bands. This may also have produced the differences in the ordering of the conduction band states. These latter differences could also be due to limitations in the perturbation approximation to the orthogonalized-plane-wave method which was used by Knox and Bassani.

One interesting observation regarding the conduction bands for argon is the similarity between these bands and those obtained for face-centered cubic iron by Wood[4] and for copper by Burdick[16] and also by Segall.[17] Aside from minor changes in the ordering of states in the 4s–4p bands (which can be explained by differences in lattice spacing), the bands are remarkably similar. This

may lend some support to the rigid band approximation, a proposal which has enjoyed fair success in explaining several aspects of the electronic properties of the transition metals and their alloys.

VI. ACKNOWLEDGMENTS

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Second-Sound Propagation in Dielectric Solids*

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The conditions necessary for the occurrence of second sound in solids are examined in some generality. The results indicate that second sound can propagate at frequencies greater than the reciprocal umklapp relaxation time and smaller than the reciprocal normal relaxation time. At frequencies less than the reciprocal umklapp relaxation time, the solutions are the same as those for normal thermal conductivity. The frequency range and damping of second sound at various temperatures is computed using relaxation times determined for sodium fluoride.

I. INTRODUCTION

SECOND sound in superfluid helium was first described as a collective phonon wave by Landau.[1] In this description, the "phonon gas" was treated as a particle gas in which harmonic phonon-density fluctuations could be propagated. This explanation seemed to describe a phenomenon so general that many authors[2] have speculated about the possibility of occurrence of similar collective waves in solids. A collective wave of a more restricted nature has been reported in CdS crystals by Kroger, Prohofsky, and Damon.[3] Their experiment involved the use of electrons drifting faster than the velocity of sound, which are therefore strongly coupled to the phonons. This problem will be discussed in a forthcoming paper.

This paper is limited (as were those by Ward and Wilks, and by Dingle[2]) to a discussion of an acoustic

phonon system which does not interact strongy with charged particles or optical phonons. We will place emphasis on those aspects of phonon dynamics associated with the periodic structure of solids. This requires that a distinction be made between normal collisions and umklapp collisions. It should be kept in mind that phonons undergo normal collisions in which the crystal momentum of all the phonons is conserved, much like the collisions of a particle gas. It is emphasized that this conservation applies regardless of the number of phonons or whether the collision involves phonons of the same or different phonon branches. The major difference between phonon and particle gases is that in addition to normal collisions the phonons may undergo umklapp collisions which have no counterpart in particle gases. In this context this paper examines in detail the collective transport phenomena of a many-phonon system and develops a description of a collective harmonic mode.

In Sec. II of this paper, the factors that determine whether or not a system will respond to a density fluctuation by diffusive or harmonic behavior are discussed qualitatively.

In Sec. III, energy and crystal-momentum conservation equations for phonons are derived from transport equations. The moments of the equations are then

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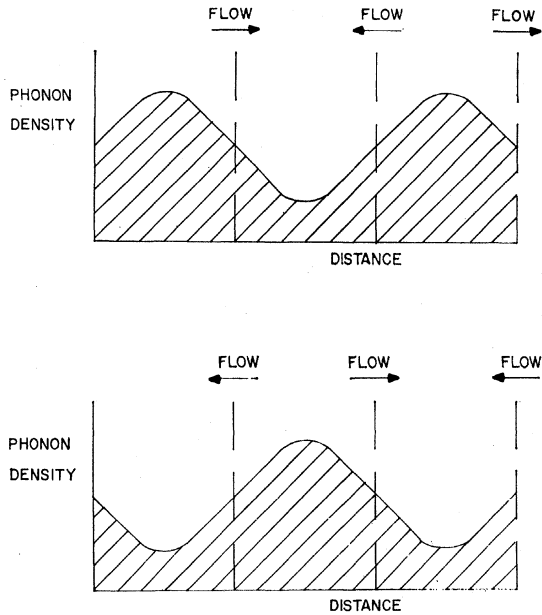
FIG. 1. Schematic instantaneous phonon distributions. That in the upper graph gives rise to a net phonon flow through the dashed vertical lines in the direction of the arrows. The resultant crystal momentum distribution causes an "overshoot" to the situation pictured in the lower graph, provided that the required transit time is short, compared to momentum-destroying relaxation times. The flow is reversed when the distribution assumes the form shown in the lower graph. The cyclic process is repetitive and gives rises to propagation of harmonic density fluctuations.

evaluated, assuming that the distortion in the phonon field can be described by using a net drift velocity and a temperature fluctuation as parameters. The error in this two-parameter description of the distribution function is expanded as a power series in the crystal momentum and shown to be small under certain conditions. Use of a power series in this manner is one feature of our present study.

Harmonic solutions for temperature fluctuations and net drift velocities are found in Sec. IV by simultaneous solution of the conservation equations. "Second-viscosity" damping for these harmonic solutions is examined.

The harmonic solutions are shown in Sec. V to become the usual thermal-conductivity solutions for very short umklapp relaxation times. In Sec. VI, the feasibility of an experimental observation of second sound is investigated, using computed values of effective relaxation times in NaF.

II. A QUALITATIVE DESCRIPTION OF SECOND SOUND IN NONCONDUCTING SOLIDS

Ward and Wilks[2] first proposed that second sound could be thought of as a density fluctuation in a "phonon gas." We wish to discuss this idea in qualitative physical terms, and by analogy with (first) sound in an ordinary particle gas.

