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Effects of Scattering-Induced Dispersion on Phonons: Thermal Conductivity[*]

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It is well known that scattering leads to dispersion. The two constitute, respectively, the imaginary and the real parts of the index of refraction, which are connected by Kramers–Kronig relations. The effects of scattering-induced dispersion on the thermal conductivity have been ignored heretofore. It is shown that for strongly interacting and/or highly concentrated systems the additional dispersion will make a significant difference to the calculated thermal conductivity. The conductivity including dispersion has been calculated and compared with experimental results for solid ^{3}He-^{4}He mixtures, and for the KCl:CN$^-$ system. In order to conform to the dispersion relations for the latter, it was necessary to use a model for which the scattering cross section varied as the phonon frequency to the fourth power, in the low-frequency limit. For a multilevel system the scattering cross section must depend on the occupation of the levels. This leads to a temperature dependence of the cross section. Expressions for the cross section appropriate to multilevel systems were derived, and employed in calculating the thermal conductivity of KCl:CN$^-$. These expressions are similar to those obtained by numerous investigators for spin systems.

INTRODUCTION

In treating the interaction between long-wavelength phonons and defects, attention has been focussed entirely (except for paramagnetic ions) on the effect on the phonon lifetime. Heretofore, most experimental data bearing on these interactions came from thermal-conductivity measurements. The analysis of the data is usually performed using a relaxation time for the phonons to provide the resistance to heat flow in a crystal which is assumed to be an isotropic Debye solid. This, of course, is the simplest model that can be used and, bearing in mind certain uncertainties inherent in the experimental technique, is more than adequate in many cases. We wish to show, however, that one of the assumptions of this model of thermal conductivity, namely, that the velocity of sound is constant, breaks down in certain cases. These changes occur for phonons near the center of the zone, and are a consequence of the scattering. It will be shown that the velocity of sound is, in fact, a function of defect concentration, and that this can significantly affect the conductivity. Furthermore, for resonance scattering, the phonon frequency ω is no longer proportional to the wave vector k near resonance, and this should permit three-phonon processes, which are forbidden otherwise.

Finally, it should be noted that the analysis of thermal-conductivity data is usually based on a solution to a Boltzmann equation, which in turn requires wave packets.[1] Now it is clear that this description will break down close to resonance when a phonon's mean free path approaches its wavelength. However, it develops that the contribution of such a mode to the conductivity is negligible, in fact, phonons begin to be scattered so strongly that they cease to be effective, quite far from resonance. Thus, for the important phonons the wave-packet description is probably valid, and it is expected to break down only for those which do not matter anyway. Therefore, while this is an important and interesting question, the breakdown of the Boltzmann equation will not be considered here, since a conventional thermal-conductivity experiment is incapable of probing close enough to resonance for such effects to be important.

DISPERSION

Propagation of a wave in any medium can be described by $A(e^{i\vec{k}\cdot\vec{x}\,\mathrm{Re}(n)}e^{-\vec{k}\cdot\vec{x}\,\mathrm{Im}(n)}e^{-i\omega t})$, where n is a complex index of refraction. The real part expresses the dispersion and the imaginary part expresses the damping of the wave caused by interaction with the medium. Causality prevents the two from being independent of each other, and the Kramers–Kronig relations express this fact.

When calculating the thermal conductivity, it is necessary to perform an integral over the states of the system. The effect of changing $\mathrm{Re}(n)$ is to change the density of states, hence the conductivity. Another useful way of considering this is to say that the presence of dispersion in the system will change the group velocity, generally making it smaller. If the interaction is large enough and the defect concentration is high, this can have a significant effect on the magnitude of the integral and hence on the calculated conductivity.

Recently, considerable attention has been focused on the interaction of phonons with low-lying resonant modes in crystals, and these have led to quite remarkably strong effects on the thermal conductivity. For these strongly scattering centers, it is also no longer possible to ignore the additional dispersion induced by the scattering.

THERMAL CONDUCTIVITY

The thermal conductivity is given, through the Boltzmann equation and the relaxation-time approximation, assuming all three polarizations give equal contribution, by[1]

$$K=\frac{k_B}{2\pi^2}\int_0^{k_{\max}}\frac{(2\beta\omega)^2e^{2\beta\omega}}{(e^{2\beta\omega}-1)^2}\,\frac{C_k^2}{\sum_i 1/\tau_i(k)}\,d^3k \quad ,$$

where $C_k=\partial\omega/\partial k$ is the group velocity in mode k, $\beta=\hbar/2k_BT$, and $\tau_i(k)$ is the relaxation time due to a process i. Assuming isotropy and changing the variable of integration to ω:

$$K=\frac{k_B}{2\pi^2}\int_0^{\omega_{\max}}\frac{(\beta\omega)^2}{\sinh^2\beta\omega}\,\frac{C_k}{\sum_i 1/\tau_i(k)}\,k^2\,d\omega \quad .$$

Dispersion requires that the integral should really be written

$$K=\frac{k_B}{2\pi^2}\int_0^{\omega_{\max}}\left(\frac{\beta\omega}{\sinh\beta\omega}\right)^2\frac{C_{k'}}{\sum_i 1/\tau_i(k')}\,k'^2(\omega)\,d\omega \quad .$$

The dispersion has been taken into account by associating a new wave vector $k'(\omega)$ with a phonon of frequency ω. Of course it would also be possible to do it by leaving k unchanged and shifting ω. For phonons, the latter is probably more reasonable from a physical point of view since the values of k are established by the crystal lattice.

