

Scattering of Long-Wavelength Phonons by Point Imperfections in Crystals*

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At very low temperatures the thermal conductivity of insulating crystals containing point defects is limited by boundary relaxation processes and by Rayleigh scattering of long-wavelength phonons: at higher temperatures resonant modifications of Rayleigh scattering and phonon-phonon scattering dominate. Experiments by Baumann and Pohl on the thermal conductivity of alkali-halide crystals containing monovalent impurities indicate that the inverse relaxation time computed from experiment for Rayleigh scattering is in some situations very much less than that calculated on the assumption that the defects are isotopic impurities, a result contrary to an analysis by Klemens. Since the scattering of phonons in a one-dimensional chain may be discussed without approximation, we have solved that problem and find that mass and spring changes round the imperfection may give compensating contributions to the scattering amplitude; the scattering power of the center may thereby be reduced to below the value calculated on the basis of pure isotope scattering. A generalization of these ideas not dependent on Born approximation is presented using formal scattering theory adapted to handle this case.

I. INTRODUCTION

POINT defects in insulating crystals scatter phonons and decrease the thermal conductivity. Pomeranchuk¹ and Klemens² discuss the scattering of low-frequency phonons, predicting a Rayleigh scattering law for phonons of frequency ω with cross section proportional to ω^4 . Experimental verification of such a mechanism has been obtained by studying isotopic scattering in Ge³ and LiF.^{4,5} Studies of the thermal conductivity as a function of temperature of alkali halides containing monatomic impurities by Walker and Pohl⁶ and Baumann⁷ reveal pronounced "dips" in the curves inexplicable in terms of the Klemens theory.

Takeno,⁸ Elliot and Taylor,⁹ Krumhansl,¹⁰ McCombie and Slater,¹¹ Klein,¹² and Thoma and Ludwig,¹³ explain the "dips" in terms of resonance-scattering processes, but at low temperatures when only long-wavelength phonons are present all these theories reduce to the Rayleigh law.

The experiments of Pohl⁶ and Baumann⁷ indicate that for some impurities the Rayleigh-scattering cross section is very much less than that calculated on the assumption that the foreign ion is an isotopic impurity.

The system KCl containing AgCl is particularly remarkable because it shows virtually no Rayleigh scattering at low temperatures, though distinct resonant-scattering "dips" appear at high temperatures as is shown in Fig. 1. Such results are contrary to the discussion of Klemens² who in computing the scattering adds the squares of matrix elements for mass-defect scattering and scattering through modified force constants; thus the cross section for isotope scattering alone is, in that approximation, a lower limit for the scattering cross section.

It is therefore of interest to examine the scattering of long-wavelength phonons for a model which may be solved exactly, but which contains the basic ingredients of the experimental situation. In this paper we discuss the scattering of phonons in a one-dimensional chain by a defect characterized by both mass and spring changes. The problem is solved both by a one-dimensional phase-shift analysis and by formal scattering theory; the results give some insight into the experimentally observed Rayleigh-scattering cross sections and clarify the range of validity of common approximations in phonon-scattering theory. This special application of the scattering properties of the one-dimensional chain extends the previous results of Ludwig.¹⁴

II. PHASE-SHIFT ANALYSIS

Consider an infinite array of equidistant mass points having the same distance a between their equilibrium positions; let the particles be numbered

$$\dots, -l, -(l-1), \dots, -1, 0, 1, \dots, (l-1), l, \dots$$

Let each particle have mass M with the exception of the particle 0 which has mass $M + \Delta M$. The displacements of the particles from their equilibrium positions will be denoted by

$$\dots, x_{-l}, x_{-l+1}, \dots, x_{-1}, x_0, x_1, \dots, x_l, x_{l+1}, \dots$$

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¹⁰ J. A. Krumhansl, *Proceedings of the International Conference on Lattice Dynamics, Copenhagen* (Pergamon Press, Inc., New York, 1964), p. 523.

