course, the ultimate solution of this problem involves the intrinsic mechanisms of A.S.R., which are not known at present. Several reasons for its coherency are, however, as follows:

(i) The wavelength hardly changes.

(ii) The beam is comparatively sharp.

(iii) The glancing angle depends on the wavelength, as expressed in Fig. 6.

(iv) A close relation to the coherent equiangular reflection is found as shown in Fig. 8.

It is seen from Fig. 7 that α has an important relation to the periodic law. This fact leads to a presumption that A.S.R. is different to some extent from the ordinary Thomson scattering. The angles α of the elements Au, Ag, and Cu are large and occupy peak positions of the curve in Fig. 7. From the fact that these three elements all belong to Group I and Series b in the Periodic Table, we can presume that A.S.R. has an important relation to the valence electrons. In this case, the behavior of the valence electrons on the surface of the material has to be considered. No definite explanation seems to be known so far as to what behavior the surplus valence electrons on the surface have, and the measurement of A.S.R. seems to offer a clue for investigating their characteristics.

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Second Sound in Solids

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A critical frequency for thermal fluctuations is calculated above which heat transport proceeds by wave propagation rather than by diffusion. This phenomenon should occur in some dielectric solids. It is the analog of second sound in helium II. A macroscopic point of view is used which relies upon a modification in the Fourier heat equation. Some quantitative results are obtained on the magnitude of this modification.

1. INTRODUCTION

EVER since the initial experiments of Peshkov[1,2] exhibiting second sound in liquid helium, considerable speculation and effort has been devoted to the possible existence of this phenomenon is solids. This effort has been stimulated, in the main, by those theories[3-6] of second sound which depend only upon the presence of a phonon gas. Since phonon gas excitations exist in any solid, second sound should be detectable in solids as well as in liquid helium. We propose that thermal waves should, indeed, be detectable in many substances but that there is a critical frequency for the onset of the phenomenon. This idea is current and has been elegantly presented by Prohofsky[7] from a microscopic point of view. Here we wish to relate the idea, heuristically, to a well-known paradox of heat transport and to derive some simple quantitative predictions on this basis. Our point of view is essentially macroscopic.

2. THERMAL DIFFUSION

It is well known that the diffusion equation for thermal transport results from the following two elementary considerations: The first is a statement of the continuity equation for heat transport in the absence of density or pressure gradients. This is given by

$$C\frac{\partial T}{\partial t}+\nabla\cdot\mathbf{q}=0, \tag{1}$$

where C is the heat capacity per unit volume, T is the absolute temperature, $\mathbf{q}$ is the thermal heat current density, t represents time, and ∇ is the spatial gradient operator. If this equation is combined with the phenomenological Fourier equation of thermal conductivity for heat flow in a solid,

$$\mathbf{q}=-K\nabla T, \tag{2}$$

the diffusion equation results. In Eq. (2), K is the thermal conductivity. But a much more physically

[1] V. Peshkov, J. Phys. U.S.S.R. **8**, 131 (1944).

[2] V. Peshkov, in *Report of an International Conference on Fundamental Particles and Low Temperatures* (The Physical Society, London, 1947), p. 19.

[3] F. London, *Superfluids* (John Wiley & Sons, Inc., New York, 1954), Vol. II, p. 101.

[4] J. C. Ward and J. Wilks, Phil. Mag. **42**, 314 (1951).

[5] J. C. Ward and J. Wilks, Phil. Mag. **43**, 48 (1952).

[6] R. B. Dingle, Proc. Phys. Soc. (London) **A65**, 374 (1952).

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

intuitive picture of heat transport is obtained if, instead of the conductivity K, we choose to think in terms of a thermal resistivity,

$$\rho = 1/K.\tag{3}$$

The diffusion equation which results from the combination of (1) and (2) is the well known

$$\rho C\frac{\partial T}{\partial t} - \nabla^2 T = 0.\tag{4}$$

3. MODIFIED FOURIER HEAT EQUATION

As has been pointed out by many people,[8-10] the diffusion equation leads to an infinite propagation velocity for a finite thermal pulse. Such a state of affairs is clearly not physical and a number of explanations have been proposed for the dilimma. One of these has a long and venerable history[11,12] and a clear physical interpretation. The dilemma is resolved by noting that the Fourier heat equation, (2), is an approximation to a more exact equation

$$\tau\frac{\partial \mathbf{q}}{\partial t} + \mathbf{q} = -K\nabla T,\tag{5}$$

where τ is a relaxation time.