This analysis still assumes that the crystal lattice has been replaced by an isotropic continuum, but $k'(\omega)$ is no longer necessarily a linear function of ω.

At the low temperatures of interest here, the boundaries are often an important source of thermal resistance. Including this explicitly,

$$\sum_i\frac{1}{\tau_i(k')}=C\left(L^{-1}+\sum_j N_j\sigma_j(k')\right) \quad , \tag{1}$$

where N_j is the number per unit volume of scatterers of type j;

$$K=\frac{k_B}{2\pi^2}\int_0^{\omega_{\max}}\left(\frac{\beta\omega}{\sinh\beta\omega}\right)^2\frac{k'^2(\omega)}{L^{-1}+\sum_j N_j\sigma_j(k')}\,d\omega \quad . \tag{2}$$

Noting the relation $k'=\omega/C_p(k')$, where $C_p(k')$ is the phase velocity, observe that k' for a given ω is increased by the interaction. Thus if boundary scattering dominates, the conductivity is increased. Other scattering mechanisms usually decrease rapidly with temperature, so that at sufficiently low temperatures the conductivity of an impure crystal should be higher than that of a pure one! However, for the case considered here, the change in $\sigma(k')$ dominates and the net result is a decrease.

It will be shown that dispersion can lead to quite drastic differences in the conductivity. Two cases will be considered here, one a strong scattering which follows a Rayleigh law, i.e., the scattering induced by the isotope in solid helium. In this case, the scattering law is known with a great deal of confidence, and it will be shown that inclusion of dispersion may account for a significant fraction of the anomalous concentration dependence of the scattering cross section.

The second will be resonant scattering by low-lying resonant modes in KCl: CN$^-$. Here the scattering law is not as well established. To introduce the dispersion corrections in a consistent fashion, expressions will be derived for the real and imaginary parts of the T matrix.

ISOTOPIC SCATTERING IN SOLID HELIUM

In general, it is possible, using dispersion relations, to relate the real part of the index of refraction which leads to dispersion, to the imaginary part which represent a damping of the excitations. However, to be useful, these require a knowledge of the scattering cross section at all frequencies. A less general approach is preferred, however, and results first obtained by Lax[2] for the change in the index of refraction of a medium due to scattering will be used:

$$k'^2 = k^2 + 4\pi N f(0) \ , \tag{3}$$

where k' is the new wave vector corresponding to frequency ω, k is the wave vector which would correspond to a frequency ω in the perfect crystal, $f(0)$ is the forward scattering amplitude, and N is the number of scatterers per unit volume.

For phonons at the low temperatures of interest here, k^{-1} is usually very large compared to the dimensions of the scattering center so that all of the scattering is contained in the first partial wave. In other words, this corresponds to S-wave scattering.

The general formula for the scattering amplitude is[3]

$$f(\theta) = (1/2ik) \sum_l \ (2l+1)(e^{2i\delta_l} - 1)P_l(\cos\theta) \ , \tag{4}$$

where δ_l is the phase shift for the partial wave l and P_l is the Legendre polynomial. The total scattering cross section is

$$\sigma = (4\pi/k^2) \sum_l \ (2l+1)\sin^2\delta_l \ . \tag{5}$$

From Eq. (4) it is clear that, if the $l=0$ wave alone contributes, the real part of the forward scattering amplitude is

$$\begin{aligned} \mathrm{Re} f(0) &= (1/k)\sin\delta\cos\delta \\ &= [(\sigma/4\pi)(1 - k^2\sigma/4\pi)]^{1/2} \ . \end{aligned} \tag{6}$$

If the phase shifts δ are small, $\cos\delta \approx 1$ and the forward scattering amplitude is given approximately by the following expression:

$$\mathrm{Re} f(0) \cong (\sigma/4\pi)^{1/2} \ . \tag{7}$$

The assumption made in deriving Eq. (5) is probably excellent for phonons in the neighborhood of 1 °K; the phase shifts δ_l for small k vary[3] as k^{2l+1}, and so all phase shifts except the zero-order shift may be safely neglected.

An approximate expression for the thermal conductivity which includes dispersion corrections will now be derived.

For mass-defect and strain-field scattering, the scattering cross section is evaluated at the perturbed wave vector, and is of the form[1]

$$\sigma = a k'^6 / \omega^2 C_g^2 \ ,$$

where C_g is the phonon group velocity, and the constant a measures the strength of the interaction. Assuming that Rayleigh scattering is predominant, and ignoring three-phonon processes, substitution in Eq. (2) yields

$$K = \frac{k_B}{2\pi^2} \int_0^{\omega_{\max}} \left(\frac{\beta\omega}{\sinh\beta\omega} \right)^2 \frac{C_p^4 C_g^2}{N a \omega^2} \, d\omega \ ,$$

where C_p is the phase velocity, $C_p = \omega/k'$.