¹¹ C. W. McCombie and J. Slater, *Proc. Phys. Soc. (London)* **84**, 499 (1964).

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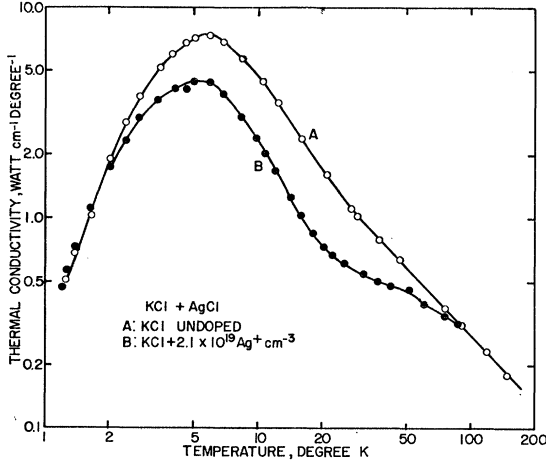


FIG. 1. Graph of log of the thermal conductivity against the log of T . A: Pure KCl. B: $\text{KCl} + 2.1 \times 10^{19} \text{ Ag}^+ \text{ cm}^{-3}$. In curve B note there is no depression of the thermal conductivity below 2°K , while the depression above 2°K is not characterized by a Rayleigh-scattering law. Experimental data by Baumann and Pohl (unpublished).

Let the harmonic force constant of the springs between the particles in the unperturbed portions of the chain be λ and the force constant in the two links adjacent to particle 0 be $\lambda + \Delta\lambda$. The model is illustrated in Fig. 2.

A wave of wave vector q is incident from the left; the solutions in various regions of the chain are:

$$\begin{aligned} x_l &= A e^{-iqla} + B e^{iqla}, & l \leq -1 \\ x_l &= C e^{-iqla} + D e^{iqla}, & -1 \leq l \leq 0 \\ x_l &= E e^{-iqla} + F e^{iqla}, & 0 \leq l \leq 1 \\ x_l &= G e^{-iqla}, & l \geq 1. \end{aligned} \quad (1)$$

Here the wave $A e^{-iqla}$ represents the incident wave, while $B e^{iqla}$ and $G e^{-iqla}$ constitute the reflected and transmitted waves, respectively.

The asymptotic waves satisfy the dispersion condition

$$\omega^2 = \omega_{\max}^2 \sin^2(qa/2), \quad (2)$$

where

$$\omega_{\max}^2 = 4\lambda/M.$$

The required continuity of solutions (1) imply the conditions:

$$A e^{iqa} + B e^{-iqa} = C e^{iqa} + D e^{-iqa}, \quad (3)$$

$$C + D = E + F, \quad (4)$$

$$E e^{-iqa} + F e^{iqa} = G e^{-iqa}. \quad (5)$$

Further, the solutions (1) must satisfy the equations of motion:

(a) For particle -1 ,

$$\begin{aligned} -M\omega^2[A e^{iqa} + B e^{-iqa}] \\ = -\lambda[A e^{iqa} + B e^{-iqa} - A e^{2iqa} - B e^{-2iqa}] \\ - (\lambda + \Delta\lambda)[A e^{iqa} + B e^{-iqa} - C - D]; \end{aligned} \quad (6)$$

(b) For particle 0,

$$\begin{aligned} -(M + \Delta M)\omega^2[C + D] \\ = -(\lambda + \Delta\lambda)[C + D - C e^{iqa} - D e^{-iqa}] \\ - (\lambda + \Delta\lambda)[C + D - E e^{-iqa} - F e^{iqa}]; \end{aligned} \quad (7)$$

(c) For particle 1,

$$\begin{aligned} -M\omega^2 G e^{-iqa} = -\lambda[G e^{-iqa} - G e^{-2iqa}] \\ - (\lambda + \Delta\lambda)[G e^{-iqa} - C - D]. \end{aligned} \quad (8)$$

