Influence of Localized Modes on Thermal Conductivity*

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The curves of the thermal conductivity versus temperature of some insulating crystals (alkali halides) which are doped with certain impurity centers exhibit a distinct indentation. This suggests a relaxation time of some resonance nature, which is independent of the temperature for molecular impurity centers ($KCl:KNO_2$, measured by Pohl) and temperature-dependent for monatomic disturbances ($KCl:NaCl$, etc., measured by Walker and Pohl). In this paper a theory is given for the influence of inelastic scattering of phonons at localized modes outside the band and at quasilocalized modes inside. The calculated relaxation time for the *third-order* process $(k\lambda)+(k'\lambda') \rightleftarrows (s)$, describing phonons and localized quanta, respectively, has been tested on the experimental data in the preceding paper by Walker and Pohl; from the very good agreement one may conclude that the indentation effect is quantitatively due to this scattering process. The analysis is also done for the scattering of phonons by internal modes of molecular perturbations. The relaxation time for the second-order process $(k\lambda) \rightleftarrows (\sigma)$, (σ)=internal quantum, is independent of temperature and of resonance form as observed for $KCl:KNO_2$.

I. INTRODUCTION

RECENT measurements by Pohl[1] have shown that the thermal conductivity of KCl crystals containing small concentrations of KNO_2 exhibits a distinct (resonance) indentation in curves of temperature dependence, which changes with the NO_2 concentration and is considerably different from the shape of the "pure" KCl thermal conductivity. Figure 1 shows experimental results.

Pohl suggested that a relaxation time τ_s of the form

$$\tau_s^{-1} = \frac{A\omega^2}{(\omega_0^2 - \omega^2)^2 + (\Lambda/\pi)^2 \omega_0^2 \omega^2}, \quad (1a)$$

be assumed for the relevant scattering process, as would characterize some resonance. With this phenomenological assumption it was possible to explain the structure of the curves in Fig. 1 by a suitable choice of the constants A and ω_0; Λ can be varied over a wide range $\Lambda \geq 0$ without altering the result noticeably. (Pohl found $\omega_0 = 2\pi \times 10^{12}$ sec^{-1} most favorable for the system $KCl:KNO_2$.)

There are, however, other systems, e.g., $KCl:NaCl$, $KCl:CaCl_2$, $KCl:KI$, etc., whose thermal conductivity, as measured by Walker and Pohl,[2] show waviness similar to Fig. 1. Here, the shape of the curves can be described only by an additional relaxation time τ_s which is temperature-dependent, for instance,

$$\tau_s^{-1} = \frac{AT^2\omega^2}{(\omega_0^2 - \omega^2)^2 + (\Lambda/\pi)^2 \omega_0^2 \omega^2}. \quad (1b)$$

Although the formulas (1a) or (1b) did fit the respective measurements rather well, there was no specific theoretical model which would support these postulates. The aim of this calculation is to give an atomistic model of the resonance-scattering process and a theoretical calculation of the proper relaxation time.

Until recently the existing calculations showed that any elastic-scattering process of phonons has a monotonic-relaxation time ($\tau \sim \omega^n$, n negative or positive).[3] Excellent presentations of these calculations are given in the review articles by Klemens,[4,5] Carruthers,[6] and Bross[7] and in a book by Peierls.[8] A superposition of such monotonic-relaxation times, τ_i, according to the law[9]

$$(\tau_{\text{total}})^{-1} = \sum_i (\tau_i)^{-1} \quad (2)$$

cannot give any waviness in the temperature dependence of the thermal conductivity. The indentation in the curves and resonance expressions of the form 1(a),(b) must be ascribed, therefore, to nonelastic or resonant-scattering processes where energy may be scattered out of or into a particular part of the phonon spectrum. An example is the resonance interaction between phonons and the electron spin of paramagnetic

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[1] R. O. Pohl, Phys. Rev. Letters **8**, 481 (1962).
[2] C. T. Walker and R. O. Pohl, preceding paper, Phys. Rev. **131**, 1433 (1963).

[3] In his important paper of 1951, P. G. Klemens (Ref. 15) noted that the thermal conductivity of elastic-phonon scattering processes at imperfections may be decomposed into two parts, $\chi = \chi_I + \chi_{II}$, both exhibiting a peak at possibly different temperatures, if one takes into account the interaction of different polarization branches [longitudinal (I) and transversal (II)] by means of Normal processes. This superposition might possibly give rise to an indentation in the over-all shape of the curves.

However, Klemens has stated that in the case of regular crystals $\chi_I \ll \chi_{II}$ except for very low temperatures at about 2°K, so that an indentation at about 10°K seems to be unlikely (Pohl, Walker). Moreover, the decomposition $\chi_I + \chi_{II}$ can be done only by an approximation which is often very poor, especially for relaxation times, which vary strongly with frequency (mass differences, e.g.), as pointed out by Carruthers (footnote 39 of Ref. 6). A more accurate calculation of the Normal process is very complicated and has not yet been carried out. If one neglects Normal processes for all scattering processes which are connected with imperfections, our statement holds, that for elastic-scattering processes there are only monotonic-relaxation times.
[4] P. G. Klemens, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 14–1, p. 198.
[5] P. G. Klemens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 1.
[6] P. Carruthers, Rev. Mod. Phys. **33**, 92 (1961).
[7] H. Bross, Physica Status Solidi **2**, 481 (1962).
[8] R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York, 1955).
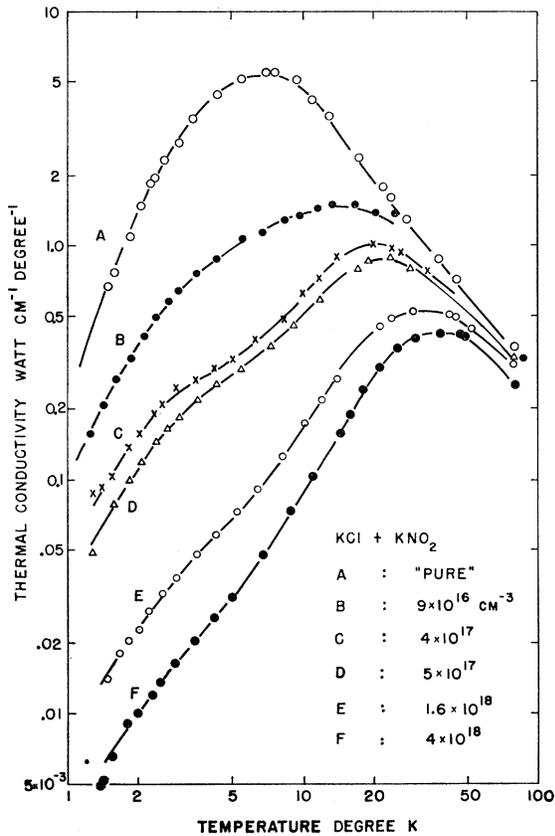[9] J. Callaway, Phys. Rev. **113**, 1046 (1959).

FIG. 1. Thermal conductivity of KCl doped with different concentrations of KNO_2 as an example of the influence of inelastic phonon scattering at localized modes. [Measurements by Pohl (Ref. 1).]

ions, which has been observed recently[10-12] and analyzed theoretically by Orbach.[13]

As seen by the experimental results,[1,2] the indentation in the curves depends on the concentration of the impurity centers in the host lattice, thus demanding that the effect be due to these impurities. This means that in addition to the Rayleigh scattering of the phonons at the impurity center[14-15] with $\tau \sim \omega^{-4}$ there must exist another scattering mechanism. One is led at once to suspect that we should consider the inelastic scattering of phonons at localized modes.

These modes are unable to transport energy (heat) and can make no contribution to the heat current. Nevertheless, they influence the heat current because they may be excited by annihilating phonons (which reduces the heat current) or de-excited by creating phonons (which increases the heat current). We can

expect that these scattering processes are responsible for the indentation in the curves of the thermal conductivity.

II. LOCALIZED MODES

To simplify the calculation as much as possible, we assume the insulating host crystal to have cubic structure (which is the case for all crystals in which the aforementioned resonance effect has been found) and only one atomic mass (which is a fairly good approximation for KCl: $M_K = 39.1$ a.u., $M_{Cl} = 35.5$ a.u.). As our physical system we can take a cubic region of N^3 lattice points in the center of which is a point defect of mass, M_s. Then the Hamiltonian in harmonic approximation is given by

$$H = \frac{1}{2} \sum_{ni} M_n \dot{x}_n{}^{i2} + \frac{1}{2} \sum_{nmij} H_{nm}{}^{ij} x_n{}^i x_m{}^j, \qquad (3)$$

where $M_n = M$ for the regular atom and $M_n = M_s$ for the disturbance in the center $[i, j = 1, 2, 3; n = a(n_1, n_2, n_3); n_i = 0, 1, 2 \cdots]$.

The Schrödinger equation is solved if we know the normal modes of the oscillating lattice. For the ideal crystal we can find them as standing or propagating plane waves by postulating (instead of the exact boundary conditions) the well-known periodicity condition.

The solution for the defect lattice, however, is much more complicated. In fact, very little is known quantitatively about localized modes although a large amount of important work has been done within the last years.[16-19] In principle, the problem is solved by the fundamental work of Lifshitz,[16,20] on the one hand, and of Montroll and Potts[17] on the other, but the explicit calculations which have been published[21-22] are restricted to special simplified cases because of the immense mathematical difficulties. At this writing there are some new developments on scattering problems[23,24] which, though apparently different in approach, are compatible with our development here.

Accordingly, we survey some general results[16] for the normal modes of the defect lattice. Under certain conditions which we need not consider here one has the possibility of discrete-localized modes in the gap between the acoustic and the optical band and above the optical band. These modes outside the bands are the "true" localized modes.

Apart from these singular solutions the alterations within the acoustic band are most interesting. Accord-

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[14] P. G. Klemens, Proc. Phys. Soc. (London) A68, 1113 (1955).
[15] P. G. Klemens, Proc. Roy. Soc. (London) A208, 108 (1951).