Using (7), substitution in (3) yields

$$k'^2 = k^2 + [N(4\pi a)^{1/2}/C_g C_p] k'^2$$

and therefore

$$k' = k[1 - N(4\pi a)^{1/2}/C_g C_p]^{-1/2} , \tag{8}$$

since $\omega = C_0 k$, where C_0 is the unperturbed velocity and $C_p = \omega/k' = C_0[1 - N(4\pi a)^{1/2}/C_g C_p]^{-1/2}$.

It is clear that ω is still proportional to k in this approximation, so $C_p = C_g$ and (2) becomes

$$K = \frac{k_B}{2\pi^2} \int_0^{\omega_{\max}} \left(\frac{\beta\omega}{\sinh\beta\omega} \right)^2 \frac{C_0^6[1 - N(4\pi a)^{1/2}/C_0^2]}{N a \omega^2} \, d\omega \ . \tag{9}$$

In deriving (9) it has been assumed that only one scattering mechanism is important, i.e., that scattering by a particular point defect is much larger than boundary or other scattering.

The effect of including dispersion has been to make the scattering amplitude appear to be concentration dependent, i.e., proportional to $a[1 - N(4\pi a)^{1/2}]^{-3}$. If the correction is written in terms of the fractional concentration as $1 - \alpha x$, where $\alpha x = N(4\pi a)^{1/2}/C_p C_g$, it can be compared with available experimental data.

At the low-concentration limit Bertman, Fairbank, Guyer, and White[4] deduce from their data that the relaxation time is

$$1/\tau = x(9.2 \times 10^{-38}\omega^4) \ .$$

Therefore,

$$\sigma = (\tau N C_0)^{-1} = \omega^4/(9.2 \times 10^{38} N_{\mathrm{He}} C_0)$$

$$=ak^4/C_0^4\ .$$

The molar volume is 19.5 cm^3/mole, thus the number of atoms per cm^3, N_{He}, is 3×10^{22} cm^{-3}. Following Bertman *et al.*, we use a Debye model and calculate C_0 from

$$C_0=(k_B\theta/\hbar)(6\pi^2N/V)^{-1/3}\ ,$$

with $\theta=30.4$ °K obtained by Bertman, White, Fairbank, and Crooks[5]

$$a/C_0^4=10^{-46}\ ,$$

therefore,

$$\alpha\cong1.1\ .$$

Reference to Eq. (9) indicates that if dispersion is ignored the experimental strength of the point-defect term would appear to be $a(1-\alpha x)^{-3}$. Thus, if the correction is not taken into account, the strength of the point-defect scattering would appear to increase with concentration. The data[4] indicate an apparent increase of a factor of 2 in scattering strength when the ^{3}He concentration changes from 1% to 10%. These computations indicate a factor of about 1.5. Thus, it is concluded that dispersion may account for a significant fraction of the increase observed.

It should be emphasized that there are two important factors which have been overlooked in arriving at this value for α:

(a) Both Berman, Bounds, and Rodgers[6] and Bertman, Fairbank, Guyer, and White[4] conclude that a major source of scattering is due to the lattice distortion about the defects. As Carruthers[1] has pointed out, a distortion of this nature behaves like a Coulomb field. This field varies too slowly with distance from the defect for the simple calculation presented here to be strictly valid. However, because of the presence of other defects, etc., the field is limited in range. If it is cut off at a distance small compared to the phonon wavelength this treatment is valid.

(b) The scattering cross sections have been obtained from thermal-conductivity data on polycrystals. In fitting the data, it is necessary to include the effect of strong three-phonon interactions.[4,6] This can lead to uncertainty for two reasons: (i) the strength assumed for the normal process affects that for the point defects, (ii) the damping due to three-phonon collisions can also lead to dispersion, and this we have ignored.

In spite of the uncertainties encountered above, it is felt that this elementary treatment shows that the effects of dispersion can be significant at high concentration in ^{3}He–^{4}He mixtures.

RESONANT SCATTERING

Scattering which is accompanied by transitions between internal states of the defect will now be considered. A simple derivation of a very general expression will be shown since this can be accomplished very briefly. This problem has been considered by Klein.[7] Griffin and Carruthers[8] and Kwok[9] have considered scattering by donor atoms in germanium. The expressions derived below differ from theirs. However, they are essentially identical to those obtained for spin systems.[10]

This derivation is applicable to all defects which scatter through transitions between internal states, including spin systems.

The Hamiltonian is

$$H=H_0+V\ ,$$

where H_0 is the uncoupled contribution from the crystal plus defect, and V is the interaction.