Equation (5) is a truncated form of an extensive relation which includes pressure and density spatial variations and which may be derived from kinetic theory in the case of an ideal gas. Such an equation was obtained by Maxwell,[11] who, realizing the magnitude of τ appropriate to his problem, casually cast out the time derivative term with a remark that it may be neglected because "the rate of conduction will rapidly establish itself." He was certainly right for the case he was treating. The more sophisticated and elaborate treatment by Grad[12] also unearths the time derivative term of Eq. (5) plus a number of other corrections to the Fourier heat equation. All of the latter depend upon the spatial variation of mechanical properties in the medium. These extra corrections are not germane to the matters which follow so we will ignore them here. However, they must certainly be included in a careful treatment dealing with a practical experimental situation. We restrict ourselves to a medium in which no spatial pressure or density variations obtain.

It should also be remarked here that the modifications to the Fourier heat equation which have been obtained theoretically have been derived for ideal gases only and not for the case at hand where the "gas" is that of excitations (or phonons). Hence, Eq. (5) still retains, somewhat, the nature of a hypothesis since it has not

been established generally either experimentally or theoretically.

The physical significance of Eq. (5) is simple. It states that there is a finite buildup time for the onset of a thermal current after a temperature gradient is clamped onto a specimen. The heat flow does not start instantaneously but rather grows gradually with a relaxation time τ. Conversely, if a thermal gradient is suddenly removed there is a lag in the disappearance of the heat current and Eq. (5) exhibits just such a relaxation, whereas Eq. (2) does not. The relaxation time τ is associated with the communication "time" between phonons (phonon-phonon collisions) for the commencement of resistive flow.

In fact, the rate $1/\tau$ must be connected with thermal resistance because τ is the time for the establishment of resistive flow. The rate $1/\tau$ refers to the frequency of collisions of a "lossful" nature, i.e., those which give rise to a thermal resistance. It is expected, therefore, that τ is proportional to K.

There is a total collision rate, R, which is higher than $1/\tau$. The rate R encompasses all types of collisions including "lossless" ones which do not give rise directly to thermal resistance.[13,14] The total collision rate R establishes an upper frequency, f_R, for phonon-distribution fluctuations, above which the concept of temperature loses its meaning. The thermal equilibrating rate is of the order of R. This means that the time $1/R$ is that necessary to establish local thermal equilibrium. This time is less than τ, the time to establish steady state resistive flow. The temperature variations contemplated here are less rapid than R but may be faster than $1/\tau$.

4. THERMAL WAVES

If instead of employing Eq. (2) in combination with (1) to obtain the differential equation for temperature, one uses the more "exact" equation (5), the result is

$$\frac{\partial^2 T}{\partial t^2} + \frac{1}{\tau}\frac{\partial T}{\partial t} - \frac{K}{\tau C}\nabla^2 T = 0,\tag{6}$$

and the temperature T is found to obey a dissipative wave equation.

It is clear that Eq. (6) resolves the dilemma of infinite propagation for a thermal signal. In fact, Eq. (6) predicts a finite upper limiting velocity for the propagation of a thermal signal. The limiting velocity, v, is given by

$$v^2 = K/\tau C\tag{7}$$

and, indeed, the modification contained in (5) was motivated by the need to produce just such a finite "propagation" velocity. Also it is to be noted that

[8] C. W. Ulbrich, Phys. Rev. 123, 2001 (1961).
[9] P. Vernotte, Compt. Rend. 246, 3154 (1958).
[10] C. Cattaneo, Compt. Rend. 247, 431 (1958).
[11] J. C. Maxwell, Phil. Trans. Roy. Soc. 157, 49 (1867).
[12] H. Grad, in Handbuch der Physik, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 12, p. 271.

[13] J. M. Ziman, Electrons and Phonons (Clarendon Press, Oxford, 1960), p. 289.
[14] P. G. Klemens, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 4.

Eq. (6) reduces, as it must, to the diffusion equation in the limit of slow time variations of temperature.

The interesting aspect of Eq. (6) obtains in the high-frequency limit of fast thermal fluctuations. If T varies at a rate, $f = (1/2\pi)(1/T)(\partial T/\partial t)$, much faster than $f_c = 1/2\pi\tau$, then Eq. (6) predicts wave propagation of temperature instead of diffusion. The frequency f_c is the critical frequency for the onset of thermal waves. This frequency is directly proportional to the thermal resistivity. It is zero if the thermal resistivity is zero.