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[17] E. W. Montroll and R. B. Potts, Phys. Rev. 100, 525 (1955); 102, 72 (1956).
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[19] J. A. Krumhansl, Suppl. J. Appl. Phys. 33, 307 (1962).
[20] I. M. Lifshitz, Zh. Eksperim. i Teor. Fiz. 18, 293 (1948).
[21] R. L. Bjork, Phys. Rev. 105, 456 (1957).
[22] H. B. Rosenstock and C. C. Klick, Phys. Rev. 119, 1198 (1960).
[23] J. Krumhansl (to be published).
[24] M. V. Klein (to be published).

ing to Lifshitz[16] the eigenvectors are no longer pure plane waves; they contain also a term which is approximately radially symmetric to the imperfection center. However, these Lifshitz solutions can still be characterized by a wave vector $\mathbf{k}$ and a polarization λ because of the plane-wave part, and because of the fact that the new $\mathbf{k}$ values lie between the ideal $\mathbf{k}$ values in such a manner that the density in k space is conserved. Moreover, the spectral density is also unchanged [only one solution $\omega(k)$ lies between two neighboring solutions of the ideal lattice].

In most regions of the acoustic spectrum the plane-wave part is predominant and we may still speak approximately of phonons. There may, however, occur small regions within the band in which the localized part is much more important than the plane-wave part.[25] Very recent calculations of Krumhansl[23] on the one hand, and Klein[24] on the other, have demonstrated this in great detail. They have shown that the scattering cross section of the phonons may have a resonance peak within the band. This means that the coherent second-order process

$$(\mathbf{k}\lambda) \rightleftarrows (\mathbf{k}'\lambda') \qquad (4)$$

is no longer a pure Rayleigh-type scattering and the relaxation time is modified by a resonance factor.

However, the scattering process (4) apparently cannot explain the experimental results of Walker and Pohl on KCl:KI, etc., because the required relaxation time must depend on temperature [Eq. (1b)]. It is natural, therefore, to consider other mechanisms such as a third-order process, but we then have to explain why the second-order process (4) might be less important.

The explanation is probably that in these systems the mass or strain defect strength is not sufficient to lead to a pronounced resonant scattering within the bands; whereas for F centers or U centers there would probably be pronounced resonant scattering of the elastic type.

Let $(\eta_{\mathbf{k}\lambda}, \eta_s)$ be the exact set of eigenvectors for the disturbed lattice (η_s represent the singular localized modes outside the bands). Then the heat current takes the form,

$$\mathbf{Q} = \sum_{\mathbf{k}\lambda} N_{\mathbf{k}\lambda} \hbar \omega_{\mathbf{k}\lambda} \mathbf{v}_{\mathbf{k}\lambda} \cdot \Delta_{\mathbf{k}\lambda}, \qquad (5)$$

where $N_{\mathbf{k}\lambda}$ is the quantum number of the mode $(\mathbf{k}\lambda)$, whereas $\mathbf{v}_{\mathbf{k}\lambda}$ is the group velocity for the plane-wave solutions of the ideal lattice. $\mathbf{Q}$ does not depend on the singular localized modes outside the bands. The function $\Delta_{\mathbf{k}\lambda}$ gives the deviation from the ideal case which depends on the exact scattering solutions. In the undisturbed lattice we have $\Delta_{\mathbf{k}\lambda} \equiv 1$ and we are back to the well-known expression of Peierls.[26] If there are impurity centers, $\Delta_{\mathbf{k}\lambda}$ has a minimum value <1 in the

[25] R. Brout and W. Visscher, Phys. Rev. Letters **9**, 54 (1962).
[26] R. Peierls, Ann. Physik **3**, 1955 (1929).

same region in $\mathbf{k}$ space where there is a resonance in the scattering cross sections of phonons as calculated by Krumhansl[23] and Klein.[24]

This consideration demonstrates that a third-order process may produce a large effectively resonant influence because two modes $(k\lambda)$, $(k'\lambda')$, lying in regions where $\Delta_{\mathbf{k}\lambda} \approx 1$, may combine to a mode $(k''\lambda'')$ with $\Delta_{k''\lambda''} \ll 1$, which reduces the heat current, and vice versa.

From these preliminaries we are led to suggest a simple conceptual device which allows us to simplify the mathematical description and make contact with the standard formulation of a Boltzmann equation. We introduce the following approximation:

(a) We define a region of G_s modes around the resonance frequency ω_s, for which we put $\Delta_{\mathbf{k}\lambda} = 0$. Then these modes do not contribute to the heat current and may be considered as "quasilocalized" modes because of this similarity to the true localized modes outside the bands, and their eigenvectors η_s have no longer a traveling part.

(b) Outside the defined region we take the ideal phonon solutions $\eta_{\mathbf{k}\lambda}^{(0)}$ instead of the real modes and put $\Delta_{\mathbf{k}\lambda} = 1$.

Thus, the heat current can be written in the old form of Peierls, but the G_s $\mathbf{k}$ values in the defined vicinity around ω_s have to be rejected from the summation,

$$\mathbf{Q} = \sum_{\mathbf{k}\lambda} N_{\mathbf{k}\lambda} \hbar \omega_{\mathbf{k}\lambda} \mathbf{v}_{\mathbf{k}\lambda} \qquad (5a)$$

$$(\omega_{k\lambda} \neq \omega_s).$$

The advantage of this conception is that we are now back in the phonon picture in lieu of a description in terms of the exact eigenmodes; this is necessary to set up the Boltzmann equations, because it is difficult to formulate the diffusion otherwise than in terms of plane-wave packets. Yet, it is important to note that the theory will contain two adjustable parameters, G_s and ω_s, the calculation of which is a task for future investigations.

According to our concept we adopt as the basic system the approximate eigenvectors,

$$(\eta_{\mathbf{k}\lambda}^{(0)}) + (\eta_s), \qquad (6)$$

where (η_s) includes the true localized modes outside and the quasilocalized modes inside the bands. Expression (6) is no longer an orthogonal set, but naturally it has to be still a complete system in the $3N^3$ space.

The interesting third-order processes are

$$(\mathbf{k}\lambda) + (\mathbf{k}'\lambda') \rightleftarrows (s), \qquad (7a)$$

with the law of energy conservation,

$$\omega(\mathbf{k}\lambda) + \omega(\mathbf{k}'\lambda') = \omega_s, \qquad (7b)$$

and

$$(\mathbf{k}\lambda) + (s) \rightleftarrows (\mathbf{k}'\lambda'), \qquad (8a)$$

$$\omega(\mathbf{k}\lambda) + \omega_s = \omega(\mathbf{k}'\lambda'), \qquad (8b)$$

which latter is only realistic if ω_s lies within the band.

III. THE HAMILTONIAN

For the Hamiltonian (3) we introduce the substitution,

$$\xi_n{}^i = M_n{}^{1/2} x_n{}^i, \qquad h_{nm}{}^{ij} = M_n{}^{-1/2} M_m{}^{-1/2} H_{nm}{}^{ij}. \qquad (9)$$

The basic set (6) does not diagonalize the matrix $h_{nm}{}^{ij}$ exactly. Projecting the Cartesian coordinates $\xi_n{}^i$ onto the basis (6) we get an expression in the normal coordinates $q_{k\lambda}$, q_s, which are connected to the standard creation-annihilation formalism by the definition[27]

$$q_{k\lambda} = (\hbar/2\omega_{k\lambda})^{1/2}(a_{k\lambda}{}^\dagger + a_{-k\lambda}); \quad q_s = (\hbar/2\omega_s)^{1/2}(a_s{}^\dagger + a_{-s}) \qquad (10a)$$

$$\dot{q}_{k\lambda} = i(\hbar\omega_{k\lambda}/2)^{1/2}(a_{k\lambda}{}^\dagger - a_{-k\lambda}); \quad \dot{q}_s = i(\hbar/2\omega_s)^{1/2}(a_s{}^\dagger - a_{-s}), \qquad (10b)$$

where $-s$ means that member of the set $[\eta_s(\mathbf{n}i)]$ which has the same eigenvalue as $\eta_s(\mathbf{n}i): \omega_s{}^2 = \omega_{-s}{}^2$ or $\eta_s{}^* = \eta_{-s}$; if there is no such member, i.e., if $\eta_s(\mathbf{n}i)$ is real, $-s$ has to be replaced by s, assuring that in this case q_s is real too. (This follows from the fact that the variables $\xi_n{}^i$ are real.) With these substitutions the Hamiltonian (3) is transformed to

$$H = H_0 + H_{int}{}^{(2)}, \qquad (11)$$

where $H_{int}{}^{(2)}$ is the nondiagonalized part and H_0 is given by

$$H_0 = \tfrac{1}{2}\sum_{k\lambda} \hbar\omega_{k\lambda}(a_{k\lambda}{}^\dagger a_{k\lambda} + a_{k\lambda}a_{k\lambda}{}^\dagger)$$
$$+ \tfrac{1}{2}\sum_s \hbar\omega_s(a_s{}^\dagger a_s + a_s a_s{}^\dagger). \qquad (12)$$

$H_{int}{}^{(2)}$ includes (a) the Rayleigh scattering $(\mathbf{k},\lambda) \rightleftarrows (\mathbf{k}'\lambda')$ at the imperfection which is already well known[14,15] and need not be considered here; (b) the scattering $(k\lambda) \rightleftarrows (s)$, which is not able to conserve energy according to our model; (c) the scattering among the quasilocalized modes $(s) \rightleftarrows (s')$, which might be of some secondary influence on the processes (7, 8), if these latter differ strongly for two quasilocalized modes s and s', but this is not to be expected in view of the fact, that the modes s have the same radial symmetry; and finally (d) double creation or annihilation of both a phonon and a localized quantum, which strongly violates the energy conservation.

It is necessary, of course, to make sure, that $H_{int}{}^{(2)}$ can be treated as a perturbation. This question has to be investigated for each special kind of impurity center in detail, but we will postpone this analysis for later study.

If $H_{int}{}^{(2)}$ is much smaller than H_0, our conception is justified, and H_0 gives rise to the following commutation relations[27]:

$$[a_{k\lambda}, a_{k'\lambda'}{}^\dagger] = \delta_{\lambda\lambda'}\delta_{kk'}; \quad [a_s, a_{s'}{}^\dagger] = \delta_{ss'}, \qquad (13)$$

where all other commutations are zero.

[27] G. Leibfried, in *Handbuch der Physik*, edited by S. Flügge (Springer Verlag, Berlin, 1955), Vol. 7, Chap. 1, pp. 196, and especially 290 ff.