If the eigenstates of H_0 are ϕ,

$$H_0\phi=E_0\phi\ ,$$

solutions ψ are sought such that

$$H\psi=E\psi\ .$$

There is a difference in energy between E and E_0 which is one of the quantities desired

$$\Delta E(k)=E(k)-E_0(k)\ ,$$

where k is the wave vector.

A T matrix may be defined such that

$$\psi=\phi+G_0T\phi\ , \tag{10}$$

where G_0 is the Green's function for the noninteracting crystal plus defect (i.e., corresponding to H_0) and G is the complete Green's function given by

$$T=V/(1-G_0V)=V+VGV\ ;$$

now

$$\langle\phi|H|\psi\rangle=E\langle\phi|\psi\rangle\ ,$$

$$\langle\phi|H_0+V|\phi+G_0T\phi\rangle=E\langle\phi|\phi+G_0T\phi\rangle\ ,$$

and therefore,

$$\Delta E=\langle\phi|T|\phi\rangle(1+G_0T\phi)^{-1}\ . \tag{11}$$

The second term in the denominator represents interference between the incident and scattered wave. To the extent that this is negligible, the energy shift is $\langle\phi|T|\phi\rangle$, a standard result.

Now to compute $\langle\phi|T|\phi\rangle$. The presently available theory for making multiple scattering corrections will be ignored because only low frequencies are of interest. At the small values of k which are important, approaches such as the coherent-potential-approximation (CPA)[11] do not yield any significant correction. This is not to say, however, that such corrections may not be important: at sufficiently long wavelengths and high concentration there is a high probability that the average defect separation is less than one wavelength. A difference could be expected between this and the situation where the defects are many wavelengths apart, however, the CPA yields no additional corrections, and, in fact, yields no difference at all as $\omega \to 0$ from the single defect approach.

In the single-defect approximation, contributions of all defects are simply added, in which case

$$\Delta E = \sum_i N_i \langle \phi | T_i | \phi \rangle \quad , \tag{12a}$$

now N_i is the *number of defects in the crystal.* However, it is important to remember that elastic scattering is being considered here and the scattered wave is coherent with the incident wave. Therefore, some care must be exercised when performing the sum in Eq. (12a); it should be remembered that[2]

$$\langle \phi(k') | T(R_i) | \phi(k) \rangle = e^{i(\vec{k}'-\vec{k})\cdot\vec{R}_i} \langle \phi(k') | T(0) | \phi(k) \rangle \; .$$

Since the forward scattering amplitude alone is needed, the energy shift is

$$\Delta E = \sum_j N_j \langle \phi | T_j(0) | \phi \rangle \quad , \tag{12b}$$

where j labels the type of defect.

The matrix element is[12]

$$\langle \phi | T | \phi \rangle = \langle \phi | V | \phi \rangle + \sum_{\phi' \phi''} \langle \phi | V | \phi' \rangle \times \langle \phi' | G | \phi'' \rangle \langle \phi'' | V | \phi \rangle .$$

If an interaction linear in the phonon operators is being considered, the first term disappears. Specialize to this case, and also consider a two-level system, call the ground state $|0\rangle$ and the excited state $|1\rangle$. The states ϕ are then $|n_k, \alpha\rangle$, where n_k is the number of phonons in mode k and α is 0 or 1.

If the defect is in the ground state, the matrix element is[12]

$$\hbar T_g = \frac{\langle k, 0 | V | 1 \rangle \langle 1 | V | k, 0 \rangle}{\omega - \omega_0 - \Delta(\omega) + i\Gamma(\omega)} - \frac{\langle k, 0 | V | 2k, 1 \rangle \langle 2k, 1 | V | k, 0 \rangle}{\omega + \omega_0 + \Delta(\omega) - i\Gamma(\omega)} \quad , \tag{13}$$

where $\hbar\omega_0$ is the energy difference between the ground and excited states of the defect, $\Delta(\omega)$ is the level shift, ω is the phonon frequency, and $\Gamma(\omega)$ is the lifetime of the excited complex formed by the absorbed phonon and the defect.

The first term in Eq. (13) corresponds to an event where the defect absorbs the phonon and then reemits it; the second to where the scattered phonon is emitted and then the incident quantum is absorbed. The first term is often called the resonant scattering, and the second the potential scattering, amplitude.

The linewidth Γ is[13] equal to the transition probability per unit time which, in first-order perturbation theory and using Fermi's golden rule, is

$$\Gamma = (\Omega k^2 / \pi \hbar^2 C_g) |\langle f | V | i \rangle|^2 \quad , \tag{14}$$

where Ω is the volume of the crystal, $|f\rangle$ refers to the metastable intermediate state (either $|n_k - 1, 1\rangle$ or $|n_k + 1, 1\rangle$ in this case), and $|i\rangle$ to the initial state. Letting

$$|\langle k_0 | V | 1 \rangle| = |\langle k, 0 | V | 2k, 1 \rangle| = |\langle f | V | i \rangle| \quad ,$$
$$\hbar T_g = \left(\frac{1}{\omega - \omega_0' + i\Gamma} - \frac{1}{\omega + \omega_0' - i\Gamma} \right) |\langle f | V | i \rangle|^2 \quad , \tag{15}$$

where the level shift has been included to give $\omega_0' = \omega_0 + \Delta(\omega)$.

