x_3^- \quad 0$	$\bar{y}_1 \quad \bar{x}_1 \quad \bar{z}_1$	$x_1 \quad y_1 \quad z_1$	$\bar{x}_0 \quad x_0 \quad 0$			

$x_3^\pm = -(z_1 \pm y_1)$

TABLE IV. Invariant subspaces of the subgroup D_{2h}.

D_{2h}	m_v^μ	m_r^μ	m_T^μ	Invariant subspaces																				
				$\bar{3}$			$\bar{2}$			$\bar{1}$			0			1			2			3		
A_{1g}	3	0	3	{0	0	z_3	y_1	x_1	0	x_1	y_1	0	0	0	0	$\bar{x}_1$	$\bar{y}_1$	0	$\bar{y}_1$	$\bar{x}_1$	0	0	0	$\bar{z}_3$}
B_{1g}	1	1	2	{$\bar{x}_3$	x_3	0	0	0	$\bar{z}_1$	0	0	z_1												
B_{2g}	1	1	2	{x_3	x_3	0	0	0	z_1	0	0	z_1												
B_{3g}	1	1	2	{0	0	0	$\bar{y}_1$	$\bar{x}_1$	0	x_1	y_1	0												
A_{1u}	1	0	1	{0	0	0	0	0	$\bar{z}_1$	0	0	z_1	0	0	0	0	0	z_1	0	0	$\bar{z}_1$	0	0	0}
B_{1u}	3	0	4	{x_3	x_3	0	y_1	x_1	0	x_1	y_1	0	x_0	x_0	0									
B_{2u}	3	0	4	{$\bar{x}_3$	x_3	0	$\bar{y}_1$	$\bar{x}_1$	0	x_1	y_1	0	$\bar{x}_0$	x_0	0									
B_{3u}	2	0	3	{0	0	z_3	0	0	z_1	0	0	z_1	0	0	z_0									

technique to record infrared spectra of molecules by introducing the molecule of interest in a crystal matrix (usually an alkali halide). It was pointed out that in our case the librational mode is a localized mode rather than a resonance (pseudolocalized) mode. This fact justifies Wagner's derivation of the phonon scattering relaxation time for the in-band librational mode[26,27] which was questioned by Maradudin.[28]

In the next section we replaced the rigid sphere by a rigid ellipsoid with two equal moments of inertia, but different from the third one. In all cases we found basically the same matrix elements as for the spherical defect molecule.

We start the discussion of what we might expect in a more realistic situation with a reminder of the approximations which we have made. All calculations were performed within the harmonic approximation which limits our study to situations where it can be assumed that the amplitudes of all the modes involved are small. Our expression for the differential scattering cross section [Eq. (7)] was based on the acoustic approximation and the correct form would contain second derivatives of the surfaces of constant square modulus of the frequency in $\vec{k}$ space as well as an energy conservation factor.

TABLE V. Compatibility conditions for the subgroup D_{4h} with the four-fold rotation axis along the [001] direction of the cube.

		Compatibility conditions																				
		A_{1g}		A_{2g}	B_{1g}	B_{2g}	E_g^1		E_g^2		A_{2u}			B_{2u}	E_u^1				E_u^2			
O_h	D_{4h}	x_1	z_3	y_1	x_1	y_1	z_1	x_3	z_2	y_3	z_0	z_1	z_3	z_1	x_0	x_1	x_2	x_3	y_0	y_1	y_2	y_3
A_{1g}	A_{1g}	a	a																			
E_g^1	$A_{1g}+B_{1g}$	a	$2\bar{a}$		-																	
E_g^2		-	-		a																	
F_{1g}^1	$A_{2g}+E_g$			-			-	-	a	$\bar{a}$												
F_{1g}^2				-			a	$\bar{a}$	-	-												
F_{1g}^3				a			-	-	-	-												
F_{2g}^1	$B_{2g}+E_g$					-	-	-	a	a												
F_{2g}^2						-	a	a	-	-												
F_{2g}^3						a	-	-	-	-												
F_{1u}^1	$A_{2u}+E_u$										-	-	-		a	b	c	c	-	-	-	-
F_{1u}^2											-	-	-		-	-	-	-	a	b	c	b
F_{1u}^3											a	b	c		-	-	-	-	-	-	-	-
F_{2u}^1	$B_{2u}+E_u$													-	0	0	a	$\bar{a}$	-	-	-	-
F_{2u}^2														-	-	-	-	-	0	a	0	$\bar{a}$
F_{2u}^3														a	-	-	-	-	-	-	-	-

Depending on the size of the defect molecule we must expect structural changes as well as alterations in the force constants in the neighborhood of the defect, which might even lead to a local instability of the lattice. The defect may take an interstitial equilibrium position which could give rise to tunneling between equivalent positions. A different equilibrium position has a greater effect on the librational than the translational motion, for the librational frequencies are highly sensitive to the crystal field at the given equilibrium position. These effects were not included in the model and for this aspect we refer to the reports of Krumhansl[29] and Imry[30] as well as the review article by Narayanamurti and Pohl.[31]