Up to this point we neglected those terms in the lattice energy which are of higher order than the second; of these the cubic terms are most important and will be the basis of our analysis. They include the scattering processes (7) and (8).

The cubic terms in the defect lattice can be written in the form

$$H_{int}{}^{(3)} = \frac{1}{3!} \sum_{nmm'}{}_{ijk} P(\mathbf{n},\mathbf{m},\mathbf{m}') H^{ijk}(\mathbf{m},\mathbf{m}')$$
$$\times \xi_n{}^i \xi_{n+m}{}^j \xi_{n+m'}{}^k. \qquad (14)$$

$H^{ijk}(\mathbf{m},\mathbf{m}')$ are the coefficients of the ideal lattice[4]; they depend only on the two vectors $\mathbf{m}$ and $\mathbf{m}'$ defining a triangular region somewhere in the crystal, but they do not depend on the absolute position within the lattice space, marked by the lattice vector, $\mathbf{n}$. The factors $P(\mathbf{n},\mathbf{m},\mathbf{m}')$ give the deviation from the idealistic behavior and destroy the translation invariance; they turn to unity if the region $(\mathbf{n},\mathbf{m},\mathbf{m}')$ is far away from the center of disturbance.

Carrying out successively the projection onto the basic set (6) and the transformation (10a, b) and quantizing according to (13) we arrive at an expression of the form

$$H_{int}{}^{(3)} = \sum_{kk'\lambda\lambda's} \rho_{k\lambda k'\lambda'}{}^s[a_{k\lambda}{}^\dagger a_{k'\lambda'}{}^\dagger a_s + a_{k\lambda}a_{k'\lambda'}a_s{}^\dagger]$$
$$+ \sum_{kk'\lambda\lambda's} \rho_{k\lambda s}{}^{k'\lambda'}[a_{k\lambda}{}^\dagger a_s{}^\dagger a_{k'\lambda'} + a_{k\lambda}a_s a_{k'\lambda'}{}^\dagger]$$
$$+ \cdots, \qquad (15)$$

where we have written down only the parts which belong to the processes (7) and (8). $H_{int}{}^{(3)}$ includes also the well-known normal and umklapp processes and some processes which are of no importance. The correlation factors $\rho_{k\lambda k'\lambda'}{}^s$ and $\rho_{k\lambda s}{}^{k'\lambda'}$ depend on the symmetry of the crystal and the symmetry of the localized modes.

The symmetry of the lattice already assumed to be cubic, we may specify the localized eigenvectors to be of a spherically symmetric form:

$$\boldsymbol{\eta}_s(\mathbf{r}) = \text{grad}\,\varphi_s(r)$$
$$= \Phi_s(r)(\cos\vartheta\,\cos\varphi, \cos\vartheta\,\sin\varphi, \sin\vartheta). \qquad (16)$$

These are perhaps not the only localized modes, but they are certainly the most important (and the ones which are localized most strongly). There is no difficulty in extending the concept to modes with a more complicated point symmetry (e.g., p, d symmetry, etc.), but to simplify the calculation we will consider only those of the form (16).

With these two presuppositions on the symmetry it is evident that the functions $\rho_{k\lambda k'\lambda'}{}^s$ can only depend on the absolute amounts $|\mathbf{k}|$ and $|\mathbf{k}'|$ and on the angle ϑ between the two wave vectors $\mathbf{k}$ and $\mathbf{k}'$:

$$\rho_{k\lambda k'\lambda'}{}^s \equiv \rho_{\lambda\lambda'}{}^s(|\mathbf{k}|, |\mathbf{k}'|; \vartheta) \qquad (17)$$

and, as the process (7) is symmetric in both involved phonons $(\mathbf{k}\lambda)$ and $(\mathbf{k}'\lambda')$, we must have

$$\rho_{\lambda\lambda'}{}^s(k,k';\vartheta)=\rho_{\lambda\lambda'}{}^s(k',k;\vartheta),\qquad(18)$$

which means an extremal value for $k=k'$. The coefficients $\rho_{\mathbf{k}\lambda s}{}^{k'\lambda'}$ are identical with $\rho_{\mathbf{k}\lambda\mathbf{k}'\lambda'}{}^s$ as will be proved later on.

The general properties (17) and (18) are insufficient, however, for getting the final result in a form where it is comparable to the measurements. To calculate the interaction factors of Eq. (15) in explicit form one has to analyze the deviation factors $P(\mathbf{n},\mathbf{m},\mathbf{m}')$. Very little is known about them, and they depend sensibly on the special impurity center. Their exact form is too complicated for further computational use.

Fortunately we can avoid the difficulty by a very plausible approximative assumption. We know that the ideal coefficients $H^{ijk}(\mathbf{m},\mathbf{m}')$ are significant only for small values of $|\mathbf{m}|$ and $|\mathbf{m}'|$, thus ensuring that the region $(\mathbf{n},\mathbf{m},\mathbf{m}')$ remains small; we may, therefore, mark it by a vector $\mathbf{R}(\mathbf{n},\mathbf{m},\mathbf{m}')$ which is some average of $\mathbf{n}, \mathbf{n}+\mathbf{m}, \mathbf{n}+\mathbf{m}'$ and replace $P(\mathbf{n},\mathbf{m},\mathbf{m}')$ by a function of $\mathbf{R}$, which has, of course, to be spherically symmetric with respect to the origin,

$$P(\mathbf{n},\mathbf{m},\mathbf{m}')=P(|\mathbf{R}|),\quad \mathbf{R}=\tfrac{1}{3}(3\mathbf{n}+\mathbf{m}+\mathbf{m}').\quad(19)$$

This approximation implies that $P(R)$ is practically constant within the region $(\mathbf{n},\mathbf{m},\mathbf{m}')$, the extension of which is determined by the nonvanishing coefficients $H^{ijk}(\mathbf{m},\mathbf{m}')$; hence,

$$P(R)\simeq P(|\mathbf{n}|)\simeq P(|\mathbf{n}+\mathbf{m}|)\simeq P(|\mathbf{n}+\mathbf{m}'|).\quad(20)$$

Using this simplification and the well-known relation for the ideal eigenvectors $\eta_{k\lambda}(\mathbf{r}j)$,

$$\eta_{\mathbf{k}\lambda}(\mathbf{n}+\mathbf{m},j)=\eta_{\mathbf{k}\lambda}(\mathbf{m}j)e^{i\mathbf{k}\cdot\mathbf{n}}.\quad(21)$$

The third-order interaction energy (14) is written in normal coordinates as

$$H_{\text{int}}^{(3)}=\frac{1}{3!}\sum_{\mathbf{k}\mathbf{k}'\lambda\lambda's}q_{\mathbf{k}\lambda}q_{\mathbf{k}'\lambda'}q_s$$

$$\times\sum_{ijk}\sum_{\mathbf{n}}P(|\mathbf{n}|)\eta_s(\mathbf{n}i)e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{n}}\sum_{\mathbf{m}\mathbf{m}'}H^{ijk}(\mathbf{m},\mathbf{m}')$$

$$\times\{\eta_{\mathbf{k}\lambda}(\mathbf{m}j)\eta_{\mathbf{k}'\lambda'}(\mathbf{m}'k)+\eta_{\mathbf{k}\lambda}(-\mathbf{m}j)\eta_{\mathbf{k}'\lambda'}(\mathbf{m}-\mathbf{m}'k)$$

$$+\eta_{\mathbf{k}\lambda}(\mathbf{m}-\mathbf{m}'j)\eta_{\mathbf{k}'\lambda'}(-\mathbf{m}'k)\}+\text{terms not be-}$$

longing to the processes (7) and (8), (22)

thus making the summations over $\mathbf{n}$ independent of $\mathbf{m},\mathbf{m}'$.

IV. LATTICE SUMMATIONS

Considering Eq. (22) we have to manipulate first summations of the form,

$$\sum_{\mathbf{n}}P(|\mathbf{n}|)\eta_s(\mathbf{n},j)e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{n}},\quad(23)$$

where the localized eigenvectors $\eta_s(\mathbf{n},j)$ are of the spherically symmetric form (16).

Without any further special statement on the function $\varphi_s(r)$ (Eq. (16)) it is now possible to simplify the summation over $\mathbf{n}$ greatly. First we replace the summation by an integration:

$$\sum_{\mathbf{n}}\cdots=\frac{1}{\tau_0}\int\cdots r^2\sin\vartheta dr d\vartheta d\varphi.\quad(24)$$

($\tau_0=$volume of the unit cell of the lattice.) Then we may carry out the integration over φ and ϑ, if we use for the latter the formula[28]

$$\int_0^\pi \sin^2\vartheta\,\cos(|\mathbf{k}+\mathbf{k}'|r\cos\vartheta)d\vartheta$$
$$=\pi J_1(|\mathbf{k}+\mathbf{k}'|r)/|\mathbf{k}+\mathbf{k}'|r.\quad(25)$$

We get

$$\sum_{\mathbf{n}}P(|\mathbf{n}|)\eta_s(\mathbf{n}j)e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{n}}=R_s(|\mathbf{k}+\mathbf{k}'|)\frac{(\mathbf{k}+\mathbf{k}')_j}{|\mathbf{k}+\mathbf{k}'|},\quad(26)$$

where $R_s(z)$ is given by

$$R_s(z)=\frac{2\pi^2}{\tau_0}\frac{1}{z}\int_0^\infty rdr\,P(r)\Phi_s(r)J_1(zr).\quad(27)$$

The formula (26) is the analog to the law of quasi-momentum conservation in the theory of normal and umklapp processes[5,6] ($\sum_{\mathbf{n}}\sim\delta_{\mathbf{k}+\mathbf{k}'+\mathbf{k}''}$).