Observe that the first term in the expression is the well-known Breit–Wigner one-level formula for the resonant forward scattering amplitude (the potential scattering term has been kept since a cross section valid far from resonance is required).

Up to this point, the theory is exact for a bilinear interaction. To make further progress make the approximation that $\Gamma_{\text{res}} = \Gamma_{\text{pot}} = \Gamma$,

$$\hbar T_g = \left(\frac{\omega_0' (\omega^2 - \omega_0'^2 - \Gamma^2) + i 2\Gamma (\omega^2 + \omega_0'^2 + \Gamma^2)}{(\omega^2 - \omega_0'^2 + \Gamma^2)^2 + 4\Gamma^2 \omega_0'^2} \right) \times |\langle f | V | i \rangle|^2 \; . \tag{16}$$

A similar expression for scattering from defects in their excited state can be obtained. The excited-state contribution is $T_e = -T_g$.

The energy shift is obtained by summing the real parts of these expressions. Taking the population of the excited state into account:

$$\Delta E = (N_d \tanh \beta \omega_0') \operatorname{Re} T_g \quad , \tag{17}$$

where N_d is the number of defects.

The other quantity required is the scattering cross section. At this point the quickest and simplest way to obtain it is to use the optical theorem[14]

$$\sigma_i = (2v / \hbar C_g) \operatorname{Im} T_i \quad ,$$

where v is the atomic volume.

The sum of the cross sections is required for the thermal conductivity:

$$\sigma_{\text{tot}} = [(2v/\hbar C_g) N_d \tanh \beta \omega_0'] \operatorname{Im} T_g \quad . \tag{18}$$

In obtaining this expression, we have used the fact that $\operatorname{Im} T_{00}^g = -\operatorname{Im} T_{00}^e$. In fact, for the Kramers–Kronig relations to hold, the temperature dependence must be identical to that for the energy shift.

The negative contribution to the cross section may be understood if it is recalled that this simply corresponds to stimulated emission of radiation.

Now to compute $\langle k, 0 | V | 1 \rangle$: the interaction has been assumed to be linear in phonon operators, i.e.,

$$V=\sum_i u_i \frac{\partial E_d}{\partial R_i} , \qquad (19)$$

where E_d is the energy of the defect and the u_i are displacements. The displacements u_i are written,

$$u_i=\sum_k (\hbar/2M\omega_k)^{1/2}(\alpha_k e^{i\vec{k}\cdot\vec{R}_i}+\alpha_k^\dagger e^{-i\vec{k}\cdot\vec{R}_i})\, e_k ,$$

where e_k is the polarization vector, α_k and $\alpha_k^\dagger$ are annihilation and creation operators, and k includes a polarization index.

If k is assumed to be small the interaction confined to the nearest neighbors, Eq. (19) can be written[15]

$$V=\sum_k k(\hbar/2M\omega_k)^{1/2}(\alpha_k+\alpha_k^\dagger)U_k , \qquad (20)$$

where U_k is an operator on the internal states of the defect and is a suitably transformed $\partial E_d/\partial R_i$. Take U_k as an experimental parameter in the sense that

$$\langle 1|V|k,0\rangle = k(\hbar/2M\omega_k)^{1/2}W , \qquad (21)$$

where $W=\langle 1|U_k|0\rangle$ is a coupling constant expressed as an energy shift per unit strain. This is, in principle, directly measurable by applying a stress to the crystal if a probe is available which can measure the energy difference between states $\langle 1|$ and $\langle 0|$. U_k has been taken to be independent of k. This has been shown to be a good approximation for spin systems.

Substituting Eqs. (21) and (16) in Eqs. (17) and (18) we obtain, finally

$$\Delta\omega = \frac{W^2k^2}{\rho\hbar\omega_k}\left(\frac{\omega_0'(\omega^2-\omega_0'^2-\Gamma^2)}{(\omega^2-\omega_0'^2+\Gamma^2)^2+4\Gamma^2\omega_0'^2}\right)\rho_D \tanh\beta\omega_0' , \qquad (22)$$

where ρ_D is now the number of defects *per unit volume* and ρ is the density of the crystal. We also obtain

$$\sigma_{\text{tot}} = \frac{2W^4k^6}{\pi\rho^2\hbar^2C_g^2\omega_k^2}\left(\frac{\omega^2+\omega_0'^2+\Gamma^2}{(\omega^2-\omega_0'^2+\Gamma^2)^2+4\Gamma^2\omega_0'^2}\right) \times\rho_D \tanh\beta\omega_0' , \qquad (23)$$

where C_g is the group velocity of phonon k.

In general Γ^2 is negligible compared with ω_0^2 and Eq. (22) yields the following expression for the fractional energy shift:

$$\Delta\omega/\omega_k \cong A(\omega^2-\omega_0^2)^{-1}\rho_D \tanh\beta\omega_0' ,$$

where $A=W^2\omega_0/C_0^2\rho\hbar$.