Figure 1 shows the density and flow situation to be

expected for propagation of a wave. It is clear that a spatial variation in the density of phonons will result in a net drift from high-density to low-density regions. However, it is not necessarily apparent that, under certain circumstances, this flow can "overshoot" repetitively, rather than simply "relaxing" to a uniform distribution. Wave propagation is familiar in the case of particle-density fluctuations, whereas diffusion is the common experience in "thermal-density" fluctuations.

We have sought to illuminate this point by considering ordinary sound propagation in a particle gas. We employ the usual hydrodynamic equations and the usual small-amplitude adiabatic assumption for plane-wave sound propagation in the x direction. An equation of state is also assumed to exist. The quantities of interest are: the particle density $\rho_0 + \rho_1(x,t)$ where ρ_0 is the equilibrium density and $\rho_1(x,t)$ is the (small) density change in the sound wave; the velocity of an element of the gas $\mathbf{u_x} = 0 + \mathbf{u_x}$, which is to say the gas is initially at rest in the reference frame. There is also an equation of state $\rho = \rho(p,T)$ where p and T are the local pressure and temperature, respectively.

The linearized hydrodynamic equations lead to

$$(\partial\rho_1/\partial t) + (\partial/\partial x)(\rho_0 \mathbf{u_x}) = 0 \qquad (2.1)$$

$$\frac{\partial(\rho_0 \mathbf{u_x})}{\partial t} = -\frac{\partial p}{\partial x} + f_x = -\left(\frac{\partial p}{\partial \rho_0}\right)\left(\frac{\partial \rho_1}{\partial x}\right) + f_x. \qquad (2.2)$$

Equation (2.1) is simply a statement of continuity, and the zero on the right-hand side indicates that there are no particle sinks or generators. Equation (2.2) is purposely written to include the force f_x in addition to the internal stress arising from the pressure gradient.

In particular, note that the left-hand side of Eq. (2.2) is the time rate of change of the particle current. Only if we neglect viscosity or inelastic impurity scattering is f_x zero. The usual undamped sound wave solutions follow when $f_x = 0$. A useful generalization is to assume a viscous damping $f_x = -(\rho_0 \mathbf{u_x}/\tau)$ where τ is a relaxation time. Such a term is appropriate in the low-frequency diffusion limit. In the absence of density gradients or applied forces, a particle current will decay with a typical relaxation time τ.

Equation (2.2) can then be rewritten

$$\frac{\partial(\rho_0 \mathbf{u_x})}{\partial t} + \frac{\rho_0 \mathbf{u_x}}{\tau} = -\left(\frac{\partial p}{\partial \rho_0}\right)\left(\frac{\partial \rho_1}{\partial x}\right), \qquad (2.3)$$

and by elimination with Eq. (2.1) we have

$$\frac{\partial^2(\rho_0 \mathbf{u_x})}{\partial t^2} + \frac{1}{\tau}\frac{\partial(\rho_0 \mathbf{u_x})}{\partial t} = \left(\frac{\partial p}{\partial \rho_0}\right)\frac{\partial^2(\rho_0 \mathbf{u_x})}{\partial x^2}. \qquad (2.4)$$

Now the fundamental distinction between wave flow and diffusive flow becomes clear. For slow variations of $\rho_0 \mathbf{u_x}$ with time, the viscous term dominates and any

density fluctuation relaxes by diffusion. When the viscous relaxation is slight and the relaxation time is long, spatial variations of the particle density will proceed in time as wavelike motions. Both diffusive and wave descriptions may therefore apply to density fluctuations in a particle gas. The choice is determined by whether $\omega\tau \ll 1$ or $\omega\tau \gg 1$, respectively.

The "phonon density" fluctuations can be discussed in the same way. The characteristic time τ for relaxation of heat current is the umklapp or combined "umklapp-plus-other-momentum-losing-process" relaxation time. The common experience that heat-density fluctuations obey the diffusive description is a consequence of the low frequency at which they are conventionally studied. The exception is in liquid helium where relaxation times are very long, thereby permitting observation of the periodic fluctuation at low frequency.

III. MOMENT EQUATIONS

The applicability of the Boltzmann transport equations to phonon wave packets was discussed by Peierls.[4] This application appears valid in most solids below Θ_D, the Debye temperature.

Associated with the Boltzmann equation is a distribution function giving the density of particles in specific modes. This distribution can be expressed as an equilibrium distribution plus small perturbations when the periods of the disturbances are long compared to the normal relaxation time τ, and the mean free path for these collisions is short compared to the wavelength of the disturbances. It may have validity outside this regime but that does not concern us here.

The full Boltzmann equation under the conditions discussed is

$$\frac{\partial f_k}{\partial t}+\frac{1}{\hbar}\left[\frac{\partial f_k}{\partial r_i}\frac{\partial \epsilon_k}{\partial k_i}-\frac{\partial f_k}{\partial k_i}\frac{\partial \epsilon_k}{\partial r_i}\right]=\left(\frac{df_k}{dt}\right)_{\text{col}}. \quad (3.1)$$

Here, f_k is the number of phonons in the mode specified by the wave vector $\mathbf{k}$, r_i is the ith component in configuration space, ϵ_k is the energy of mode $\mathbf{k}$, k_i is the ith component in $\mathbf{k}$ space, and col refers to the effect of collision processes. We will assume (i) there are no external fields acting on the system, (ii) the system is homogeneous, and (iii) renormalization effects due to phonon interactions are small. It will be understood throughout the remaining discussion that all quantities are assumed to be (coarse-grained) local in space and time. Under these conditions

$$\partial \epsilon_k/\partial r_i=0. \quad (3.2)$$

and, by definition

$$(1/\hbar)(\partial \epsilon_k/\partial k_i)=v_i, \quad (3.3)$$

[4] R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, London, 1955), p. 45.