For the evaluation of (27) we need the explicit structure of the functions $P(r)$ and $\Phi_s(r)$ which requires a detailed investigation of the changes in the lattice produced by the special kind of impurity center. This detail would extend the inquiry unduly and obscure the essential features; therefore, we postpone the question for future study. To get some (in fact, quite good) estimate we put

$$P(r)=1,\quad(28)$$

which means that the third-order correlations are not at all affected by the disturbance. Even in this case there are processes of the form (7) and (8) suggesting that the alterations of third-order coupling constants are not so very important for these processes because of the fact that the existence of localized modes is caused by the alterations in the harmonic terms. For the function $\varphi_s(r)$ [Eq. (16)] we choose a behavior which is suggested by the characteristic radial vibrations of a homogeneous sphere in the theory of elasticity,[29] modified, however, by a decreasing exponential factor, paying regard to the disturbance in the central region and establishing with this independence of boundary conditions,

$$\varphi_s(r)=a(\alpha,\beta)\frac{\sin\beta r}{\beta r}e^{-\alpha r};\quad \Phi_s=\frac{d}{dr}\varphi_s(r),\quad(29)$$

[28] I. M. Ryshik and I. S. Gradstein, *Tafeln* (VEB Deutscher Verlag der Wissenschaften, Berlin, 1957), p. 195. $J_1(z)$ is the Bessel function of the first kind.
[29] L. D. Landau and E. M. Lifshitz, *Elasticity* (Pergamon Press, Inc., London, 1958), p. 102.

where the constant $a(\alpha,\beta)$ is defined by the normalization condition for $\eta_s(\mathbf{n}i)$ as

$$a^2(\alpha,\beta) = \frac{\alpha\tau_0}{\pi}. \tag{30}$$

With the choice (28) and (29) we can perform the integration (27),

$$R_s(|\mathbf{k}+\mathbf{k}'|) = -\frac{4\pi^2 a(\alpha,\beta)\alpha}{\tau_0 r_1 r_2}[(r_1+r_2)^2-4\beta^2]^{-1/2}, \tag{31}$$

where the formula[30]

$$\int_0^\infty e^{-\alpha r}\sin\beta r J_0(|\mathbf{k}+\mathbf{k}'|r)dr$$
$$= \frac{2\alpha\beta}{r_1 r_2}[(r_1+r_2)^2-4\beta^2]^{-1/2} \tag{32}$$

has been used, and r_1, r_2 have the meaning,

$$\begin{aligned} r_1^2 &= \alpha^2 + (\beta+|\mathbf{k}+\mathbf{k}'|)^2, \quad r_1>0 \\ r_2^2 &= \alpha^2 + (\beta-|\mathbf{k}+\mathbf{k}'|)^2, \quad r_2>0. \end{aligned} \tag{33}$$

When (26) is substituted into (22) we are left with the summation problem,

$$\sum{}^{(a)}\cdots = -G^{-1}\sum_{ijk}e_{\mathbf{k}''1}{}^i e_{\mathbf{k}\lambda}{}^i e_{\mathbf{k}'\lambda'}{}^k$$
$$\times\sum_{\mathbf{m}\mathbf{m}'}e^{i(\mathbf{k}\cdot\mathbf{m}+\mathbf{k}'\cdot\mathbf{m}')}H^{ijk}(\mathbf{m},\mathbf{m}'), \tag{34}$$

and two other summations $\sum^{(b)}$ and $\sum^{(c)}$, but it can be proved after some elementary transformations that both are identical with $\sum^{(a)}$. The $e_{\mathbf{k}\lambda}{}^i$ are the unit amplitudes of the modes $(\mathbf{k}\lambda)$, keeping in mind the definition of the eigenvectors $\eta_{\mathbf{k}\lambda}$,

$$\eta_{\mathbf{k}\lambda}(\mathbf{r}j) = G^{-1/2}e_{\mathbf{k}\lambda}{}^i \exp(i\mathbf{k}\cdot\mathbf{r}), \quad (G=N^3). \tag{35}$$

In particular, $\lambda=1$ indicates the longitudinal wave, i.e.,

$$e_{\mathbf{k}1}{}^j = k_j/|\mathbf{k}|. \tag{36}$$

Moreover, we have used in (34) the abbreviation,

$$\mathbf{k}'' = -(\mathbf{k}+\mathbf{k}'). \tag{37}$$

The summation (34) appears also in the case of the ideal lattice. An accurate computation yields extremely complicated expressions.[27] To approximation, (34) can be expressed in terms of the elastic constants of the crystal; we refer to the book by Ziman.[31] The simplest possibility is to express (34) by one single constant γ,

the so-called Grüneisen[32] constant. Klemens[4,5] gives the formula,

$$\sum{}^{(a)} = +i(3!)^{1/2}\frac{M}{Gv}\gamma\omega\omega'\omega''\delta_{\mathbf{k}+\mathbf{k}'+\mathbf{k}''}, \tag{38}$$

($v=$sound velocity) whereas in the result of Leibfried and Schloemann[33] the numerical factor $(3!)^{1/2}$ is replaced by 1.23. A typical value for γ is 2 (e.g., $\gamma_{\mathrm{KCl}}=1.6$).

We use the approximation (38), which is also well accepted in the theory of normal and umklapp processes, although it is rather bad. More accurate but more complicated expressions would burden the further calculation too much.

With (38) and the two approximate assumptions,

$$\omega(\mathbf{k}\lambda) = v_\lambda|\mathbf{k}|, \quad (\text{``acoustic approximation''}) \tag{39a}$$

and

$$v_\lambda = v_{\lambda'} = v, \tag{39b}$$

which are both usually in the theory of heat current[5,6] and already included in (38), the scattering Hamiltonian for three quantum processes finally takes the form

$$H_{\mathrm{int}}{}^{(3)} = \frac{i}{2}(3!)^{1/2}\frac{Mv^2}{G}\gamma\sum_{\mathbf{k}\mathbf{k}'\lambda\lambda's}R_s(|\mathbf{k}+\mathbf{k}'|)$$
$$\times|\mathbf{k}+\mathbf{k}'||\mathbf{k}||\mathbf{k}'|q_{\mathbf{k}\lambda}q_{\mathbf{k}'\lambda'}q_s, \quad +\cdots, \tag{40}$$

which may be written in the creation-annihilation form (15) by means of the transformation (10a). Doing so, we find the concrete expressions for the interaction factors $\rho_{\mathbf{k}\lambda\mathbf{k}'\lambda'}{}^s$, $\rho_{\mathbf{k}\lambda s}{}^{\mathbf{k}'\lambda'}$, namely,

$$\rho_{\mathbf{k}\lambda\mathbf{k}'\lambda'}{}^s = \rho_{\mathbf{k}\lambda s}{}^{\mathbf{k}'\lambda'} = i2^{-5/2}(3!)^{1/2}G^{-1}(M\omega_s)^{-1/2}v\hbar^{3/2}\gamma$$
$$\times R_s(|\mathbf{k}+\mathbf{k}'|)|\mathbf{k}+\mathbf{k}'||\mathbf{k}|^{1/2}|\mathbf{k}'|^{1/2}. \tag{41}$$

Expressions which are very similar to these were derived by Klemens[34] when he calculated the anharmonic attenuation of a singular localized mode outside the bands; yet they are not identical, because he used another form than (29) for the localized mode.

The coefficients (41) evidently satisfy the relations (17) and (18) and are independent of λ, λ'. From now on we suppress the indices λ, λ' at all quantities which do not depend on them, especially

$$\omega(\mathbf{k}\lambda) \equiv \omega(\mathbf{k}) = \omega(k), \tag{39c}$$

which follows from (39a, b).

V. MOLECULAR VIBRATIONS

So far the mathematical description has been restricted to the case where the impurity center is mon-

[30] H. Bateman, *Tables of Integrable Transforms* (McGraw-Hill Book Company, Inc., New York, 1954), Vol. II, p. 10.
[31] F. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, 1960), p. 131.

[32] E. Grüneisen, in *Handbuch der Physik*, edited by H. Geiger and Karl Scheel (Julius Springer, Berlin, 1926), Vol. 10. p. 1.
[33] G. Leibfried and E. Schloemann, Nachr. Akad. Wiss. Göttingen Math. Physik. Kl. IIa 4, 71 (1954).
[34] P. G. Klemens, Phys. Rev. **122**, 443 (1961).

atomic, i.e., a regular ion of the lattice is replaced by a foreign one. The treatment of polyatomic or molecular impurity centers, where more than one irregular atom occupy a single unit cell of our (monatomic) lattice, is simpler in some senses.

Let us assume that there are ν foreign masses in the unit cell $(0,0,0)$, or $3(\nu-1)$ new degrees of freedom; and let us, further on, alter the meaning of the lattice vector $\mathbf{n}$:

$$\mathbf{n} = \mathbf{a}(n_1, n_2, n_3) \text{ for } n_1^2 + n_2^2 + n_3^2 \neq 0, \ n_i = 0, 1, 2, \cdots$$
$$= \mathbf{n}_0^{(1)}, \mathbf{n}_0^{(2)}, \cdots, \mathbf{n}_0^{(\nu)} \text{ for } n_1^2 + n_2^2 + n_3^2 = 0. \quad (42)$$

Then we have again to look for the eigensolutions of the matrix $h_{\mathrm{nm}}{}^{ij}$ which is now of a higher rank. There are once more the "lattice modes" discussed in Sec. II, in which the molecule acts (roughly speaking) as a unity with mass M_0; for them the spectral density is unchanged. But in addition one has $3(\nu-1)$ new modes either outside the bands or inside. In the case of the system $KCl:KNO_2$, for instance, the internal vibrations of the free NO_2^- atom are practically unchanged in the lattice and lie high above the lattice modes, whereas the rotational vibrations of the NO_2^- center lie in the acoustic band.