For a multilevel system this is easily generalized to

$$\frac{\Delta\omega}{\omega_k} = \rho_D\sum_i \frac{A_i}{\omega_i}\left(\frac{\omega^2}{\omega_i^2}-1\right)^{-1}\left(\frac{1-g_i\exp-\beta\omega_i}{1+\sum_i g_i\exp-\beta\omega_i}\right) , \qquad (24)$$

where g_i is the degeneracy of level i, and a similar generalization can be performed on Eq. (23).

COMPARISON WITH EXPERIMENT

There are two features of Eq. (24) which are confirmed directly by experiment: the temperature dependence of the fractional phonon frequency shift and the independence of this shift on frequency in the limit of low frequencies.

Byer and Sack[16] have measured sound velocities and the ultrasonic attenuation at frequencies between 30 and 200 MHz for modes of E_g and T_{2g} symmetry for a variety of alkali-halide crystals doped with impurities which are resonant scatterers. Their results for KCl : CN$^-$ directly confirm Eq. (24) in the low-frequency limit: The change in velocity of sound is independent of frequency and the observed T^{-1} temperature dependence at high temperatures is also in agreement with (24).

The level structure of the KCl: CN$^-$ system is discussed fully in an article by Narayanamurti and Pohl.[17] Of interest here are the three lowest tunnel-split levels and the librational level at 13.5 cm^{-1}. The tunnel splittings have been measured by Hetzler and Walton,[18] and lie at 1.1 and 2.0 cm^{-1} above the ground state.

Byer and Sack observed that the E_g mode was essentially only coupled to the libration level, and the T_{2g} mode only to the tunneling levels. Unfortunately, their data do not go to sufficiently low frequencies to allow a complete separation of the contribution from each tunneling state: The coupling to the level at 2.0 cm^{-1} would be expected to saturate below about 1.5 °K, becoming temperature independent, and the remaining temperature dependence would yield the magnitude of the coupling constant to the 1.1-cm^{-1} level. A rough estimate of the fraction to be assigned to each level is obtainable from the data of Hetzler and Walton, and the contribution from the higher transition appears to be about twice that from the lower. When allowance is made for the ω^4 frequency dependence of the scattering cross section, the constants A_i/ω_i in Eq. (24) are approximately in the ratio 6 : 1. The magnitude of the coupling constants were then obtained from Byer and Sack's data in the high-temperature limit: $(A/\omega)_{1.1}=1.2\times10^{-20}$ cm^{-3} and $(A/\omega)_{2.0}=2\times10^{-21}$ cm^3.

The resulting dispersion relations are plotted in Fig. 1 for a CN$^-$ concentration of 4.9×10^{19} cm^{-3}. It is clear that there is considerable perturbation of the phonons in the vicinity of both resonant frequencies. The obvious question which arises now is what effect do the resulting large changes in sound velocity have on the thermal conductivity?

In an attempt to answer this question, the thermal conductivity for KCl doped with CN$^-$ at concentration of 9×10^{17}, 8.4×10^{18}, and 4.9×10^{19} cm^{-3} has been calculated and compared with the data of

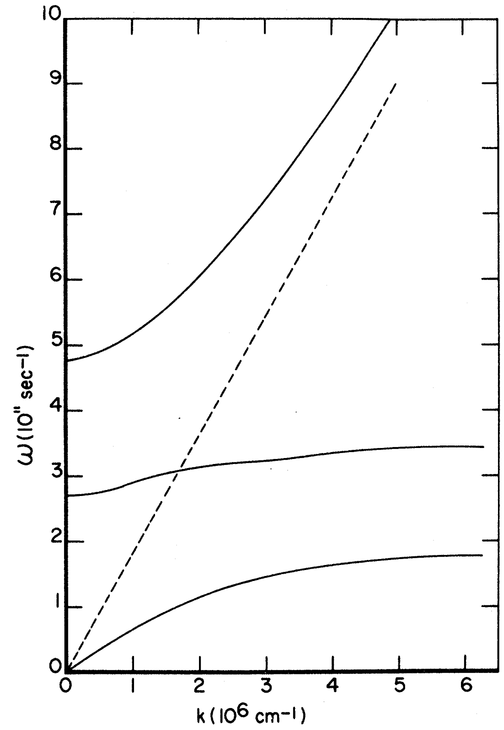

FIG. 1. Dispersion relations for KCl doped with 4.9×10^{19} cm^{-3} CN$^-$. The coupling constants were calculated from the data of Byer and Sack (Ref. 16), with strengths apportioned between the two levels from data of Hetzler and Walton (Ref. 18).

Seward and Narayanamurti.[19] The constants required for this calculation were obtained in the following way: in conventional fashion a fit was obtained to the experimental conductivity of the pure KCl crystal. Then additional scattering terms due to the CN$^-$ ion were included in the denominator of Eq. (2).