The six equations (3)–(8) contain seven unknowns and may be solved to find the amplitude-reflection coefficient B/A , and hence the energy-reflection coefficient $R = |B/A|^2$. In the limit of long-wavelength modes, i.e., q small, we find

$$\frac{B}{A} = -i \left(\beta + \frac{2\gamma}{1 + \gamma} \right) \left(\frac{\omega}{\omega_{\max}} \right), \quad (9)$$

where

$$\beta = (\Delta M/M) \quad \text{and} \quad \gamma = (\Delta\lambda/\lambda),$$

and therefore

$$R(\beta, \gamma) = \left| \frac{B}{A} \right|^2 = \left(\beta + \frac{2\gamma}{1 + \gamma} \right)^2 \left(\frac{\omega}{\omega_{\max}} \right)^2. \quad (10)$$

For the case of pure isotope scattering, i.e., $\gamma = 0$, this result agrees with that obtained by Maradudin¹⁵ using Green's function techniques and Ludwig,¹⁴ if their solutions are also examined in the long-wavelength limit.

III. APPLICATION OF FORMAL SCATTERING THEORY

We now discuss the same problem within the framework of formal scattering theory and attempt to generalize the ideas inherent in this model. The purpose of carrying out this alternative method of solution is to exhibit features which may be generalized to three dimensions, in principle. We follow the methods due originally to Lifshitz¹⁶ and applied by Krumhansl¹⁰ and others, which describe the phonon scattering in terms familiar in quantum-mechanical scattering problems. Use the convention:

$|\varphi\rangle \equiv$ vector displacement field on lattice sites (a column or row matrix),

$A \equiv$ matrix operator, e.g., potential-energy matrix.

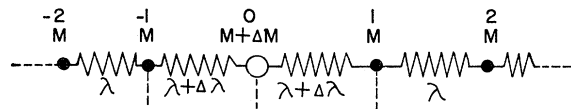


FIG. 2. One-dimensional model.

¹⁵ A. A. Maradudin, in *Phonons and Phonon Interactions*, edited by T. A. Bak (W. A. Benjamin and Company, Inc., New York, 1964), p. 462.

¹⁶ I. M. Lifshitz, *Nuovo Cimento Suppl.* 3, 716 (1956).

For a perfect lattice unperturbed by a defect we have the free-field solution $|\varphi_0\rangle$ given by

$$(L-\omega^2)|\varphi_0\rangle=0, \quad (11)$$

where L is the mass-reduced potential-energy matrix for the unperturbed lattice.

When the lattice is perturbed by the presence of a point defect, we obtain a perturbed field $|\varphi\rangle$ characterized by

$$(L-\omega^2)|\varphi\rangle=-P|\varphi\rangle, \quad (12)$$

where P is the perturbation-energy matrix for the defect.

The solution of Eq. (12) takes the form of a complementary function, which is just the free-field solution given in Eq. (11), and a particular integral:

$$|\varphi\rangle=|\varphi_0\rangle+(L-\omega^2)^{-1}(-P)|\varphi\rangle, \quad (13)$$

where $(L-\omega^2)^{-1}\equiv G_0$ is the mass-reduced Green's-function operator for the perfect lattice.

In the scattering problem $|\varphi_0\rangle$ is given by

$$|\varphi_0\rangle\equiv|\varphi_{\text{inc}}\rangle=e_{\mathbf{q}}^{\nu}\exp[i(\omega t-\mathbf{q}\cdot\mathbf{r}(l/k))], \quad (14)$$

where \mathbf{q} is the wave vector of the incident wave, the $\mathbf{r}(l/k)$ define the lattice points, $e_{\mathbf{q}}^{\nu}$ gives the polarization of the ν th mode of wave vector \mathbf{q} , and ω satisfies a dispersion relation $\omega^2=\omega_{\mathbf{q}}^2$.