We are only interested in the new modes within the acoustic band. They may well lie in spectral regions, where the "lattice modes" are phonons, i.e., where the heat current is given by the Peierl's formula. Then we have the possibility of the second-order process,

$$(\mathbf{k}\lambda) \rightleftarrows (\sigma) \quad (43)$$

with a strong influence on the thermal conductivity. To describe this process we use the basic system[35]

$$(\eta_{\mathbf{k}\lambda}{}^{(0)}) + (\eta_\sigma), \quad (44)$$

which includes all the $3N^3$ ideal eigenvectors $\eta_{\mathbf{k}\lambda}{}^{(0)}$ together with $3(\nu-1)$ localized vectors η_σ which represent the molecular vibrations. They are solutions of the eigenvalue equation

$$\sum_{\mathbf{m}j} h_{\mathrm{nm}}{}^{(\sigma)ij}\eta_\sigma(\mathbf{m}j) = \omega^2(\sigma)\eta_\sigma(\mathbf{n}i), \quad (45)$$

where $h_{\mathrm{nm}}{}^{(\sigma)ij}$ is identical with $h_{\mathrm{nm}}{}^{ij}$ in the neighborhood of the origin (i.e., for small $|\mathbf{n}|$, $|\mathbf{m}|$) and zero for larger values of $|\mathbf{n}|$, $|\mathbf{m}|$ in order to assure that η_σ is strongly localized. The interaction Hamiltonian then takes the form

$$H_{\mathrm{int}}{}^{(2)} = \tfrac{1}{2}\sum_{\mathbf{k}\lambda\sigma} \hbar(\omega(\mathbf{k}\lambda)\omega(\sigma))^{1/2}\left(\frac{\omega_\sigma}{\omega_{\mathbf{k}\lambda}}+1\right)$$
$$\times [\Omega_{\mathbf{k}\lambda}{}^{\sigma*}a_{\mathbf{k}\lambda}{}^\dagger a_\sigma + \Omega_{\mathbf{k}\lambda}{}^\sigma a_\sigma{}^\dagger a_{\mathbf{k}\lambda}] + \cdots, \quad (46)$$

where we have suppressed those terms which belong to double creations or annihilations and those of the

processes $(\mathbf{k}\lambda) \rightleftarrows (\mathbf{k}'\lambda')$ and $(\sigma) \rightleftarrows (\sigma')$. Moreover, some additional contributions to the process (43) are negligible according to the relations,

$$|(\mathbf{k}\lambda|h^{(\sigma)}|\sigma)| \gg |(\mathbf{k}\lambda|h-h^{(\sigma)}|\sigma)|, \quad (47a)$$

$$|(\sigma|h^{(0)}|\mathbf{k}\lambda)| \gg |(\sigma|h-h^{(0)}|\mathbf{k}\lambda)|, \quad (47b)$$

and not written down in (46). $\Omega_{\mathbf{k}\lambda}{}^\sigma$ is the scalar product of the two vectors $\eta_{\mathbf{k}\lambda}{}^{(0)}$ and η_σ.

The rank of the matrix $h_{\mathrm{nm}}{}^{(\sigma)ij}$ is a small number, although larger than $3(\nu-1)$, and there are, therefore, no practical difficulties for the evaluation of $\omega^2(\sigma)$ and $\eta_\sigma(\mathbf{n}i)$. For the set (44) we choose the most localized solutions. It is not necessary that the solutions remain localized if we go to the limit $h_{\mathrm{nm}}{}^{(\sigma)ij} \equiv h_{\mathrm{nm}}{}^{ij}$. Hence, the molecular vibrations, represented by the most localized solutions of (45), are possibly not stationary eigenvibrations of the lattice at all, but they are quasi-stationary vibrations with a long decay time.

VI. THE SCATTERING PROCESS

The scattering Hamiltonians for two and three quantum processes being established, we may turn to the formulation of the scattering process. We have to look for the alterations in time for the occupation numbers $N_{\mathbf{k}\lambda}, N_s$, and N_σ which are due to the respective scattering process. Starting with an initial state ψ_i each of the scattering processes (7), (8), and (43) defines in a natural way two final states $\psi_f{}^{(1)}$ and $\psi_f{}^{(2)}$ (occupation numbers either unchanged or changed by ± 1). The time derivatives $\dot{N}_{\mathbf{k}\lambda}$, etc., are then the difference of gain and loss per unit time, where gain and loss are given by the transition probability to one of the two final states, respectively, the transition probability being determined by the interaction Hamiltonians.

All this is standard procedure[4,5] and need not be reproduced here in detail. For the second-order process (43), however, there arises a strong implication because of the quasi δ behavior of the transition probability $W_{if}(t)$ as given by elementary quantum mechanics.[36] Namely, it is customary to go the limit $t \to \infty$ and use the formula[37]

$$\lim_{t\to\infty} \sin^2\alpha t/\pi t\alpha^2 = \delta(\alpha) \quad (48)$$

which, of course, is physically of no sense, taken literally, because it would imply that the change of any state, caused by the perturbation, would be vanishingly small for infinite times. Nevertheless, one can use (48) in all cases where the limiting process does not influence the result essentially, i.e., if there is a summation over a dense spectrum. Yet in the second-order process (43) the expression for $\dot{N}_{\mathbf{k}\lambda}$ contains a summation over a small number of discrete (molecular) frequencies ω_σ only.

[35] The eigenamplitudes $\eta_{\mathbf{k}\lambda}$ for the points $\mathbf{n}_0^{(1)}, \mathbf{n}_0^{(2)}, \cdots$ are all the same and identical with $\eta_{\mathbf{k}\lambda}(0,i)$ in the $3N^3$-dimensional description, $\eta_{\mathbf{k}\lambda}(\mathbf{n}_0^{(1)}i) = \eta_{\mathbf{k}\lambda}(\mathbf{n}_0^{(2)}i) = \cdots = \eta_{\mathbf{k}\lambda}(0,i)$.

[36] E.g., L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), p. 197 ff.

[37] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon Press, Inc., London, 1958), p. 146.

It is, therefore, necessary to take account somehow of the finite decay time of internal vibrational excitations of molecular defects, which are of a quasistationary character. This is done in elementary quantum mechanics[38] by replacing the discrete energy by an energy distribution in the vicinity of the discrete value. In our case we write the law in the form,

$$w(\hbar\omega)d(\hbar\omega) = \frac{\Gamma_\sigma}{\pi} \frac{d(\hbar\omega)}{(\hbar\omega - \hbar\omega_\sigma)^2 + \Gamma_\sigma{}^2}, \qquad (49)$$

where $\Delta(\hbar\omega)_\sigma = \Gamma_\sigma$ is the so-called *breadth of the distribution* around the central value $\hbar\omega_\sigma$ and is given as some average over the breadths of the quasistationary states $(N_\sigma + 1)\hbar\omega_\sigma$, $N_\sigma\hbar\omega_\sigma$, $(N_\sigma - 1)\hbar\omega_\sigma$, namely

$$\Gamma_\sigma = 2\Gamma(N_\sigma). \qquad (50)$$

$\Gamma(N_\sigma)$ is related to the average lifetime $\tau(N_\sigma)$ of the state $N_\sigma\hbar\omega_\sigma$ by $\tau(N_\sigma) = \hbar/2\Gamma(N_\sigma)$. This lifetime $\tau(N_\sigma)$ is defined by the scattering process (43) itself, if we put $N_{k\lambda} = 0$ in the formula for $\dot{N}_\sigma$,

$$\frac{d}{dt}N_\sigma(t) = -\frac{N_\sigma(t)}{\tau(N_\sigma)}, \quad (N_{k\lambda} = 0). \qquad (51)$$

We multiply now the expression for $\dot{N}_{k\lambda}$ with $w(\hbar\omega) \times d(\hbar\omega)$, as given by (49), and integrate over $\hbar\omega$. Then the limiting process $t \to \infty$ no longer critically influences the result, whence we may use it. Let us, further on, replace summations over $\mathbf{k}$ by integrations in $\mathbf{k}$ space (V = volume of the system),

$$\sum_{\mathbf{k}} \cdots = \frac{V}{(2\pi)^3} \int \cdots d^3k$$

$$= \frac{V}{(2\pi)^3} \frac{1}{v^3} \int \cdots \omega^2 \sin\vartheta\, d\omega d\vartheta d\varphi, \quad (52)$$

and summarize the results in explicit form. For the second-order scattering (43) we get

$$\frac{d}{dt}N_{k\lambda}(t) = 2\sum_\sigma |\Omega_{k\lambda}{}^\sigma|^2 \frac{\Gamma_\sigma\omega^2(k)}{(\omega(k) - \omega_\sigma)^2 + (\Gamma_\sigma/\hbar)^2}$$

$$\times [N_\sigma - N_{k\lambda}], \quad (53a)$$

$$\frac{d}{dt}N_\sigma(t) = \frac{V}{(2\pi)^2} \frac{\omega_\sigma{}^4}{v^3} \sum_\lambda \int |\Omega_{k\lambda}{}^\sigma(\omega(k) = \omega_\sigma)|^2$$

$$\times [N_{k\lambda} - N_\sigma] \sin\vartheta d\vartheta d\varphi, \quad (53b)$$

where, by means of (50) and (51),

$$\Gamma_\sigma = \frac{\hbar}{\tau(N_\sigma)} = \hbar \frac{V}{(2\pi)^2} \frac{\omega_\sigma{}^4}{v^3} \sum_\lambda \int |\Omega_{k\lambda}{}^\sigma(\omega(k) = \omega_\sigma)|^2$$

$$\times \sin\vartheta d\vartheta d\varphi \quad (54)$$

[38] E.g., D. I. Blochinzew, *Grundl. d. Quantenmechanik* (VEB Deutscher Verlag der Wissenschaften, Berlin, 1953), p. 360.

which demonstrates that Γ_σ in fact does not depend on N_σ; this is plausible as no third-order effects were included. For the third-order processes (7) and (8) there are no implications concerning the limit $t \to \infty$, and for the scattering (7) we have

$$\frac{d}{dt}N_{k\lambda}(t)$$

$$= \frac{V}{(2\pi)^2} \frac{\omega'^2}{\hbar^2 v^3} \sum_{\lambda's} \int |\rho^s(\omega,\omega';\vartheta')|^2 \sin\vartheta' d\vartheta' d\varphi'$$

$$\times [N_s(N_{k\lambda} + 1)(N_{k'\lambda'} + 1) - (N_s + 1)N_{k\lambda}N_{k'\lambda'}], \qquad (55a)$$

$$\frac{d}{dt}N_s(t)$$

$$= \frac{V^2}{(2\pi)^5} \frac{\omega'^2}{\hbar^2 v^6} \sum_{\lambda\lambda'} \int \omega^2 d\omega \sin\vartheta d\vartheta d\varphi$$

$$\times |\rho^s(\omega,\omega';\vartheta')|^2 \sin\vartheta' d\vartheta' d\varphi' \qquad (55b)$$

$$\times [(N_s + 1)N_{k\lambda}N_{k'\lambda'} - N_s(N_{k\lambda} + 1)(N_{k'\lambda'} + 1)],$$

where

$$\omega' = \omega_s - \omega. \qquad (56)$$

This condition follows from the integration over the δ function and is nothing but the law of energy conservation already written down in (7b). The two-phonon frequencies must be in the acoustic band (ω, $\omega' \leq \omega_g$ = acoustic boundary; we may put $\omega_g = \omega_D$ = Debye frequency). Whence, (55) is correct only if we make the restrictions

$$\omega_s - \omega_g \leq \omega \leq \omega_g \quad \text{for} \quad \omega_s \geq \omega_g \qquad (57a)$$

and

$$0 \leq \omega \leq \omega_s \quad \text{for} \quad \omega_s = \omega_s{}^B \leq \omega_g. \qquad (57b)$$

Otherwise the right-hand sides of (55a, b) are zero.