where v_i is the ith component of the group velocity, or the velocity of the phonon packet. Equation (3.1) then becomes

$$\partial f_k/\partial t+\text{div}\langle \mathbf{v}f_k\rangle=(\partial f_k/\partial t)_{\text{col}}. \quad (3.4)$$

If one now sums this equation over all values of $\mathbf{k}$ one obtains

$$(\partial/\partial t)\langle n\rangle+\text{div}\langle n\mathbf{v}\rangle=\Delta n_{\text{col}}, \quad (3.5)$$

where $\langle n\rangle$ is the local number of phonons, $\langle n\mathbf{v}\rangle$ is the net local number current, and Δn_{col} is the change, due to collisions, in the local number of phonons. If both the right and left sides of (3.4) are multiplied by ϵ_k and then summed over all $\mathbf{k}$ one obtains

$$\partial\langle E\rangle/\partial t+\text{div}\langle n\epsilon\mathbf{v}\rangle=\Delta\epsilon_{\text{col}}, \quad (3.6)$$

where $\langle E\rangle$ is the total energy, $\langle n\epsilon\mathbf{v}\rangle$ is the net energy flow, and $\Delta\epsilon_{\text{col}}$ is the energy gained in collisions. Multiplying (3.4) by $\hbar k_i$ and then summing over all $\mathbf{k}$ leads to the equation

$$\frac{\partial}{\partial t}\langle \pi_i\rangle+\sum_j\frac{\partial}{\partial x_j}\langle v_j n\hbar k_i\rangle=\Delta\pi_{i\text{col}}. \quad (3.7)$$

$\langle \pi_i\rangle$ is the ith component of the net quasimomentum, $\langle v_j n\hbar k_i\rangle=\langle v_j\pi_i\rangle$ is the quasimomentum flow, $\Delta\pi_{i\text{col}}$ is the change in quasimomentum through collisions. The general distribution function is written as

$$f_k=f_k{}^0+f_k{}', \quad (3.8)$$

where $f_k{}'$ is assumed to be small compared to $f_k{}^0$. The two important departures from equilibrium in second sound are assumed to be variations in temperature from the ambient temperature, and net energy fluxes. Landau[5] has shown that a steady net flow of phonons, has a distribution function

$$f(\mathbf{v})=\{\exp[(\epsilon_k-\boldsymbol{\lambda}\cdot\hbar\mathbf{k})/k_BT]-1\}^{-1}, \quad (3.9)$$

where $\boldsymbol{\lambda}$ is the net drift velocity.

To account for slight temperature variations we set

$$T=T_0+T_1. \quad (3.10)$$

Here, T_0 is the ambient temperature, assumed constant throughout the system, and T_1 is the small change in temperature. If the temperature and the drift velocity change in time, the system may have a slight distortion from equilibrium which cannot be described in terms of drifts and thermodynamic temperature changes. This extra perturbation can be expressed as a power series in $\mathbf{k}$. The proposed form of the distribution function, as then, is

$$f_k=\left[\exp\left(\frac{(\epsilon_k-\boldsymbol{\lambda}\cdot\hbar\mathbf{k}-\varphi k^2\hbar^2-\mu\hbar^3k^3-\cdots)}{k_B(T_0+T_1)}\right)-1\right]^{-1}$$

$$(3.11)$$

[5] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Ltd., London, 1958), p. 204.

for λ, φ, μ, and T_1 all very small, this can be expanded to

$$f_k = [\exp\epsilon/k_B T_0 - 1]^{-1}$$

$$+ \frac{\lambda \cdot \hbar \mathbf{k} + \varphi \hbar^2 k^2 + \mu \hbar^3 k^3 + \cdots + \epsilon_k(T_1/T_0)}{k_B T_0}$$

$$\times \frac{\exp(\epsilon_k/k_B T_0)}{[\exp(\epsilon_k/k_B T_0) - 1]^2} \quad (3.12)$$

$$= f^0 + \frac{\lambda \cdot \hbar \mathbf{k} + \varphi \hbar^2 k^2 + \mu \hbar^3 k^3 + \cdots + \epsilon_k(T_1/T_0)}{k_B T_0} f^0(f^0 + 1)$$

$$= f^0 + \alpha f^0(f^0 + 1).$$

Again the distribution function applies to cells within the system which are small compared to the macroscopic distance measurements.

The role of T_1 is to increase the local number and thus the average local energy in a symmetrical way which corresponds to a locally higher temperature. The λ term gives rise to a distortion in velocity space, but does not change the local number or average energy. The φ term distorts the distribution away from that expected in thermal equilibrium. A positive φ increases the number of phonons at higher energies; a negative φ decreases that number. The terms of higher order allow further generality, but are not important in establishing the general features of second sound.