In our study of the librational motion of the spheroidal defect molecule we assumed the force constants to be the same as in the case of the spherical molecule. We now drop this assumption and ask if there could now be a coupling of the librational motion to longitudinally polarized lattice waves. The necessary condition is that in the decomposition of the modes A_{1g}, E_g, and F_{1g} due to the lower symmetry, there must be at least one irreducible representation in common. This is indeed the case if the molecule is oriented either along a body diagonal (Table VI, E_g) or parallel to a face diagonal (Table VII, B_{3g}). However, the above-mentioned condition is not sufficient, and indeed from the compatibility conditions it follows that the corresponding invariant subspaces (carrier spaces of the irreducible representations) are in fact mutually exclusive. Yet there may be reasons to relax these compatibility conditions, for example if the defect is no longer assumed to be rigid. Then there exists a possibility that it would be energetically favorable for the neighboring atoms to follow the internal motion of lower symmetry of the defect, and no longer to be governed by the over-all cubic symmetry of the crystal. This means that from corresponding experimental results one could conclude to what extent a molecular defect which leads to a lower symmetry at the defect site affects the dynamics of the host lattice.

Indeed, Pohl[32] found that the low-temperature heat conductivity of alkali-halide crystals containing molecular impurities decreases below the value characteristic for heat transfer by longitudinal phonons alone. He interpreted the fact that longitudinal phonons get scattered as well as transverse ones by noting that boundary scattering could mix longitudinal and transverse phonons continuously and hence be responsible for the unexpected result. As we have seen, there is also the possibility that the molecular defect governs the dynamics of the crystal at the defect site to a larger extent than anticipated, having the consequence that longitudinal phonons as well are scattered by the librational mode due to the additional degrees of freedom of the defect molecule.

TABLE VI. Compatibility conditions for the subgroup D_{3d} with the three-fold rotation axis along the [111] direction of the cube.

		Compatibility conditions																						
		A_{1g}		A_{2g}	E_g^1			E_g^2			A_{1u}	A_{2u}			E_u^1				E_u^2			
O_h	D_{3d}	x_1	y_1	y_1	x_1	y_1	z_1	x_1	y_1	z_1	y_1	x_0	x_1	y_1	x_0	x_1	y_1	z_1	x_0	x_1	y_1	z_1
A_{1g}	A_{1g}	a	0																			
E_g^1	E_g				a	0	0	-	-	-												
E_g^2					-	-	-	a	0	0												
F_{1g}^1	$A_{2g}+E_g$			$2\bar{a}$	0	0	$3a$	0	$2\bar{a}$	$\bar{a}$												
F_{1g}^2				$2a$	0	0	$3a$	0	$2a$	a												
F_{1g}^3				$\bar{a}$	-	-	-	0	$2a$	a												
F_{2g}^1	$A_{1g}+E_g$	0	$2a$		0	$2\bar{a}$	a	0	0	$3\bar{a}$												
F_{2g}^2		0	$2a$		0	$2\bar{a}$	a	0	0	$3a$												
F_{2g}^3		0	a		0	$2a$	$\bar{a}$	-	-	-												
F_{1u}^1	$A_{2u}+E_u$											$2a$	$2b$	$2c$	a	b	c	$2\bar{c}$	$3\bar{a}$	$3b$	$3\bar{c}$	0
F_{1u}^2												$2a$	$2c$	$2b$	a	c	b	$2\bar{b}$	$3a$	$3\bar{c}$	$3b$	0
F_{1u}^3												a	c	b	$\bar{a}$	$\bar{c}$	$\bar{b}$	$2b$	-	-	-	-
F_{2u}^1	$A_{1u}+E_u$										$2a$				0	0	$3a$	0	0	0	$\bar{a}$	$2\bar{a}$
F_{2u}^2											$2\bar{a}$				0	0	$3a$	0	0	0	a	$2a$
F_{2u}^3											a				-	-	-	-	0	0	a	$2a$

TABLE VII. Compatibility conditions for the subgroup D_{2h} with the two-fold rotation axis oriented along the [110] direction of the cube.

		Compatibility conditions																				
		A_{1g}			B_{1g}		B_{2g}		B_{3g}		A_{1u}	B_{1u}				B_{2u}				B_{3u}		
O_h	D_{2h}	x_1	y_1	z_3	z_1	x_3	z_1	x_3	x_1	y_1	z_1	x_0	x_1	y_1	x_3	x_0	x_1	y_1	x_3	z_0	z_1	z_3
A_{1g}	A_{1g}	a	0	a																		
E_g^1	$A_{1g}+B_{3g}$	a	0	$2\bar{a}$					-	-												
E_g^2		-	-	-					a	0												
F_{1g}^1	$B_{1g}+B_{2g}+B_{3g}$				$\bar{a}$	$\bar{a}$	a	$\bar{a}$	-	-												
F_{1g}^2					a	a	a	$\bar{a}$	-	-												
F_{1g}^3					-	-	-	-	0	a												
F_{2g}^1	$A_{1g}+B_{1g}+B_{2g}$	-	-	-	$\bar{a}$	a	a	a														
F_{2g}^2		-	-	-	a	$\bar{a}$	a	a														
F_{2g}^3		0	a	0	-	-	-	-														
F_{1u}^1	$B_{1u}+B_{2u}+B_{3u}$											a	b	c	c	$\bar{a}$	b	$\bar{c}$	$\bar{c}$	-	-	-
F_{1u}^2												a	c	b	b	a	$\bar{c}$	b	b	-	-	-
F_{1u}^3												-	-	-	-	-	-	-	-	a	b	c
F_{2u}^1	$A_{1u}+B_{1u}+B_{2u}$										-	0	0	a	$\bar{a}$	0	0	$\bar{a}$	a			
F_{2u}^2											-	0	0	a	$\bar{a}$	0	0	a	$\bar{a}$			
F_{2u}^3											a	-	-	-	-	-	-	-	-			