5. EVALUATION OF τ

The interesting and important question about the foregoing concerns the value of τ. This is the crucial parameter. It determines the critical frequency and the attenuation of the "thermal wave." It is at this point that our discussion diverges from the previous work of Ulbrich and Vernotte. We evaluate τ quantitatively on the physical grounds that the square of the thermal wave propagation velocity v^2 must be just one third of the square of the phonon velocity, s^2, in the medium.

$$v^2 = \tfrac{1}{3}s^2. \tag{8}$$

This, of course, is only true for a medium in which the transport of heat occurs via the phonon gas. It may not be true, for example, in an electrical conductor. It would obtain though for an insulating solid or for a fluid.

The deduction of Eq. (8) is based on the following. The thermal wave ($f > 1/2\pi\tau$) constitutes a coherent propagation of density disturbances in the phonon gas. This is what one would mean by a temperature wave. And this is precisely the description used for the case of second sound in liquid helium II. Now, the limiting velocity of propagation of second sound (low-temperature limit) has been calculated theoretically on just this notion of the transport of a phonon density disturbance.[3-6] Ward and Wilks[4,5] were the first to calculate the velocity of second sound with this model in place of the two-fluid one used by Landau.[15] Their result was the same as Landau's and is that exhibited in Eq. (8).

Equation (8) can be understood physically in the following manner for the case of liquid helium. The phonons may be viewed as a gas of particles, each of which moves with the same speed s. (We limit ourselves here, of course, to an idealized elastic medium which is dispersionless.) The phonons move in random directions, however. Therefore, the average root mean square velocity of a group of phonons in any one particular direction is

$$v = s/\sqrt{3}.$$

[15] L. Landau, J. Phys. U.S.S.R. 5, 71 (1941).

This results from the combination of

$$s^2 = s_x{}^2 + s_y{}^2 + s_z{}^2, \tag{9}$$

with

$$\langle s_x{}^2\rangle_{\mathrm{av}} = \langle s_y{}^2\rangle_{\mathrm{av}} = \langle s_z{}^2\rangle_{\mathrm{av}} = v^2. \tag{10}$$

In particular, an energy disturbance in the phonon gas is carried with this mean velocity, v, in the direction of propagation of the disturbance. The forgoing is not meant to constitute a proof of Eq. (8) but merely a physical view of it. Perhaps the clearest and most detailed derivation of Eq. (8) is given by London[3] in a section of his book entitled "Compression Waves of the Phonon Gas." There, following Ward and Wilks, he introduces the average momentum current density tensor which yields the factor $\tfrac{1}{3}$ in exact analogy to Eq. (10) and for the same reasons.

The connection to the case of solids is simply that a thermal wave represents the same microscopic phenomena whether it exists in He II or in a solid. A thermal wave is the propagation of a phonon density disturbance. Hence, such a wave should always propagate with a velocity, v, related by Eq. (8) to the sound (phonon) velocity, s. Indeed, the implication that second sound should exist in solids, since its appearance depends merely upon the presence of a phonon gas, was remarked upon by Ward and Wilks in their paper[4] and speculated upon by Peshkov[2] in his. However, no note was taken of the fact that there is a critical frequency for the onset of the phenomenon. For liquid He II this critical frequency is zero, but for other substances it is given by

$$f_c = \frac{1}{2\pi\tau} = \frac{s^2}{6\pi}\frac{C}{K}. \tag{11}$$

6. CONCLUSION

A quantitative estimate of the relaxation time τ in terms of known and measurable macroscopic parameters has been obtained [combination of Eqs. (7) and (8)].

$$\tau = \frac{3}{s^2}\frac{K}{C}. \tag{12}$$

And the connection to second sound or thermal wave propagation has been indicated with the result that there is a critical lower frequency, f_c, given by Eq. (11), below which thermal wave propagation will not exist. As noted earlier, there is also an upper frequency limit f_R above which the concept of temperature becomes hazy and again thermal waves will not exist.

With regard to the magnitudes involved and the practicality of detecting second sound in solids it should be mentioned that certain alkali halides—especially KCl—look promising if the experiment is carried out at low temperatures. We are undertaking experiments presently to detect the effect.