The scattered solution $|\varphi^+\rangle$ consists of outgoing waves superposed on the incident waves, G_0^+ being the Green's function for outgoing solutions. In practice the problem is simplified by the perturbation P being non-zero for only a small subspace $|\theta\rangle$ of the total space. Thus

$$|\theta^+\rangle=|\theta_{\text{inc}}\rangle+g_0^+(-P)|\theta^+\rangle, \quad (15)$$

where g_0^+ is the operator G_0^+ defined in subspace $|\theta\rangle$. Hence

$$|\theta^+\rangle=(1+g_0^+P)^{-1}|\theta_{\text{inc}}\rangle. \quad (16)$$

From the viewpoint of the scattering problem we are interested in the asymptotic form of the scattered field which is given by $|\varphi^+_{\text{scatt}}\rangle$

$$|\varphi^+_{\text{scatt}}\rangle=|\varphi^+\rangle-|\varphi_0\rangle=G_0^+(\infty)(-P)|\theta^+\rangle, \quad (17)$$

where $G_0^+(\infty)$ is the asymptotic form of the perfect-lattice Green's function.

Specializing to the one-dimensional model discussed in II, $G_0^+(\infty)$ takes the form

$$G_0^+(\infty)\equiv G_0^+(l,l')=\frac{e^{-i\mathbf{q}|l'-l|a}}{i\omega\omega_{\text{max}}[1-(\omega/\omega_{\text{max}})^2]^{1/2}}, \quad (18)$$

where the l' are the sites of the defect perturbation and l is a site remote from the defect. For the reflected wave $l\ll l'$,

$$G_0^+(\infty)=\frac{|e^{i\mathbf{q}la}|(e^{-i\mathbf{q}l'a})|}{i\omega\omega_{\text{max}}[1-(\omega/\omega_{\text{max}})^2]^{1/2}} \quad (19)$$

which defines the scattered solution $|\varphi^+_{\text{REF}}\rangle$:

$$|\varphi^+_{\text{REF}}\rangle=\frac{|e^{i\mathbf{q}la}|}{i\omega\omega_{\text{max}}[1-(\omega/\omega_{\text{max}})^2]^{1/2}}T_{\mathbf{q},-\mathbf{q}}, \quad (20)$$

where $T_{\mathbf{q},-\mathbf{q}}$ is the transition-matrix element defined by

$$T_{\mathbf{q},-\mathbf{q}}=-(e^{-i\mathbf{q}a'l'}|P(1+g_0^+P)^{-1}|e^{-i\mathbf{q}a'l''}) \quad (21)$$

and the energy-reflection coefficient R is

$$R=[1/\omega^2\omega_{\text{max}}^2[1-(\omega/\omega_{\text{max}})^2]]|T_{\mathbf{q},-\mathbf{q}}|^2. \quad (22)$$

For the model considered here the operator $P(1+g_0^+P)^{-1}$ spans only the subspace x_0, x_1, x_{-1} , i.e., it is an operator in a three-dimensional subspace; here P is given by

$$P=\begin{bmatrix} 2\alpha-\beta\omega^2 & -\alpha & -\alpha \\ -\alpha & \alpha & 0 \\ -\alpha & 0 & \alpha \end{bmatrix}, \quad (23)$$

where $\alpha=\Delta\lambda/M$ and $\beta=\Delta M/M$ while g_0^+ is given by

$$g_0^+=f(\omega)\begin{bmatrix} 1 & e^{i\theta} & e^{i\theta} \\ e^{i\theta} & 1 & e^{i\theta} \\ e^{i\theta} & e^{i\theta} & 1 \end{bmatrix}, \quad (24)$$

where

$$f(\omega)=1/i\omega\omega_{\text{max}}[1-(\omega/\omega_{\text{max}})^2]^{1/2}$$

and $\theta=-qa$.