In the classical thermal-conductivity experiment[12] it is more difficult to detect the narrow resonance associated with the librational mode (hence also the interference term) even if its magnitude is substancially larger than that of the broad resonance due to the motion of the center of mass. However, there are good reasons to believe that due to the modulation of the magnitude of the moment of inertia θ by the other internal motions of the molecule, the former resonance will not be as sharp as shown in the model calculation (rigid sphere). Furthermore, the new heat-pulse technique (phonon generation by tunneling in superconductors)[33-38] promises to provide a powerful tool not only in regard to sensitivity but also in the possibility of separating the contributions to the scattering cross section with respect to polarization.

ACKNOWLEDGMENTS

The author wishes to express his sincere gratitude to Professor Frank J. Blatt for the kind hospitality extended to him during his stay at Michigan State University as well as for many discussions and much encouragement throughout the course of this work. Concerning the lattice dynamics aspect, the author benefited from the experience of Dr. W. M. Hartmann. Thanks are also due to Dr. B. I. Lundqvist for making the author familar with the experimental results of Professor Pohl's group and to Dr. M. Boon for a critical reading of the manuscript.

APPENDIX

To solve the dynamical problem it is not necessary to work in the whole (often high dimension) defect space. From group-theoretical theorems we conclude (see Paper I) that this space can be decomposed into smaller subspaces, i.e., the carrier spaces of the irreducible representations into which the total representation splits. There is a natural way of obtaining the correct dynamical eigenvectors belonging to each *invariant subspace*. [By invariant subspace we mean the maximal part of the whole space which carries (a multiple of) some irreducible representation of the group.] One uses the symmetry elements of the group[39] to decompose the total space into its invariant constituents. In Tables I–IV the invariant subspaces of interest for the simple cubic structure are listed, giving the decomposition of the 21-dimensional total space according to the irreducible representations for the full cubic group O_h as well as for the subgroups D_{4h}, D_{3d}, and D_{2h}. In the first column only those irreducible representations of the (sub)-group are listed which are part of the total representation. In the next three columns the multiplicities m_i^μ of the corresponding irreducible representations are given. The first of these is for the case where we allow for vibrations only; the next corresponds to librational (quasirotational) motions only; and the last includes all degrees of freedom. Clearly, the difference $m_t^\mu = m_T^\mu - (m_v^\mu + m_r^\mu)$ is associated with the translational degrees of freedom, and the translation of the center of mass has to be excluded explicitly. The remaining columns give the components of the displacements ϵ_j^n (for the numbering of the lattice points see Fig. 1) which span the m_T^μ-dimensional invariant subspace associated with the μth irreducible representation. The entries left blank in the tables can be filled in using the relations between the displacement at a point n: ϵ_j^n, and that of the inverted point $\bar{n}$: $\epsilon_j^{\bar{n}}$ ($j = g$: even, u: odd): $\epsilon_g^n = \bar{\epsilon}_g^{\bar{n}}$, $\epsilon_u^n = \epsilon_u^{\bar{n}}$. A bar above any entry (e.g., $\bar{1}$, $\bar{x}$) denotes the inverse or negative of the unbarred quantity (1, x).

If one introduces a molecule into a crystal lattice, then in general the symmetry of the system is reduced depending on the shape of the molecule and its orientation with respect to the crystallographic axes. This leads to relations between the free parameters of the invariant subspaces involved (see Paper I), since the invariant subspaces of a subgroup frequently have a higher dimension that the corresponding invariant subspaces of the group of higher order. These conditions are what we call *compatibility conditions*. They are given in Tables V–VII for the cases considered in Sec. IV. In the first column the irreducible representations of the full cubic group are listed and in the next column the correlation table[40] of the respective subgroup is reproduced. For all components of the invariant subspaces of the subgroup, the relations imposed by the group of higher symmetry are tabulated under the appropriate heading. A bar (¯) means that the particular invariant subspace is not contained in the subspace carrying a certain row of the irreducible representation given at the left.

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[*] Supported partially by the U.S. National Science Foundation.

[†] Preliminary results have been announced in Phys. Letters 35A, 395 (1971) and a short report of this work has been presented at the International Conference on Phonon Scattering in Solids, Paris, July 3–6, 1972.

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