The moments can be written as a constant part and a small variable part:

$$\langle n \rangle = \langle n \rangle_0 + \langle n \rangle_1,$$
$$\langle n\mathbf{v} \rangle = 0 + \langle n\mathbf{v} \rangle_1,$$
$$\langle E \rangle = \langle E \rangle_0 + \langle E \rangle_1, \quad (3.13)$$
$$\langle n\epsilon\mathbf{v} \rangle = 0 + \langle n\epsilon\mathbf{v} \rangle_1,$$
$$\langle \Pi \rangle = 0 + \langle \Pi \rangle_1,$$
$$\langle \mathbf{v}_j \pi_i \rangle = \langle \mathbf{v}_j \pi_i \rangle_0 + \langle \mathbf{v}_j \pi_i \rangle_1.$$

All the constant terms are to be associated with the f_0 term in the distribution function. Since these moments are only to be used in the differential Eqs. (3.5)–(3.7), there will be no contribution from the constant terms and they need not be considered further.

In macroscopic lattices the phonon level spacing is small and the summation can be performed by integration. These integrals can be broken into a sum of terms, one for each term in the expansion of the distribution function:

$$\langle n \rangle_1 = \langle n \rangle_\lambda + \langle n \rangle_{T_1} + \langle n \rangle_\varphi + \langle n \rangle_u \cdots . \quad (3.14)$$

An examination of the form of these moments shows that every power of k inside the integral requires another power of T_0 to make the integral dimensionless. All terms of higher power in k will be of correspondingly higher powers of T/Θ_D. At low temperatures. $T_0 \ll \Theta_D$,

the effect of these higher order terms in the density is negligible. This reasoning holds for all the moments needed in the moment equations.

For the rest of this development the terms in the distribution function with powers of k higher than two will therefore be neglected. The term $\varphi \hbar^2 k^2 f^0(f^0 + 1)$ will be an estimate of our ability to describe the system as having temperature variations and net drift velocities. If this term is large, the system can no longer be described well in thermodynamic terms. The evaluation of these moments is straightforward. For isotropic materials, the results are

$$\langle n \rangle_1 = AT_1 + B_\varphi \approx AT_1 + (CT_0/\langle v^2 \rangle_{\text{av}})\varphi, \quad (3.15)$$

$$\langle n\mathbf{v} \rangle_1 = F\lambda \approx \tfrac{1}{3} AT_0 \lambda, \quad (3.16)$$

$$\langle E \rangle_1 = CT_1 + D\varphi, \quad (3.17)$$

$$\langle n\epsilon\mathbf{v} \rangle = N\lambda \approx \tfrac{1}{3} CT_0 \lambda, \quad (3.18)$$

$$\langle \Pi \rangle = Y\lambda \approx \tfrac{1}{3}(CT_0/\langle v^2 \rangle_{\text{av}})\lambda, \quad (3.19)$$

$$\langle \mathbf{v}_j \pi_i \rangle = \gamma CT_1 + \gamma D\varphi \approx \tfrac{1}{3}CT_1 + \tfrac{1}{3}D\varphi. \quad (3.20)$$

Because normal collisions involve phonons of different branches of the phonon spectrum, the constants in Eqs. (3.15)–(3.20) must be appropriate averages over the branches. For example,

$$N = \frac{1}{8\pi^3} \sum_\sigma \int_\Omega \int_0^{Q_\sigma} \hbar v_\sigma k(v_\sigma \cos\theta) \frac{\hbar k \cos\theta}{k_B T_0} f^0(f^0 + 1)k^2 dk d\Omega$$

$$\approx \sum_\sigma \frac{1}{v_\sigma{}^3} J_4\left(\frac{\Theta_\sigma}{T_0}\right), \quad (3.21)$$

and

$$Y = \frac{1}{8\pi^3} \sum_\sigma \int_\Omega \int_0^{Q_\sigma} \hbar k \cos\theta \frac{\hbar k \cos\theta}{k_B T_0} f^0(f^0 + 1)k^2 dk d\Omega$$

$$\approx \sum_\sigma \frac{1}{v_\sigma{}^5} J_4\left(\frac{\Theta_\sigma}{T_0}\right). \quad (3.22)$$

In these equations, σ is the phonon branch index, J_4 is the fourth-order Debye function, Q_σ is the maximum $\mathbf{q}$ value of branch σ, Ω is the total solid angle, and Θ_σ is the Debye temperature for branch σ. The other constants are functions of T_0, but not of T_1, λ, etc. The constant C is the specific heat. The simplifications indicaded in Eqs. (3.5)–(3.22) are valid in the Debye approximation. Details of the integration have been described by Prohofsky.[6]

Although phonons behave like Bose particles, their number is not necessarily conserved on collision. In fact, one expects three-phonon collisions to be the dominant type at low temperatures. The equation given by Ziman[7] for the collision rate of three-phonon colli-

[6] E. W. Prohofsky, thesis, Cornell University, 1963 (unpublished).

[7] J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, England, 1960), p. 275.

sions is

$$\Delta n_3 = \int\int\int [\alpha_k - \alpha_{k'} - \alpha_{k''}] P_k{}^{k'k''} d^3k\, d^3k'\, d^3k'', \quad (3.23)$$

where $P_k{}^{k'k''}$ is the equilibrium probability of phonon k splitting into phonons k' and k''. $P_k{}^{k'k''}$ contains factors which insure that the net change in the $\mathbf{k}$ vector is either zero or a reciprocal-lattice vector, and that the total energy is conserved. In our terminology,

$$\alpha_k = \frac{1}{k_B T_0}(\boldsymbol{\lambda} \cdot \hbar\mathbf{k} + \epsilon_k T_1/T_0 + \varphi \hbar^2 k^2). \quad (3.24)$$