We use the symmetry property of the defect under inversion to factorize the operators into a direct sum of a two-dimensional matrix operator and a one-dimensional operator by applying a similarity transformation which transforms the basis displacements into symmetry-adapted basis displacements

$$x_{u1}=x_0, \quad x_{u2}=\frac{1}{2}(x_1+x_{-1}) \quad \text{and} \quad x_{\sigma}=\frac{1}{2}(x_1-x_{-1}).$$

In the new basis system we find

$$P'=\begin{bmatrix} 2\alpha-\beta\omega^2 & -\sqrt{2}\alpha & 0 \\ -\sqrt{2}\alpha & \alpha & 0 \\ 0 & 0 & \alpha \end{bmatrix}\equiv\begin{bmatrix} P_u & 0 \\ 0 & P_{\sigma} \end{bmatrix} \quad (25)$$

and

$$(g_0^+)=f(\omega)\begin{bmatrix} 1 & \sqrt{2}e^{i\theta} & 0 \\ \sqrt{2}e^{i\theta} & (1+e^{2i\theta}) & 0 \\ 0 & 0 & (1-e^{2i\theta}) \end{bmatrix} \\ \equiv\begin{bmatrix} (g_0^+)_u & 0 \\ 0 & (g_0^+)_\sigma \end{bmatrix}. \quad (26)$$

The transition matrix $T_{\mathbf{q},-\mathbf{q}}$ is now the sum of two terms

$$T_{\mathbf{q},-\mathbf{q}}=T_{\mathbf{q},-\mathbf{q}}^u+T_{\mathbf{q},-\mathbf{q}}^{\sigma}, \quad (27)$$

where $T_{\mathbf{q},-\mathbf{q}}^u$ and $T_{\mathbf{q},-\mathbf{q}}^{\sigma}$ are evaluated from the two-dimensional operator and one-dimensional matrix operators, respectively.

Now $T_{q,-q}^g$ is easily given by

$$T_{q,-q}^g = -\left[\frac{1}{2}(e^{-i\theta} - e^{+i\theta}) \right. \\ \left. \times \left| \frac{\alpha}{1 + \alpha f(\omega)(1 - e^{2i\theta})} \right| \frac{1}{2}(e^{-i\theta} - e^{+i\theta}) \right] \quad (28)$$

which, in the limit of long wavelength, i.e., the limit of small ω and θ yields

$$T_{q,-q}^g = [2\gamma/(1+\gamma)]\omega^2, \quad (29)$$

where as before

$$\gamma = \Delta\lambda/\lambda.$$

The quantity $T_{q,-q}^u$ is somewhat more complicated but yields

$$T_{q,-q}^u = \beta\omega^2, \quad (30)$$

i.e., in the long-wavelength limit $T_{q,-q}^u$ is independent of spring changes.

Thus the reflected amplitude is in the long-wavelength limit

$$|\varphi_{\text{REF}}^+| = -i \left(\beta + \frac{2\gamma}{1+\gamma} \right) \left(\frac{\omega}{\omega_{\text{max}}} \right) |e^{iq\ell a}|, \quad (31)$$

and the energy-reflection coefficient by

$$R(\beta, \gamma) = \left(\beta + \frac{2\gamma}{1+\gamma} \right)^2 \left(\frac{\omega}{\omega_{\text{max}}} \right)^2 \quad (32)$$

in agreement with the previous solution. The forward "scattered" wave amplitude $|\varphi_{\text{FORWARD}}^+|$ may similarly be shown to be

$$|\varphi_{\text{FORWARD}}^+| = -i \left(\beta - \frac{2\gamma}{1+\gamma} \right) \left(\frac{\omega}{\omega_{\text{max}}} \right) |e^{-iq\ell a}| \quad (33)$$

while the total forward amplitude is

$$\left[1 - i \left(\beta - \frac{2\gamma}{1+\gamma} \right) \frac{\omega}{\omega_{\text{max}}} \right] |e^{-iq\ell a}|. \quad (34)$$