It is characteristic of the effect of resonance scattering that quite a large band of phonons about the resonance frequency are ineffective in heat transport. Thus, long before a frequency is reached where the damping term $4\Gamma^2\omega_0^2$ in Eq. (23) becomes important, the phonons in question have ceased to contribute. For this reason, Eq. (23) was rewritten

$$\sigma_{\text{tot}} \cong N_d \sum_i \frac{4A_i^2C_0^2}{\pi C_p^2 C_g^2}\left(\frac{\omega^4}{(\omega^2-\omega_i^2)^2}\right)\left(\frac{1-e^{-\beta\omega_i}}{1+\sum_i g_i e^{-\beta\omega_i}}\right) ,$$

where N_d is the number of CN$^-$ per unit volume.

The phase velocity C_p was obtained from Eq. (24) and

$$\Delta\omega/\omega_k = (C_p/C_0) - 1 \quad .$$

The group velocity C_g was obtained from

$$C_g = \frac{\partial\omega}{\partial k} = C_p + k\,\frac{\partial C_p}{\partial k} \quad .$$

The known values of the resonant frequencies listed above were used. The coupling constant A_i to the two tunneling levels was computed as outlined above, and that to the librational level at 13.5 cm^{-1} was treated as an adjustable parameter. With these values the solid lines shown in Fig. 2 were computed. The concentrations employed were the spectroscopically determined values listed in the figure.

The computed conductivities which would have been obtained if the dispersion had been neglected, i.e., $C_p = C_g = C_0$ are shown as the dashed lines in Fig. 2. It is clear that for the highest doping, the changes in velocity of sound resulting from the scattering make a substantial difference to the calculated conductivity at the lowest temperature.

DISCUSSION

The main objective of this paper has been to investigate the effects of dispersion on the thermal conductivity. It has been found that these effects are important at high concentrations for strongly

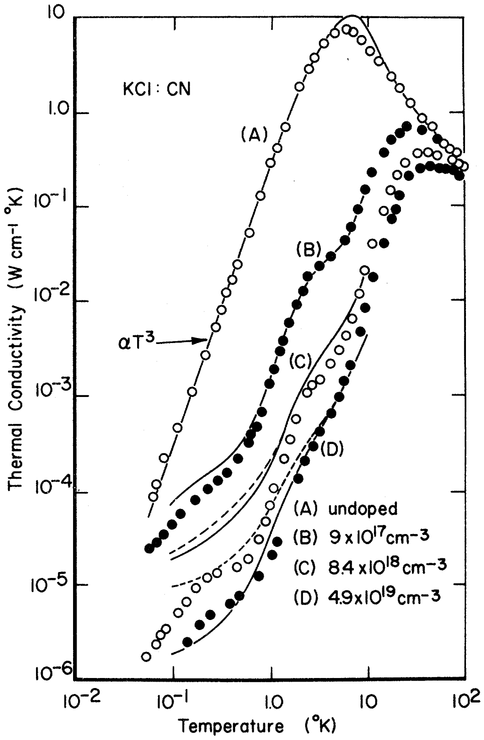

FIG. 2. Calculated thermal conductivities for KCl : CN$^-$ with the same constants used in obtaining Fig. 1 compared with the measurements of Seward and Narayanmurti (Ref. 19). The coupling constant to the level at 13.5 cm^{-1} was treated as an adjustable parameter. The solid lines are calculated with, and the dashed lines without, including dispersion.

coupled systems and are most important for resonant scatterers. In calculating thermal conductivities, the imaginary part of the T matrix, which leads to damping of the phonons, is most important. Thus, the calculated effect of the real part of the T matrix which leads to the dispersion depends on the corresponding imaginary part. Some confidence in the expression derived here for resonant systems is inspired by the fact that they fit the measured thermal conductivities with only one adjustable parameter, the coupling to the librational level. *All other parameters were determined independently by other techniques*. It is true that the agreement is not as good for the KCl + 8.4×10^{18} cm^{-3} CN^- crystal as that obtained by Seward and Narayanamurti.[19] However, it should be noted that in addition to varying the resonance frequencies and coupling constants, they allowed the concentration of CN^- to vary in order to obtain their curves. This was not done here since it was felt that the temperature dependence of the thermal conductivity is too insensitive to the details of a scattering mechanism to be able to yield these if such a procedure is followed. Needless to say, when such a procedure was followed, agreement with all the measured curves was readily obtained which was well within the experimental error. However, it was also found that a variety of combinations of the parameters yielded essentially identical results.

Excepting the intermediate-concentration low-temperature data, the expressions used here in calculating the conductivity yield adequate agreement between theory and experiment with only one adjustable parameter. It is felt, therefore, that they are an adequate approximation to the real situation. Using these expressions, it was found that the inclusion of dispersive effects made a difference of as much as a factor of 6 in the calculated conductivity. Thus, it appears that effects of dispersion do, in fact, make an important difference and must be included.

A straightforward curve-fitting procedure was followed in order to fit data obtained by Baumann *et al.*[20] for Li in KCl: The four tunneling levels were replaced by a two-level system, and the coupling constant and resonance frequency were varied until a best fit was obtained. This fit was as good as that obtained by the original authors. Again, it was found that dispersion made a large difference to the calculated conductivities at the low temperatures, in this case, a factor of 3.