One can assume that relaxation times involve averages weighted by the energy content of the modes. Under these conditions, the collision terms are shown in Appendix A to be

$$\Delta n_{3\,\text{col}} = -(CT_0/\langle v^2\rangle_{\text{av}})(1/\tau)\varphi, \quad (3.25)$$

$$\Delta \epsilon_{\text{col}} = 0, \quad (3.26)$$

$$\Delta \pi_{\text{col}} = -(CT_0/\langle v^2\rangle_{\text{av}})(\tfrac{1}{3})(1/\tau_U)\boldsymbol{\lambda}, \quad (3.27)$$

$$1/\tau = 1/\tau_N + 1/\tau_U. \quad (3.28)$$

τ_N is the relaxation time for all interactions which conserve crystal momentum within the phonon distribution. τ_U is the relaxation time for all interactions in which crystal momentum is lost by the phonon distribution. We may generalize τ_U to include all crystal momentum losing processes such as boundary and impurity scattering. It is emphasized that these relaxation times are weighted averages over the phonon distribution.

If higher-order collisions are considered, the form of the collision terms remains the same. The relaxation times, of course, become more complicated functions.

The moments can be substituted into the moment Eqs. (3.5)–(3.7) to give the "phonon gas equivalents" of the linearized hydrodynamic equations

$$(\partial/\partial t)(AT_1 + B\varphi) + \text{div} f\boldsymbol{\lambda} = -(CT_0/\langle v^2\rangle_{\text{av}}\tau)\varphi, \quad (3.29)$$

$$(\partial/\partial t)(CT_1 + D\varphi) + \text{div} N\boldsymbol{\lambda} = 0, \quad (3.30)$$

$$(\partial/\partial t)Y\boldsymbol{\lambda} + \gamma\, \text{grad}(CT_1 + D\varphi)$$
$$= -(CT_0/3\langle v^2\rangle_{\text{av}}\tau_U)\boldsymbol{\lambda}. \quad (3.31)$$

The coefficients A, C, D, etc. are functions only of the material and its ambient temperature T_0. The only parameters to vary with time and space are T_1, $\boldsymbol{\lambda}$, and φ.

IV. PROPAGATION SOLUTIONS

To find a solution which would be similar to a plane wave of second sound, assume

$$T_1 = T_1{}^0 \exp[i(\omega t - \mathbf{q}\cdot\mathbf{r})], \quad (4.1)$$

$$\boldsymbol{\lambda} = \boldsymbol{\lambda}^0 \exp[i(\omega t - \mathbf{q}\cdot\mathbf{r})], \quad (4.2)$$

$$\varphi = \varphi^0 \exp[i(\omega t - \mathbf{q}\cdot\mathbf{r})]; \quad (4.3)$$

substituting into Eqs. (3.30)–(3.32)

$$i\omega AT_1{}^0 + [i\omega B + (CT_0/\langle v^2\rangle_{\text{av}}\tau)]\varphi^0 - i\mathbf{q}\cdot\boldsymbol{\lambda}^0 F = 0, \quad (4.4)$$

$$i\omega CT_1{}^0 + i\omega D\varphi^0 - i\mathbf{q}\cdot\boldsymbol{\lambda}^0 N = 0, \quad (4.5)$$

$$i\gamma\mathbf{q} CT_1{}^0 - i\gamma\mathbf{q} D\varphi^0 + [i\omega Y + (CT_0/\langle 3v^2\rangle_{\text{av}}\tau_U)]\boldsymbol{\lambda}^0 = 0. \quad (4.6)$$

From Eq. (4.6) it can be seen that $\mathbf{q} \| \boldsymbol{\lambda}^0$ and the vectorial notation may be dropped. For the plane wave to exist, these equations must have a solution; i.e., the determinant of the coefficient of the parameters $T_1{}^0$, $\boldsymbol{\lambda}^0$, and φ^0 must equal zero. The solutions are

$$\left(\frac{\omega}{q}\right)^2 = \frac{\gamma N}{Y + (CT_0/3i\omega\tau_U\langle v^2\rangle_{\text{av}})} \approx \frac{\langle v^2\rangle_{\text{av}}}{3}, \quad (4.7)$$

$$\omega = \frac{iC^2 T_0}{\langle v^2\rangle_{\text{av}}\tau(CB - AD)}. \quad (4.8)$$

Equation (4.7) corresponds to forward and backward propagation of second sound. In Eq. (4.8), ω is imaginary, hence this solution corresponds to a pure decay mode.

The relationships between λ^0, φ^0, and $T_1{}^0$ can be found from Eqs. (4.4)–(4.6).

$$\lambda^0 = -\frac{\omega}{q}\frac{CB - AD + (C^2T_0/i\omega\tau\langle v^2\rangle_{\text{av}})}{NB - FD + (NCT_0/i\omega\tau\langle v^2\rangle_{\text{av}})}T_1{}^0. \quad (4.9)$$

$$\varphi^0 = -\frac{AN - CF}{NB - DF + (CT_0/i\omega\tau\langle v^2\rangle_{\text{av}})}T_1{}^0. \quad (4.10)$$

If the pure imaginary solution Eq. (4.8) is substituted into Eq. (4.9)

$$\lambda = 0. \quad (4.11)$$

Hence, solution (4.8) applies to temperature fluctuations which have no associated transport. Where a net quasi-momentum exists, only umklapp collisions [Eq. (4.7)] can cause relaxation.