IV. DISCUSSION

The reflection of long-wavelength waves in a one-dimensional chain is characterized by an energy-reflection coefficient proportional to ω^2 : the reflection is therefore Rayleigh-like, the frequency dependence being an inherent property of a one-dimensional model. The mass and spring changes may make reinforcing or cancelling contributions to the scattering amplitude as may be seen from Eqs. (9) and (31). In particular, if ΔM and $\Delta\lambda$ have opposite signs cancellation between the two terms in the expression $(\beta + 2\gamma/(1+\gamma))$ tends to occur, and the reflection coefficient may be much less than for the case of pure isotopic substitution. In Fig. 2 a graph is drawn of $[R(\beta, \gamma)/R(\beta, 0)]$ against γ for the

particular case $\beta=2$ (dark line): that is, we examine the scattering power of the center relative to the scattering power of the corresponding isotopic defect as a function of the spring-change parameter. For positive values of γ the contributions to the scattering amplitude from mass and spring changes are additive and the scattering power of the center is enhanced over that for the pure isotope, but for a range of negative values of γ the scattering power of the center is very much less than for the isotopic defect with a null scattering condition at $\gamma=-0.5$. As $\gamma \rightarrow -1$ the scattering due to the spring changes dominates over the isotopic effect, and once more the scattering power of the center may assume a value greater than for the isotopic defect. It must be emphasized that this cancellation condition holds only in the long-wavelength limit and, other than at very low temperatures where only long-wavelength phonons are present, such considerations would not cause a suppression of the scattering power of the center. A particular example may be the case Ag^+ in KCl for which $\beta \approx 2$; further, the magnitude of the $\text{Ag}^+\text{-Cl}^-$ nearest-neighbor interaction calculated, for example, by Fukai¹⁷ suggests that the nearest-neighbor dynamical coupling is significantly less than the corresponding $\text{K}^+\text{-Cl}^-$ interaction, in qualitative agreement with the results presented here. Experiments by Sievers¹⁸ on the infrared absorption of $\text{KCl}:\text{Ag}^+$ further suggest the $\text{Ag}^+\text{-Cl}^-$ interaction is dynamically soft.

The results of the phase-shift method and the scattering treatments above are identical, but it is of interest to examine how these arise. In the former case it is essential to superimpose the classical scattering amplitudes from both mass and spring changes before squaring the total scattering amplitude to give the energy-reflection coefficient. In the other case it is analogously necessary to add all the matrix-element components of the transition-matrix element $T_{q,-q}$ before squaring to give the reflection coefficient. This has not been done in the Klemens approximation.

Even in the long-wavelength limit there are differences between the exact solution presented here and the first Born approximation commonly used in such situations. The first-order Born approximation gives for the matrix element $T_{q,-q}$ of Eq. (21)

$$T_{q,-q} = -(e^{-iq\ell a} |P| e^{-iq\ell a'}), \quad (35)$$

which may be easily shown to give

$$R(\beta, \gamma) = (\beta + 2\gamma)^2 (\omega/\omega_{\text{max}})^2, \quad (36)$$

a result which agrees with that derived by Ludwig.¹⁴ For the case of mass scattering the first Born approximation and true solution are in exact agreement, i.e., in the long-wavelength limit the operators P and $P(1+g_0^+P)^{-1}$ are equivalent. However, the scattering

¹⁷ Y. Fukai, J. Phys. Soc. Japan **18**, 1413 (1963).

¹⁸ A. J. Sievers, Phys. Rev. Letters **13**, 310 (1964).

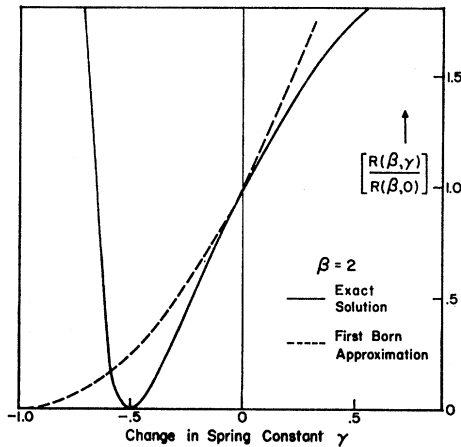


FIG. 3. Graph of $R(\beta,\gamma)/R(\beta,0)$ against γ for the case $\beta=2$.

arising from spring changes is not given exactly from first-order Born approximation and to have the true solution one must "substitute" $2\gamma(1+\gamma)^{-1}$ for 2γ . The deviation from the first Born approximation is very great for negative values of γ , as may be seen from comparing the exact solution (dark line) and the first-Born-approximation solution (dotted line) in Fig. 3. The exact solution corresponds to the solution obtained by summing an infinite number of terms in the Born expansion.