Not included in the result (55a, b) are double creations or annihilations of the mode ($\mathbf{k}\lambda$), which occur in the special case $\mathbf{k}\lambda \equiv \mathbf{k'}\lambda'$. But as the additional contributions from this process to $\dot{N}_{k\lambda}, \dot{N}_s$ contain one summation over the $\mathbf{k}$ space less than (55a, b), we may neglect them.

In the same way we may establish the equations for the scattering process (8), but it turns out that this process is of no physical significance because its relaxation time has a monotonic functional behavior. This is quite plausible as (8) is not symmetric in both involved phonons. Moreover, (8b) yields $\omega' \geq \omega_s$ which shows that (8) becomes effective at higher temperatures than (7), where both ω and ω' are below ω_s.

VII. THE BOLTZMANN EQUATIONS

The further mathematical description conforms to the other work done on thermal conductivity and is indicated in the fundamental work by Peierls.[26] We

may, therefore, be very brief and refer to the review articles by Klemens[4,5] and Carruthers.[6]

We look at the phonons as particles moving with the group velocity

$$\mathbf{v_k} = \text{grad}_k \omega(k) = v\mathbf{k}/|\mathbf{k}| . \tag{58}$$

Their density distribution $N_{k\lambda}(\mathbf{r},t)$, given as a function of space and time, depends in our case on both the scattering and the diffusion process. In the steady state the total rate of change of the distribution function per time must vanish

$$\dot{N}_{k\lambda}]_{\text{scatt}} + \dot{N}_{k\lambda}]_{\text{diff}} = 0. \tag{59}$$

These are the Boltzmann equations in our special case. But they are incomplete yet. The localized quanta are not able to transport energy in one direction and cannot be taken as particles. Their total rate of change in time is given by the scattering with phonons, and in the steady state we have, therefore,

$$\dot{N}_s]_{\text{scatt}} = 0, \text{ or } \dot{N}_\sigma]_{\text{scatt}} = 0, \tag{60a, b}$$

respectively, which is to be considered as a subsidiary condition to the Boltzmann equations (59).

$\dot{N}_{k\lambda}, \dot{N}_s, \dot{N}_\sigma]_{\text{scatt}}$ are given by the appropriate expressions of the last section, whereas $\dot{N}_{k\lambda}]_{\text{diff}}$ is usually taken in the convenient but also rather accurate approximation,

$$\dot{N}_{k\lambda}]_{\text{diff}} = -(\mathbf{v_k} \cdot \nabla T) C_{\text{ph}}(\omega)/\hbar\omega, \tag{61}$$

where $C_{\text{ph}}(\omega)$ is the contribution of the mode $(\mathbf{k}\lambda)$ to the specific heat,

$$C_{\text{ph}}(\omega) = \frac{(\hbar\omega)^2}{kT^2} \frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT}-1)^2}. \tag{62}$$

The essential quantity for describing the heat current is the deviation of the quantum numbers $N_{k\lambda}$, N_s, N_σ from thermal equilibrium

$$N_k^{(0)} = [\exp(\hbar\omega/kT)-1]^{-1}, \text{ etc.}, \tag{63}$$

and we write

$$N_{k\lambda} = N_k^{(0)} + n_\lambda(\mathbf{k}), \text{ etc.} \tag{64}$$

We adopt also the *principle of detailed balance*,[39] which reads for the second-order process (43),

$$N_k^{(0)} = N_\sigma^{(0)}; \tag{65a}$$

and for the third-order process (7),

$$N_s^{(0)}(N_k^{(0)}+1)(N_{k'}^{(0)}+1)$$
$$= (N_s^{(0)}+1)N_k^{(0)}N_{k'}^{(0)}, \tag{65b}$$

and is, in both cases, a consequence of the law of energy conservation.

Using the foregoing expressions, the Boltzmann equations (59) with the appropriate subsidiary conditions (60) can now be established in explicit form. Inserting

[39] Cf. for example, Ref. 31, p. 264 ff.

(53a) and (61) into Eq. (59) and (53b) into Eq. (60b) we have for the second-order process (43),

$$(\mathbf{v_k} \cdot \nabla T)\frac{C_{\text{ph}}(\omega)}{\hbar\omega} = 2\sum_\sigma |\Omega_{k\lambda}{}^\sigma|^2 \frac{\omega^2\Gamma_\sigma}{(\omega-\omega_\sigma)^2+(\Gamma_\sigma/\hbar)^2}$$
$$\times[n_\sigma - n_\lambda(\mathbf{k})] \tag{66}$$

with the subsidiary conditions,

$$\sum_\lambda \int |\Omega_{k\lambda}{}^\sigma(\omega=\omega_\sigma)|^2 [n_\lambda(\mathbf{k})-n_\sigma] \sin\vartheta d\vartheta d\varphi = 0,$$
$$(\omega=\omega_\sigma). \tag{67}$$

The corresponding equations for the third-order process (7) are found, if one inserts (55a), (61) into (59) and (55b) into (60a),

$$(\mathbf{v_k} \cdot \nabla T)\frac{C_{\text{ph}}(\omega)}{\hbar\omega}$$
$$= \frac{V}{(2\pi)^2} \frac{\omega'^2}{\hbar^2 v^3} \sum_{\lambda' s} \int |\rho^s(\omega,\omega';\vartheta')|^2 \sin\vartheta' d\vartheta' d\varphi'$$
$$\times[n_s(N_k^{(0)}+N_{k'}^{(0)})-n_\lambda(\mathbf{k})(N_{k'}^{(0)}-N_s^{(0)})$$
$$-n_{\lambda'}(\mathbf{k'})(N_k^{(0)}-N_s^{(0)})+\text{high. terms}] \tag{68}$$

with the subsidiary conditions,

$$\sum_{\lambda\lambda'} \int \omega^2 d\omega \sin\vartheta d\vartheta d\varphi |\rho^s(\omega,\omega';\vartheta')|^2 \sin\vartheta' d\vartheta' d\varphi'$$
$$\times[n_{\lambda'}(\mathbf{k'})(N_k^{(0)}-N_s^{(0)})-n_s N_k^{(0)}+\text{high. terms}] = 0, \tag{69}$$

where ω' is given by (56).

The Eqs. (68), (69) are nonlinear integral equations. It is customary[39] (but also necessary) to linearize such equations in transport theory, which we do by neglecting the terms of higher order in n_s, $n_\lambda(\mathbf{k})$, assuming the deviations from thermal equilibrium to be small. The equations for the second-order process, on the other hand, are exactly linear, as the second-order terms $n_\sigma n_\lambda(\mathbf{k})$ cancel.

The quantity $\Omega_{k\lambda}{}^\sigma$ is the scalar product of the two basic vectors $\eta_{k\lambda}$ and η_σ; it takes the form,

$$\Omega_{k\lambda}{}^\sigma = (\eta_{k\lambda}|\eta_\sigma) = \sum_i \eta_{k\lambda}{}^*(0,i) \sum_{n_0(\mu)}^\nu \eta_\sigma(\mathbf{n_0}^{(\mu)}i)$$
$$+ \sum_{\substack{ni \\ (n\neq n_0(\mu))}} \eta_{k\lambda}{}^*(ni)\eta_\sigma(ni), \tag{70}$$

where the first term on the right-hand side is independent of $\mathbf{k}$ according (35). Looking at $|\Omega_{k\lambda}{}^\sigma|^2$ as a function in $\mathbf{k}$ space, this function is radially symmetric to the origin if the amplitudes $\eta_\sigma(ni)$ outside the molecule $(\mathbf{n}\neq\mathbf{n_0}^{(\mu)}, \mu=1, 2, \cdots\nu)$ are radially symmetric in

n space; this is not exactly true for the single molecular impurity. But it is true in a statistical sense, i.e., if we average over a large number of impurities, and we put, therefore,

$$|\Omega_{k\lambda}{}^{\sigma}|^2 = |\Omega_{\lambda}{}^{\sigma}(\omega)|^2. \tag{71}$$

Doing so, it is evident that the ansatz

$$n_{\sigma}=0, \quad n_{\lambda}(\mathbf{k})=n_{\lambda}(\omega)(\mathbf{v_k}\cdot\nabla T) \tag{72}$$

is compatible with the subsidiary conditions (67), and from (66) we have

$$n_{\lambda}(\omega)=-\frac{C_{\mathrm{ph}}(\omega)}{2\hbar\omega}\left[\sum_{\sigma}|\Omega_{\lambda}{}^{\sigma}(\omega)|^2\frac{\omega^2\Gamma_{\sigma}}{(\omega-\omega_{\sigma})^2+(\Gamma_{\sigma}/\hbar)^2}\right]^{-1} \tag{73}$$

as solution of the Boltzmann equations for the second-order process.