In closing, it is again observed that the temperature dependence of the thermal conductivity is clearly severely limited in its ability to provide detailed information and is incapable of yielding the frequency and temperature dependence of the scattering cross section: It is, after all, a broad band spectrometer whose bandwidth is many times greater than the width of the resonance being studied. Furthermore, in using the temperature dependence of the thermal conductivity as a test for independently obtained expressions it is important that the dispersion introduced by the scattering be included.

SOME OTHER PROBABLE CONSEQUENCES

The dispersion introduced by the resonant scattering is frequency dependent, and leads to dispersion relations for phonons which are curved. Thus, three-phonon processes which are forbidden when there is a linear relationship between ω and k are now allowed. The result is that normal processes should become important at longer wavelengths and become effective at lower temperatures.

A second consequence arises from the decreased velocity of sound. In the long-wavelength limit, the phase velocity becomes constant and less than the velocity in the pure crystal. Thus, the thermal conductivity at sufficiently low temperature should become greater than that for the pure crystal. For a crystal with a high concentration of strongly interacting defects, the measured K vs T should eventually cross the pure-crystal curve at low temperatures. There are some indications that this effect has already been observed for spin systems.[21]

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Electron-Paramagnetic-Resonance and Optical-Absorption Study of $BrCl^-$ and Associated Centers in Doped KCl Crystals. II*

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Correlated optical and EPR studies have shown that after x or γ irradiation and proper thermal treatment, $BrCl^-$ molecule ions aligned along the six ⟨110⟩ directions are present in crystals of KCl doped with a small amount of KBr and $PbCl_2$. When such a crystal is warmed to near 275 K, this $BrCl^-$ center is thermally destroyed and another center, a $BrCl^-$ with a positive-ion vacancy in a nearest-neighbor position to both nuclei of the molecule ion, is formed. The internuclear axis of the latter center lies in a {100} plane and makes an angle of 12.5° with a ⟨110⟩ direction; the bromine end of the molecule ion lies closest to the vacancy. This $BrCl^-$ associated with a positive-ion vacancy has a strong σ-polarized transition at 368 nm and a weak σ-polarized transition at 910 nm; optical excitation at 4.2 K can cause preferential orientation of these molecule ions. It is found that this center reorients thermally by making what corresponds, in ⟨110⟩-oriented $BrCl^-$, to 90° jumps at 45 K and what corresponds to 60° jumps at 55 K. The mechanism of formation, the structure, the reorientation, and other properties of this center are discussed.

I. INTRODUCTION

An earlier paper[1] (hereafter called DSY-I) described the method of production, some thermally induced reactions, the EPR and optical properties, and the mechanism of reorientation in the lattice of the V_K-type ⟨110⟩-oriented $BrCl^-$ molecule ions (hereafter referred to as $BrCl^-$) in doped KCl crystals. During that study it became apparent that in KCl : KBr : $PbCl_2$ crystals another type of $BrCl^-$ could be produced which is associated with a lattice defect.[2] The purpose of the present investigation is to determine the exact nature of this center through a study of the mechanism of formation, the EPR and optical absorption, and the mechanism of reorientation of this center in the lattice.

II. EXPERIMENTAL PROCEDURE

The crystals used in these experiments were grown in air by the Kyropoulos method, from a melt of KCl containing 0.2-mole% KBr and 0.27-mole% $PbCl_2$. Since Br^- does not segregate appreciably in KCl, the concentration of Br^- in the grown single crystal is almost the same as that in the melt, but the Pb^{++} concentration is reduced by approximately a factor of 10. KCl : KBr crystals were also grown containing AgCl and a combination of AgCl and $CaCl_2$. The color centers were produced at 77 K either by x irradiation from a 50-kV 50-mA Machlett tube with a tungsten target filtered by ~1-mm fused silica or with γ rays from a 2000-Ci ^{60}Co source. Before irradiation, the Pb^{++}-doped crystals were heated to about 520 K for a few minutes and then quenched to room temperature. This treatment apparently disperses agglomerated lead in the crystal, increasing the concentration of electron traps. As a result, it is found that the hole-center concentration is increased by about a factor of 3 with respect to the unquenched crystals. The Ca^{++}-doped crystals were also quenched. Details of the EPR measurements at and above 77 K have been given before.[3] For the few EPR measurements taken at 4.2 K a superheterodyne spectrometer operating at *X*-band microwave frequencies was used.[4] Optical-absorption spectra were obtained by using a Cary 14R recording spectrophotometer. Polarized light was produced by means of an Ahrens prism. Optical excitation of the crystals was accomplished by exposure to light from an HBO-500 high-pressure mercury arc lamp or a 750-W tungsten filament lamp in conjunction with appropriate interference and/or Corning glass filters. The correlation of the optical absorption and EPR measurements was done on different crystal specimens, cleaved from the same large single crystal and treated identically.