Equations (31) and (33) show that when both mass and spring changes are involved the forward and backward scattering amplitudes are unequal. Two aspects of this are worthy of comment. First, the sum of the square moduli of (31) and the total forward amplitude (34) should be unity. If, in fact, this is computed from these expressions, it will be found necessary to carry an additional real term to order ω^2 in (34) to be over-all consistent to that order; but no fundamental physical difficulty arises here. A second aspect of the use of (31) and (33) refers to the computation of "relaxation times" as frequently done for phonon scattering in the Boltzmann equation. If a "total cross section" is calculated as the sum of the square moduli of (31) and (33) (the one-dimensional analog of integrating over all scattering angles in the three-dimensional case), it is apparent that this is not the physically relevant quantity; no destructive interference between mass scattering and force-constant scattering can occur. There is no inconsistency, however, for in a one-dimensional system it is only the reflection amplitude which determines the energy transport properties, while in a three-dimensional system the effective cross section appropriate for the calculation of thermal resistance involves a weighted sum of the cross sections for scattering in various directions. The weighting factors reflect the effectiveness of the scattering process in destroying momentum, and are important if the scattering amplitudes are anisotropic. Such factors rarely

appear in detailed thermal conductivity calculations, but Klemens¹⁹ notes their significance.

The problem of scattering of long-wavelength phonons in a three-dimensional lattice may be approached by the same formal scattering technique as that used here. The cross section $T_{\mathbf{q},\mathbf{q}',\nu,\nu'}$ for scattering of a phonon of wave vector \mathbf{q} to \mathbf{q}' is of the form¹⁰

$$\sigma_{\mathbf{q},\mathbf{q}',\nu,\nu'} \propto |T_{\mathbf{q},\mathbf{q}',\nu,\nu'}|^2,$$

where

$$T_{\mathbf{q},\mathbf{q}',\nu,\nu'} = \left[e_{\mathbf{q}'\mu\nu'} \exp \left[-i\mathbf{q}'\mu \cdot \mathbf{r} \left(\frac{l'}{k'} \right) \right] \right. \\ \left. \times |P(1+g_0^+P)^{-1}| e_{\mathbf{q}\nu} \exp \left[-i\mathbf{q} \cdot \mathbf{r} \left(\frac{l}{k} \right) \right] \right] \quad (37)$$

and $\mathbf{q}'\mu$ is defined by analogy with Ref. 10.

For the case of a point defect in an alkali halide of the NaCl structure in which the interaction with the nearest neighbors is modified, the defect matrix P is a 21×21 . The point symmetry of the center may be exploited to express $T_{\mathbf{q},\mathbf{q}',\nu,\nu'}$ as in Eq. (27) as a sum of terms characterizing the various irreducible representations of the O_h point group. In the long-wavelength limit away from resonance no single one of these terms dominate and destructive or constructive interference in contributions to the scattering amplitude is possible as before.

The effective integrated scattering cross section may then be obtained from a weighted sum over polarizations and wave vectors. If the mass and force constant change conditions are such as to greatly reduce the cross sections for the large-angle scattering processes which mainly contribute to thermal resistivity the Rayleigh scattering cross sections may be very much less than those calculated on the assumption of pure isotope scattering. Generally, $T_{\mathbf{q},\mathbf{q}',\nu,\nu'}$ should also include a contribution from the strain field set up around the defect, as another possible source of interference effects in the scattering amplitude, but no detailed discussion will be presented here.