For the third-order process it is clear by consideration of (68) and (69) that $n_{\lambda}(\mathbf{k})$ cannot depend on the polarization λ of the phonons; replacing summations over λ by the factor 3 we can drop this index. Apart from that we try an ansatz similar to (72),

$$n_s=0, \quad n(\mathbf{k})=n(\omega)(\mathbf{v_k}\cdot\nabla T), \tag{74}$$

which satisfies the subsidiary conditions (69), and after some elementary transformations the system (68) is reduced to the simple form,

$$\frac{C_{\mathrm{ph}}(\omega)}{\hbar\omega}=-\sum_s p_1{}^s(\omega)\omega'^2[N^{(0)}(\omega')-N_s{}^{(0)}]n(\omega)$$

$$-\sum_s p_2{}^s(\omega)\omega'^2[N^{(0)}(\omega)-N_s{}^{(0)}]n(\omega');$$

$$(\omega'=\omega_s-\omega), \quad (75)$$

with the abbreviations,

$$p_1{}^s(\omega)=\frac{3V}{2\pi\hbar^2v^3}\int_0^{\pi}|\rho^s(\omega,\omega';\vartheta)|^2\sin\vartheta d\vartheta, \tag{76a}$$

$$p_2{}^s(\omega)=\frac{3V}{2\pi\hbar^2v^3}\int_0^{\pi}|\rho^s(\omega,\omega';\vartheta)|^2\sin^2\vartheta d\vartheta. \tag{76b}$$

This system of linear equations for the set $n(\omega)$ is easily solved; we have only to write down the parallel equation with ω, ω' interchanged obtaining then two equations with the two unknown quantities $n(\omega)$ and $n(\omega')=n(\omega_s-\omega)$.

We prefer, however, a somewhat simpler procedure to get the relaxation times, which consists in the separation of the Boltzmann equation (75) into two parts.

VIII. THE RELAXATION TIME

If we write down the general Boltzmann equation in abstract form,

$$X=(P_1+P_2+\cdots)\cdot n,$$
$$X\equiv(X(k)), \quad n\equiv(n(k)), \tag{77}$$

where $X(k)$ and $n(k)$ are defined by (61) and (64), respectively, $[X(k)=-N(k)_{\mathrm{scatt}}]$ and $P_1, P_2, \cdots$ are integral operators transforming the set $n(k)$, then it can be shown[39] that the total relaxation time is given by the superposition (2). τ_i is the relaxation time of one single scattering type, following from the equation,

$$X=P_i\cdot n, \tag{78}$$

namely,

$$(\tau_i)^{-1}=-X(k)/n_i(k), \tag{79}$$

if $n_i(k)$ is the solution of (78). The relation (2) is exactly true, if all the Eqs. (78) have the same solution, apart from some constant multiplier. Otherwise, (2) is only a good approximation. It is closely connected with the Matthiessen rule (Matthiessen, 1862) but more accurate as this.

A. The Second-Order Process (5)

Inserting (73) and (61) into (79) we have for the relaxation time,

$$(\tau_{\lambda}(\omega))^{-1}=+2\sum_{\sigma}|\Omega_{\lambda}{}^{\sigma}(\omega)|^2\frac{\omega^2\Gamma_{\sigma}}{(\omega-\omega_{\sigma})^2+(\Gamma_{\sigma}/\hbar)^2} \tag{80}$$

which is of a resonance structure. But to be comparable to the experimental results one has to know the functional behavior of $|\Omega_{\lambda}{}^{\sigma}(\omega)|^2$, which is only possible if one analyzes the molecular vibrations in the special case. We postpone this question for future study.

B. The Third-Order Process (7)

By defining

$$P_1\equiv P_1(\omega,\omega'')=-\sum_s p_1{}^s(\omega)\omega'^2[N^{(0)}(\omega')-N_s{}^{(0)}]\delta_{\omega,\omega''}$$

$$(\omega'=\omega_s-\omega), \quad (81a)$$

$$P_2\equiv P_2(\omega,\omega'')=-\sum_s p_2{}^s(\omega)\omega'^2[N^{(0)}(\omega)-N_s{}^{(0)}]\delta_{\omega',\omega''}, \tag{81b}$$

we may divide (75) into two equations of the form (78) which yield, according to (79), the two relaxation times,

$$(\tau_1(\omega,T))^{-1}=-P_1(\omega,\omega)=\sum_s p_1{}^s(\omega)f_1{}^s(\omega,T) \tag{82a}$$

$$(\tau_2(\omega,T))^{-1}=-P_2(\omega',\omega)\frac{X(\omega)}{X(\omega')}=\sum_s p_2{}^s(\omega')f_2{}^s(\omega,T), \tag{82b}$$

where

$$f_1{}^s(\omega,T)=\omega'^2[N^{(0)}(\omega')-N_s{}^{(0)}]$$

$$=\omega'^2\frac{e^{\hbar\omega'/kT}(e^{\hbar\omega/kT}-1)}{(e^{\hbar\omega_s/kT}-1)(e^{\hbar\omega'/kT}-1)},$$

$$f_2{}^s(\omega,T)=\omega\omega'\frac{C_{\mathrm{ph}}(\omega)}{C_{\mathrm{ph}}(\omega')}[N^{(0)}(\omega')-N_s{}^{(0)}] \tag{83b}$$

$$=\frac{\omega^3}{\omega'}\frac{e^{\hbar\omega/kT}(e^{\hbar\omega'/kT}-1)}{(e^{\hbar\omega_s/kT}-1)(e^{\hbar\omega/kT}-1)}.$$

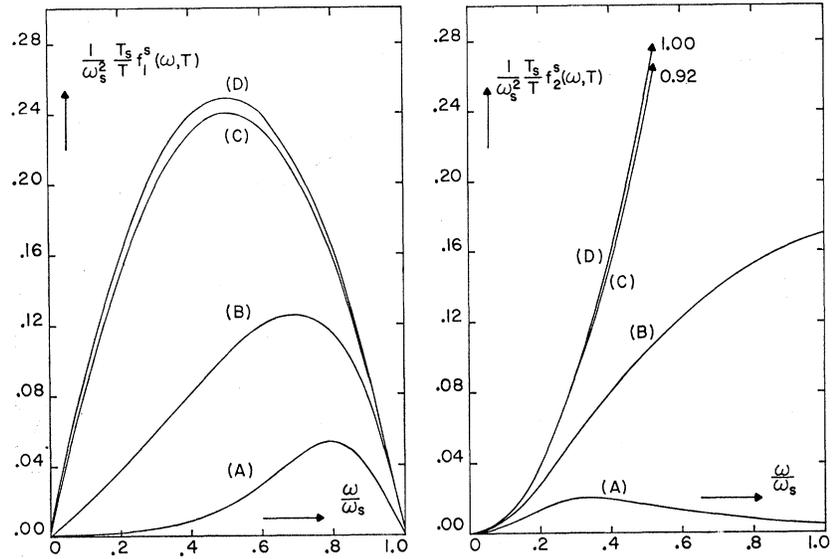FIG. 2. The functional behavior of the functions $f_1(\omega,T)$, $f_2(\omega,T)$, given by Eq. (105a). They represent, apart from the less important factors $p_1{}^s(\omega)$, $p_2{}^s(\omega)$, the two relaxation times of the three quantum process $(\mathbf{k}\lambda)+(\mathbf{k}'\lambda')\rightleftarrows (s)$. A, $T=T_s/10$; B, $T=T_s/5$; C, $T=T_s$; D, $T\to\infty$. $(kT_s=\hbar\omega_s)$.

The functions $f_1{}^s(\omega,T)$, $f_2{}^s(\omega,T)$ which determine the temperature dependence of the relaxation times are shown in Fig. 2. It is seen that $f_1{}^s$ has always a maximum; it goes to $\omega_{\max}=\frac{1}{2}\omega_s$ at high temperatures. The function $f_2{}^s$, on the other hand, has a (small) maximum only at low temperatures, whereas it exhibits a monotonic increase at higher temperatures.

Next we consider the temperature-independent factors in (82a, b). According to (76a, b) and using (41), (31), and (30) we can write them in the form,

$$p_1{}^s(\omega)=Q_sI_1{}^s(\omega), \quad p_2{}^s(\omega)=Q_sI_2{}^s(\omega). \quad (84a, b)$$

The constant Q_s has the value[4]

$$Q_s=\frac{9}{2}\pi^2\mu_s\gamma^2\frac{\hbar\tau_0\alpha^3}{M\omega_s v}, \quad (85)$$

where μ_s is the concentration of defects (i.e., the number of impurity centers per volume).

The two integrals

$$I_1{}^s(\omega)=|\mathbf{k}||\mathbf{k}'|\int_0^\pi \frac{|\mathbf{k}+\mathbf{k}'|^2\sin\vartheta d\vartheta}{r_1{}^2r_2{}^2[(r_1+r_2)^2-4\beta^2]}, \quad (86a)$$

$$I_2{}^s(\omega)=|\mathbf{k}||\mathbf{k}'|\int_0^\pi \frac{|\mathbf{k}+\mathbf{k}'|^2\sin^2\vartheta d\vartheta}{r_1{}^2r_2{}^2[(r_1+r_2)^2-4\beta^2]} \quad (86b)$$

give the frequency dependence. With the substitution,

$$q^2=|\mathbf{k}|^2+|\mathbf{k}'|^2+2|\mathbf{k}||\mathbf{k}'|\cos\vartheta, \quad (\omega'=\omega_s-\omega) \quad (87)$$

[40] V is the volume which contains one single-impurity center. G the number of unit cells in it, or $V=G\tau_0$, which is used in (85), It follows that $(1/V)$ is just the concentration μ_s of impurity centers/unit volume.

they are transformed to

$$I_1{}^s(\omega)=\int_{|k-k'|}^{(\omega_s/v)} \frac{q^3 dq}{r_1{}^2r_2{}^2[(r_1+r_2)^2-4\beta^2]},$$

$$I_2{}^s(\omega)=\int_{|k-k'|}^{(\omega_s/v)} \frac{q^3 \sin\vartheta(q,\omega)dq}{r_1{}^2r_2{}^2[(r_1+r_2)^2-4\beta^2]}. \quad (88a, b)$$

The two integrands are drawn in Fig. 3. It is easily seen that both integrals are symmetrical about the point $\omega=\frac{1}{2}\omega_s$, have the value zero at $\omega=0$ and $\omega=\omega_s(|k-k'|=|2\omega-\omega_s|/v\to\omega_s/v)$ and that always

$$I_1{}^s(\omega)\geq I_2{}^s(\omega) \quad \text{or} \quad p_1{}^s(\omega)\geq p_2{}^s(\omega). \quad (89)$$