Equation (4.10) bears out the assumption that for $\omega\tau \ll 1$, $\varphi \to 0$. In this limit, the system can be described as a temperature wave with very small higher-order distortions. The dispersion relations for the second-sound wave [Eq. (4.7)] can be reduced to

$$q^2 = (3\omega^2/\langle v^2\rangle_{\text{av}}[1 + (i\omega\tau_U) - 1] \quad (4.12)$$

for spherical symmetry. This can be solved for real and imaginary parts:

$$q_R{}^2 = (3\omega^2/2\langle v^2\rangle_{\text{av}})\{1 + [1 + (\omega\tau_U)^{-2}]^{1/2}\} \quad (4.13)$$

$$q_I{}^2 = (3\omega^2/2\langle v^2\rangle_{\text{av}})\{[1 + (\omega\tau_U)^{-2}]^{1/2} - 1\}. \quad (4.14)$$

The expected second-solution occurs when the damping due to umklapp collisions is small, i.e., $\omega\tau_U \ll 1$. In this limit Eqs. (4.13) and (4.14) lead to

$$v_{\text{II}} = \frac{\omega}{q_R} = \left(\frac{\langle v^2\rangle_{\text{av}}}{3}\right)^{1/2}[1 - \tfrac{1}{8}(\omega\tau_U)^{-2} + \cdots] \approx \frac{\langle v_{\text{I}}\rangle_{\text{av}}}{\sqrt{3}}, \quad (4.15)$$
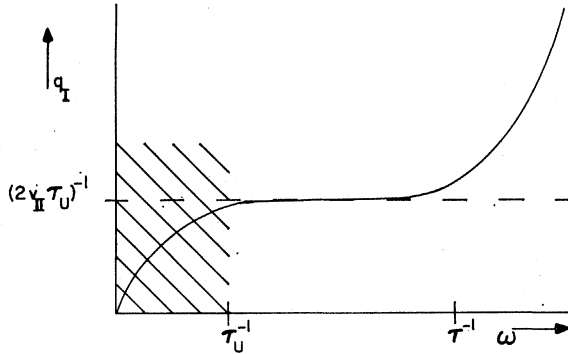
FIG. 2. Damping as a function of second-sound frequency. The frequency "window" $\tau_U^{-1} < \omega < \tau^{-1}$ is the region of second-sound propagation. In the cross-hatched area, the real and imaginary parts of the wave vector for second sound are equal, hence no harmonic propagation exists; it is the region of ordinary thermal conductivity. In the region for which $\omega > \tau^{-1}$, second sound is damped by "second viscosity"; thermal conductivity is limited by boundary scattering.

where

$$\langle v_I \rangle_{av} = \left(\frac{N}{Y}\right)^{1/2} \approx \left[\frac{\sum_\sigma (1/v_\sigma^3) J_4(\Theta_\sigma/T_0)}{\sum_\sigma (1/v_\sigma^5) J_4(\Theta_\sigma/T_0)}\right]^{1/2} \quad (4.16)$$

and

$$q_I \approx -\tfrac{1}{2} 1/v_{II}\tau_U. \quad (4.17)$$

Applying the limit $\omega\tau_U \ll 1$ to Eq. (4.9) gives

$$\lambda^0 = \omega/q(C/N)T_1^0, \quad (4.18)$$

and Eqs. (4.13) and (4.14) become

$$q_R^2 = q_I^2 = 3\omega/2\langle v^2 \rangle_{av}\tau_U. \quad (4.19)$$

The limit given in Eq. (4.19) will be shown to be equivalent to the usual equation of thermal conductivity in Sec. V.

When the combined relaxation rate τ^{-1} is small, i.e., at very high frequencies, we would expect individual phonons to travel unhindered from one region to the next and any disturbance will propagate with the velocity v_I rather than v_{II}. As $v_{II} \approx \langle v_I \rangle_{av}/\sqrt{3}$, it is clear that second-sound is a statistically collective propagation utilizing the phonons, and cannot be maintained for $\omega\tau \gg 1$.

To the second-sound wave the lack of normal collisions appears as a leaking of particles out of the coherent wave. We follow the treatments of related problems in liquid helium[8] and suggest that the effects of this loss can be described in terms of a "second viscosity." The wave propagation will be expected to have velocity v_I in the "collision-free" situation ($\omega\tau \gg 1$) and to have second-sound velocity v_{II} in the completely satistical situation ($\omega\tau \ll 1$). Large dispersion due to "second viscosity" will occur for $\omega\tau \approx 1$

This situation is treated quite generally by Landau

and Lifshitz.[9] Their results, when applied to this situation, give an additional imaginary part q_I' to the second-sound wave vector:

$$q_I' = (-\omega^2\tau/2v_{II}^3)(v_I^2 - v_{II}^2) \approx -\omega^2\tau/v_{II}. \quad (4.20)$$

The total imaginary part of the wave vector in the second-sound region ($\omega\tau_U \gg 1$) then becomes

$$q_I \approx (-1/v_{II})[(1/2\tau_U) + \omega^2\tau]. \quad (4.21)$$

The imaginary part of the wave vector is shown as a function of ω in Fig. 2. It can be seen from Eqs. (4.14) and (4.21) that the conditions for second-sound propagation are

$$\tau_U^{-1} < \omega < \tau^{-1}. \quad (4.22)$$

V. THERMAL CONDUCTIVITY AND THE DIFFUSION LIMIT

The amount of thermal energy transferred by the phonon system is the moment $\langle n\epsilon v \rangle$ from Eq. (3.18):

$$Q = \langle n\epsilon v \rangle = N\lambda,$$

where N is related to the total energy density of the system. From Eq. (3.9), λ is seen to be a net drift velocity of the excitations when the assumptions about the distribution function hold. In the spherically symmetric approximation

$$Q = \tfrac{1}{3} C T_0 \lambda. \quad (5.1)$$

In the case of phonons, this is equivalent to the product of the total energy density and the drift velocity. This formula is identical to that appearing in the expression for superfluid heat transfer.