Because we have dealt explicitly with the classical field (though applying the methodology of quantum scattering theory) it may be thought that we would have to examine the problem for particular quantum features. Actually no new features appear; for, if one uses a second-quantized representation of the phonon field, the appropriate field operators obey just the classical equations considered. Interpretation of the intensity of the classical phonon field as the local number density in the quantum case connects classical and quantum descriptions for the phonons.

V. CONCLUSION

In summary, we repeat that it is essential to superimpose different matrix-element contributions to the

¹⁹ P. G. Klemens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 29.

scattering amplitude before squaring to compute a scattering cross section, an obvious point theoretically but one which has not usually been considered in detailed calculations. Further, we have shown how even in the long-wavelength limit the first Born approximation may be significantly in error. These two factors are of general importance in determining Rayleigh-scattering cross sections.

Note Added in Proof. A recent paper by M. Yussouff and J. Mahanty [Proc. Phys. Soc. (London) **85**, 1223 (1965)] discusses impurity scattering in the long-wavelength limit for a three dimensional model with equal nearest-neighbor central and noncentral forces. Their relaxation time is obtained from an unweighted total scattering cross section by application of the optical

theorem and therefore contains no interference terms between scattering amplitudes corresponding to different irreducible representations of the point group of the impurity. We contend that a more detailed treatment of thermal conductivity with their model, in which the various scattering cross sections are consistently weighted according to their efficiency in destroying quasimomentum, will reveal results similar to those presented here.

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Relativistic Effects on the Electronic Band Structure of Compound Semiconductors*†

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The effects of the three relativistic interaction terms, mass-velocity, Darwin, and spin-orbit coupling, on the electronic levels of covalent-bond compound semiconductors BN, SiC, AlP, and GaAs have been investigated. Quantitative relativistic shifts and spin-orbit splittings of the appropriate Bloch states at Γ , X , and L points in the Brillouin zone have been obtained using orthogonalized-plane-wave crystal wave functions. Comparisons between available experimental data and calculations of the spin-orbit splittings of GaAs show a maximum discrepancy of 11%. The inclusion of the relativistic shifts of the energy levels did not change very significantly the band structure obtained by the nonrelativistic calculations. These effects increase, however, as the atomic numbers of the constituent atoms increase.

I. INTRODUCTION

WHEN correlation effects are neglected, the system of electrons in a solid can be described by a one-electron equation, which is the well-known Hartree-Fock equation. However, no corresponding equation has been derived for the relativistic electrons. Thus we have to rely on the Dirac equation for an electron interacting with a crystal potential. After applying successive canonical transformations of the Foldy-Wouthuysen¹ type to the Dirac equation, the positive and the negative energy states can be decoupled to successively higher orders of α , where α is the fine-structure constant. To the order of α^2 , there appear in the transformed Hamiltonian three extra terms in addition to the usual nonrelativistic kinetic energy and the crystal poten-

tial V :

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) - \frac{1}{2mc^2} \frac{\mathbf{p}^4}{4m^2} + \frac{\hbar^2}{8m^2c^2} \nabla^2 V(\mathbf{r}) + \frac{\hbar}{4m^2c^2} \boldsymbol{\sigma} \cdot (\nabla V(\mathbf{r}) \times \mathbf{p}). \quad (\text{I.1})$$

The first two terms in the above Hamiltonian give the nonrelativistic Hamiltonian and the last three terms are the mass-velocity term, the Darwin term, and the spin-orbit interaction term. The first of these acquired its name because it could be obtained by simply substituting into the nonrelativistic Hamiltonian the relativistic expression for the electron mass and then making a power-series expansion in terms of (v/c) . The second term was named after Darwin² who first introduced it; it may be attributed to the interaction of the electron, whose coordinates fluctuate over distances comparable to a Compton wavelength with a somewhat smeared-out Coulomb potential. The last term de-

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¹ L. L. Foldy and S. A. Wouthuysen, Phys. Rev. **78**, 29 (1950).

² C. G. Darwin, Proc. Roy. Soc. (London) **A118**, 654 (1928).