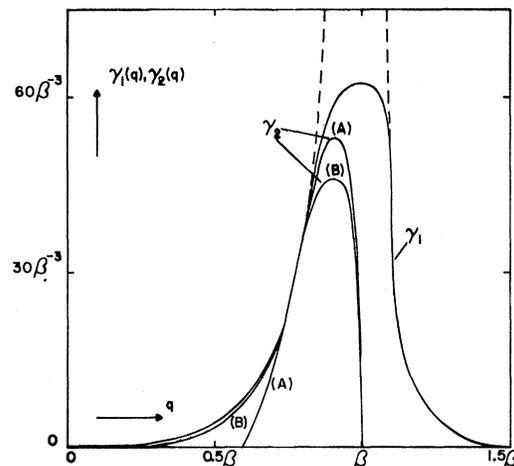$I_1{}^s(\omega)$ has a maximum at $\omega=\frac{1}{2}\omega_s$ for the simple reason,

FIG. 3. The integrands $\gamma_1(q)$, $\gamma_2(q)$ of (110a) and (110b), respectively, for the special case $\alpha=\beta/10$, $\omega_s=v\beta$. $\gamma_2(q)$ depends on ω; A, $\omega=0.8\omega_s$; B, $\omega=0.6\omega_s$.
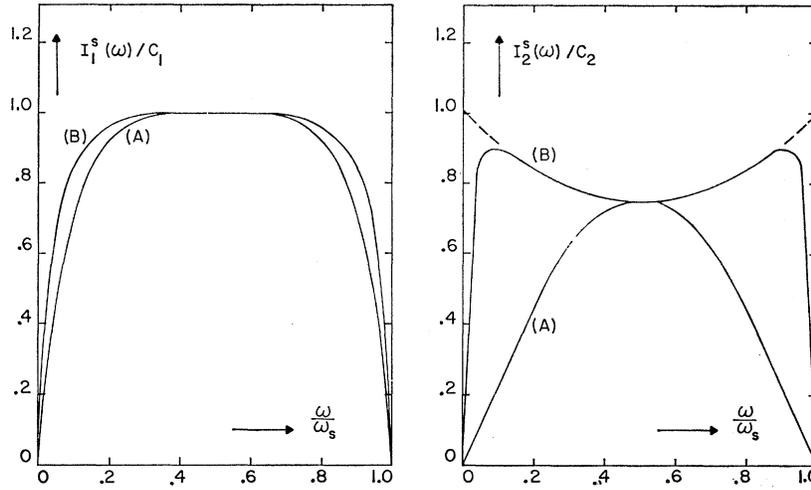
FIG. 4. The integrals $I_1{}^s(\omega)$ and $I_2{}^s(\omega)$, both suitably normalized. A, $(\alpha/\beta)=0.1$; B, $(\alpha/\beta)=0.01$.
$[C_1=(-1+(1+4\alpha/\beta)$
$\qquad\times\ln(1+4\alpha/\beta/4\alpha/\beta))/8\alpha^2$;
$\qquad\qquad\qquad\qquad C_2=\pi/8\alpha^2.]$

that the integration interval is maximal and the integrand does not depend on ω. $I_2{}^s(\omega)$, on the other hand, can have a slight minimum at $\tfrac{1}{2}\omega_s$.

To illustrate the properties somewhat more in detail we make the approximation,

$$r_1{}^2r_2{}^2[(r_1+r_2)^2-4\beta^2]$$

$$=4\beta^2\alpha^2(\beta^2-q^2+4\alpha\beta) \quad \text{for} \quad \beta^2-q^2\geq 0, \quad (90a)$$

$$=4(q^2-\beta^2)^3+16\alpha^3\beta^3 \quad \text{for} \quad \beta^2-q^2\leq 0, \quad (90b)$$

which follows from (33) by assuming $\beta\gg\alpha$; this is physically quite reasonable. Remembering now that $\varphi_s(r)$ [Eq. (29)] was chosen as a characteristic radial vibration of a homogeneous elastic sphere modified by an exponential decreasing factor we may as well take over another relation from elasticity; namely, in the problem of the vibrating sphere the constant β is connected with the frequency ω_s by[29]

$$\beta=\omega_s/v. \quad (91)$$

This means that the upper limit of the integrals (88a, b) is just β, and, using (90a) they are easily evaluated:

$$I_1{}^s(\omega)=\frac{1}{8\alpha^2\beta^2}\left[-4kk'+\beta^2\left(1+\frac{4\alpha}{\beta}\right)\ln\frac{kk'+\alpha\beta}{\alpha\beta}\right] \quad (92a)$$

$$I_2{}^s(\omega)=\frac{\pi}{8\alpha^2\beta^2}\left\{-kk'+\frac{\beta^2+4\alpha\beta}{kk'}\right.$$

$$\left.\times\left[kk'+2\alpha\beta\left(1-\left(1+\frac{kk'}{\alpha\beta}\right)^{1/2}\right)\right]\right\}. \quad (92b)$$

The result is shown in Fig. 4.

Looking at the functional behavior of both $f_2{}^s(\omega,T)$ and $I_2{}^s(\omega)$ it is evident that the relaxation time $\tau_2(\omega,T)$ has a much smaller resonance structure than $\tau_1(\omega,T)$; it does not make any considerable contribution to the physical effect we are interested in, and we are allowed

to neglect it. Then we are left with the expression (82a).

Further on we consider the fact that the quasi-localized modes inside the acoustic band lie in the vicinity of a mean frequency, and there is no harm in replacing ω_s by this frequency; whence, we may substitute the summation over s by G_s, where G_s is the number of quasilocalized modes inside the band, or $G_s=1$ for the true localized mode outside the regular spectrum. Thus, we are left with the final result

$$(\tau_{kk}{}^s(\omega,T))^{-1}=Ef(\omega,T)g(\omega), \quad (93)$$

where

$$E=\tfrac{9}{16}\pi^2\mu_s\gamma^2\frac{\hbar\tau_0\alpha}{M\omega_s v}G_s, \quad (94)$$

$$g(\omega)=\left(1+4\frac{\omega_\alpha}{\omega_s}\right)\ln\left\{\left[\frac{\omega}{\omega_s}\left(1-\frac{\omega}{\omega_s}\right)+\frac{\omega_\alpha}{\omega_s}\right]\bigg/\frac{\omega_\alpha}{\omega_s}\right\}$$

$$-4\frac{\omega}{\omega_s}\left(1-\frac{\omega}{\omega_s}\right), \quad (\omega_\alpha=\alpha v), \quad (95)$$

and $f(\omega,T)$ is given by the expression (83a). This result was used by Walker and Pohl for discussing the experimental data.

IX. SUMMARY AND DISCUSSION

We can summarize the results of the present investigation as follows:

(1) Interpretation of the measured thermal conductivity in KCl crystals containing atomic or molecular impurities definitely requires an additional relaxation time of nonmonotonic (resonance) character. It is likely that this is due in many cases to the inelastic scattering of phonons interacting harmonically or anharmonically with localized modes. The latter make no contribution to the heat current.

(2) The second-order process $(\mathbf{k}\lambda)\rightleftarrows(\sigma)$ can only

occur in the case of polyatomic impurity centers, where there is a molecular frequency (internal mode) within the phonon spectrum. The relaxation time for this scattering process does not depend on temperature and has a resonance behavior, in accord with the experimental results of Pohl.[1] It has a factor which is given by the scalar product of the eigenvectors of the lattice modes (phonons) and the molecular modes and cannot be determined without investigating the latter in detail; this is a task for future study.

(3) For monatomic-impurity centers which are not extremely strong mass or strain defects the third-order processes are dominant. The computed relaxation time differs radically from monotonic behavior for the process $(k\lambda)+(k'\lambda') \rightleftarrows (s)$ and is given by Eq. (93). Its temperature-dependent factor is given at low temperatures by

$$f(\omega,T) = (\omega_s-\omega)^2 \exp[-\hbar(\omega_s-\omega)/kT]$$

with its maximum value proportional to T^2 at $(\omega_s-\omega_{max}) = 2kT/\hbar$, and at high temperatures by

$$f(\omega,T) = (kT/\hbar\omega_s)\omega(\omega_s-\omega)$$

with its maximum proportional to T at $\omega_{max}=\frac{1}{2}\omega_s$. The temperature-independent factor $g(\omega)$ has a broad maximum at $\omega=\frac{1}{2}\omega_s$ and is symmetric about this point. The functional form of the expression (93) has been tested by Walker and Pohl in the preceding paper[2] and found to be in very good agreement with the experimental result.

To assign a second-order scattering process to the effect in the system $KCl:KNO_2$ and a third-order process to the effect in the monatomic systems $KCl: NaCl$, etc., could have been guessed without introducing a specific model, because the indentation in the curves of Pohl[1] (Fig. 1) for the former lies below the maximum in a region where other second-order processes become predominant (e.g., the elastic scattering by the strain-field and the mass-difference of point defects[6,14,15]). The indentation in the curves of Walker and Pohl,[2] for the latter, on the other hand, lies above the maximum where normal and umklapp processes have their greatest importance.

There is no contradiction in our consideration of second-order interaction for lattice waves and molecular modes and of the third-order interaction between phonons and the true localized modes outside the bands. But there is some question in taking the form (16) or even (29) for the quasilocalized modes within the band, and defining a fixed number G_s of them.

Inside the band all the modes consist of both a travelling and a localized part. Usually the latter is negligible and one has phonon solutions; but in certain regions of the spectrum the localized part is predominant.[16] To define a fixed number G_s of localized modes, it is necessary to invoke physical plausibility; we could take the expression (5a) by Peierls for the heat current, with unchanged (ideal) group velocities then we would have to reduce the density of phonon solutions in the vicinity of ω_s down to zero for $\omega=\omega_s$ itself. The total number of plane-wave solutions thus removed is just the number G_s of localized modes which have been put in instead. This definition allows us to neglect the travelling part of the G_s quasilocalized solutions around ω_s, and one is left with eigenvectors of the general form (16). Specifically, in the case of third-order interactions one may well use the single eigenvector for the mode with $\omega=\omega_s$, which has (practically) no travelling part at all; this is justified by the fact that the maximum interaction takes place with phonons with $\omega\simeq\frac{1}{2}\omega_s$, which is far from the ω_s of quasilocalized solutions.

As to the special choice (29) for the localized eigenvectors in the band, there is no other justification but physical plausibility. Future calculation may reveal a different formula for η_s; that would change $g(\omega)$ somewhat, although very slightly. Yet, the more important factor $f^s(\omega,T)$ [Eq. (83a)] does not depend at all on the form of the localized mode.

ACKNOWLEDGMENTS