If one now substitutes Eq. (4.18) into Eq. (5.1),

$$Q = N(\omega/q)(C/N)T_1 = CT_1(\omega/q), \quad (5.2)$$

and for $\omega\tau_u \gg 1$

$$q_I \approx 0; \quad (5.3)$$

whence

$$\omega/q \approx \omega/q_R = v_{II} \quad (5.4)$$

and

$$Q = CT_1 v_{II}. \quad (5.5)$$

Equations (5.1) and (5.5) both describe heat transfer. Equation (5.1) applies to the transfer of energy by a fluid flow, whereas Eq. (5.5) describes propagation of the energy by a wavelike mechanism.

Equation (5.2) can be written in the more usual form involving a temperature gradient, as

$$T_1 = T_1^0 \exp i(\omega t - \mathbf{q}\cdot\mathbf{r}) \quad (4.1)$$

$$\operatorname{grad}T = T_1^0(-iq)[\exp i(\omega t - \mathbf{q}\cdot\mathbf{r})]; \quad (5.6)$$

whence

$$Q = C(\omega/-iq^2)\operatorname{grad}T_1, \quad (5.7)$$

[8] C. T. Lane, *Superfluid Physics* (McGraw-Hill Book Company, Inc., New York, 1962), p. 67.

[9] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon Press, Ltd., London, 1959), p. 304.

and in the limit, where $\omega\tau_U\ll1$,

$$q_R{}^2=q_I{}^2=3\omega/2\langle v^2\rangle_{\mathrm{av}}\tau_U \qquad (4.19)$$

$$Q=C\tfrac{1}{3}\langle v^2\rangle_{\mathrm{av}}\tau_U\ \mathrm{grad}T. \qquad (5.8)$$

This is the equation found in the usual derivation of thermal conductivity if the heat-current relaxation is very rapid. The region of $\omega\tau_U\ll1$, then, is the usual diffusive thermal conductivity region, as noted in the qualitative discussion in Sec. II.

VI. FEASIBILITY OF EXPERIMENTAL OBSERVATION

In order for second sound to be possible in solids, there must exist an appreciable difference between the reciprocal normal and reciprocal umklapp relaxation times. At low temperatures, the normal relaxation time varies as some power of T_0, while the umklapp relaxation time varies exponentially with T_0. It therefore seems reasonable that, below some temperature, a "window" will appear in the frequency spectrum wherein the propagation of second-sound becomes possible.

A rough experimental evaluation of the relaxation times can be obtained from thermal conductivity measurements. The relaxation times shown in Table I are average relaxation times as defined in Eqs. (3.25),(3.27), (3.28), computed by us and based on data by Walker.[10] At about 10°K, the calculated τ_U and τ_N differ by more than a factor of 10^4, indicating that a frequency in the range 10^3–10^5 sec^{-1} should satisfy the inequalities of Eq. (4.22).

In Table I, ν_c represents the frequency at which heat conduction becomes more like fluid flow than diffusion. Above 15°K, no second-sound effects would be seen for frequencies below 1 Mc/sec. Below 9°K, second sound could be present for frequencies above one cycle/sec, were it not for the decreased probability of normal collisions.

The column $\nu_c/2$ in Table I represents the damping of the second-sound wave by umklapp processes; $\frac{1}{3}\omega^2\tau_N$ shows the damping due to second viscosity; and ω_I which is the total damping given by $\omega_I=q_I/v_{II}$. All these figures are for $\omega=10^5$ sec^{-1}. The smallest total damping occurs at 10°K, at which temperature the dissipation is not so large as to rule out experimental observation

of second sound. It should be emphasized that the foregoing statements in this section apply only in an infinite, pure crystal. In a real experiment, allowances must be made for boundary and impurity scattering.

In either a pulse experiment or a standing-wave experiment, it is essential that a major fraction of a wavelength be contained within the crystal. With the usual size of pure crystals (~1 cm), frequencies of the order of 10^5 sec^{-1} are necessary because of the large velocity of sound (10^5 cm/sec). The generation and detection of these high frequencies make the observation of second sound in solids more difficult than is the case in liquid helium (where $v_I\sim10^3$ cm/sec), where lower frequencies can be used. An additional consequence of the use of higher frequencies is the increased damping due to second viscosity.

It may therefore be necessary to use much larger crystals in order to observe the effect. A larger crystal would permit the use of lower frequencies and would thereby reduce the effect of second viscosity. The experiment could then be performed at lower temperatures, where damping by umklapp processes is diminished.

The ease with which second sound can be propagated in a given material can qualitatively be determined from curves showing thermal conductivity as a function of temperature. A large value of the maximum low-temperature thermal conductivity indicates a long umklapp relaxation time, which, in turn, suggests small amounts of umklapp damping of second-sound waves. The size of the crystal used in the measurement of the thermal conductivity determines the minimum wavelength for which a collective wave may be propagated in that crystal at the temperature of the conductivity peak. Therefore, for a crystal and frequency appropriately matched, the optimum temperature for observation of second sound will be slightly higher than that of the conductivity peak.

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APPENDIX A

We wish to show and define the relevant moment transfer via collision terms listed in Eqs. (3.25)–(3.27). Let $\Delta n_{3\lambda}$ be associated with the contribution to Δn_3 from the λ term in α_k of Eq. (3.12). Let Δn_{3T} be associated with the T_1 term, etc.

$$\Delta n_{3\lambda}=\int\int\int\frac{\lambda\cos\theta}{k_BT_0}(k-k'-k'')P_k{}^{k'k''}d^3k. \qquad (A1)$$

For normal processes,

$$\Delta n_{3\lambda}=0. \qquad (A2)$$

TABLE I. Computed relaxation times and damping coefficients as a function of temperature in sodium fluoride.

°K	τ_U (sec)	$\nu_c=1/\tau_U$ (sec^{-1})	τ_N (sec)	$\nu_c/2$ (sec^{-1})	$\frac{1}{3}\omega^2\tau_N$ (sec^{-1})	ω_I (sec^{-1})
20	2.2×10^{-7}	4.9×10^6	1.6×10^{-8}	2.4×10^6	5.5×10^1	2.4×10^6
15	5.2×10^{-6}	1.9×10^5	7.0×10^{-8}	9.1×10^4	2.3×10^2	9.1×10^4
12	1.1×10^{-4}	9.5×10^3	2.1×10^{-7}	4.7×10^3	7.1×10^2	5.4×10^3
11	3.8×10^{-4}	2.7×10^3	4.3×10^{-7}	1.3×10^3	1.4×10^3	2.8×10^3
10	1.9×10^{-3}	5.4×10^2	5.3×10^{-7}	2.7×10^2	1.8×10^3	2.0×10^3
9	1.1×10^{-2}	8.8×10^1	9.0×10^{-7}	4.4×10	3.0×10^3	3.0×10^3
7	2.2	4.6×10^{-1}	3.2×10^{-6}	2.3×10^{-1}	1.0×10^4	1.0×10^4
5	7.9×10^3	1.3×10^{-4}	1.7×10^{-5}	6.3×10^{-5}	5.7×10^4	5.7×10^4

[10] C. T. Walker (private communication).

For processes in which quasimomentum is lost,

$$\Delta n_{3\lambda} = -\sum_G \frac{\boldsymbol{\lambda}\cdot\mathbf{G}}{kBT_0}\frac{1}{\tau_G}. \tag{A3}$$

τ_G is the relaxation time associated with an umklapp process in which crystal momentum $\hbar G$ is lost.

In the symmetric case we can assume that the G vectors have reflection symmetry and that the sum over G includes both a positive term and a negative term for each magnitude of G. Therefore, Eq. (A3) is also zero.

$$\Delta n_{3T} = \int\int\int \frac{T_1}{kBT_0{}^2}(\epsilon_k - \epsilon_{k'} - \epsilon_{k''})P_k{}^{k'k''}d^3k = 0, \tag{A4}$$

as $(\epsilon_k - \epsilon_{k'} - \epsilon_{k''}) = 0$ for all collisions.

$$\Delta n_{3\varphi} = \int\int\int \frac{\varphi\hbar^2}{k_BT_0}(k^2 - k'^2 - k''^2)P_k{}^{k'k''}d^3k. \tag{A5}$$

The contribution to the specific heat of a single mode is

$$dC = \frac{1}{k_BT_0{}^2}\hbar^2v^2k^2f^0(f^0+1)\frac{d^3k}{(2\pi)^3}. \tag{A6}$$

Using Eq. (A6) and the usual assumptions concerning averaging of relaxation times weighted by the energy content of the single-particle modes we can rewrite Eq. (A5) as

$$\Delta n_{3\varphi} = \frac{T_0}{v^2}\int\int\int \frac{\varphi\hbar^2v^2}{k_BT_0{}^2}(k^2 - k'^2 - k''^2)P_k{}^{k'k''}d^3k, \tag{A7}$$

$$\Delta n_{3\varphi} = -\frac{T_0}{\langle v^2\rangle_{av}}\frac{C}{\tau}\varphi. \tag{A8}$$

Here, C/τ represents a reciprocal collision relaxation time weighted with the energy content of the various modes and

$$1/\tau = 1/\tau_N + 1/\tau_U. \tag{A9}$$

The $\Delta\epsilon_{col}$ term in Eq. (3.2) can be found by multiplying each collision in Eq. (3.23) by $(\epsilon_k - \epsilon_{k'} - \epsilon_{k''})$. This factor will be zero for all allowed collisions. The energy is conserved at all times.

$$\Delta\epsilon_{col} = 0. \tag{A10}$$

The $\Delta\pi_{i\,col}$ term similarly can be found by multiplying Eq. (3.23) by $\hbar(k - k' - k'')\cos\theta$.

$$\Delta\pi_{i\,col} = +\frac{\hbar}{k_BT_0}\int\int\int (k - k' - k'')$$

$$\times\cos\theta(\alpha_k - \alpha_{k'} - \alpha_{k''})P_k{}^{k'k''}d^3k \tag{A11}$$

$$= +\frac{\hbar^2\lambda_i}{k_BT_0}\int\int\int (k - k' - k'')^2$$

$$\times\cos^2\theta P_k{}^{k'k''}d^3k \tag{A12}$$

$$= 0 \text{ for normal processes}, \tag{A13}$$

$$= -\frac{T_0}{\langle v^2\rangle_{av}}\frac{1}{3}\frac{C}{\tau_U}\lambda_i. \tag{A14}$$

By symmetry arguments,

$$\Delta\pi_{Tcol} = \Delta\pi_{\varphi col} = 0. \tag{A15}$$