Scattering of Phonons by a Square-Well Potential and the Effect of Colloids on the Thermal Conductivity. I. Experimental*

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The thermal conductivity of sodium-chloride crystals containing silver colloids has been measured between 0.2 and 2°K. The effect of a transition from Rayleigh scattering to geometrical scattering is readily apparent in the results. Good agreement is obtained between the experimental values and thermal conductivities which were calculated assuming the colloids to be monodisperse spheres and using the bulk elastic constants for silver.

I. INTRODUCTION

THE use of the thermal conductivity as a (somewhat imperfect) tool for the study of phonon-scattering processes has become firmly established. Point defects have received a great deal of attention with particular emphasis recently on the resonance effects which sometimes appear.

It is the purpose of this research to investigate the scattering by a square-well potential. This simple case corresponds to the scattering of phonons by a sphere whose elastic properties differ from those of the matrix. The problem is to be considered in the continuum approximation. Thus the radius of the sphere must be large enough for this approximation to be meaningful, and colloids rather than point defects are of interest here.

The relationship between the scattering cross section and the thermal conductivity has been reviewed in a number of publications and will not be pursued any further here. Briefly, three pieces of information are required to account for the temperature dependence of the conductivity: (a) a solution to the transport equation; (b) a knowledge of the intrinsic scattering in the "pure" crystal; (c) a knowledge of the scattering cross section as a function of frequency for the defect being studied.

The scattering of a sound wave by an isotropic elastic sphere in an isotropic continuum has been treated by Ying and Truell[1] for an incident longitudinal wave, and by Einspruch *et al.*[2] for an incident transverse wave. These calculations are simply partial-wave analyses of the problem, and reliable numerical values for the cross section can be obtained from them for any value of the energy of the incident wave. It is possible, then, to obtain dependable theoretical information on the resonance and other phenomena which occur when the limit of applicability of the Born approximation is passed.

The most interesting effects can be expected to occur in the region where the wavelength of the incident wave is of the order of the radius of the colloid. Since rather large particles are being considered, these wavelengths will be relatively long, and they will manifest themselves through the thermal conductivity at low temperatures.

It will develop that these temperatures are well below that of the peak in the thermal conductivity. It is likely, then, that it will be possible to neglect the effect of phonon-phonon collisions. If this is justified, it is possible to solve the Boltzmann equation exactly, since all the scattering is elastic.[3] The temperatures of interest are temperatures which correspond to the boundary scattering region in the pure crystal. In our crystals the effect of residual defects and impurities may be neglected. Since phonon-phonon collisions can be neglected, the only scattering process intrinsic to the pure crystal will be that due to its boundaries, and this is relatively well understood. The interpretation of our results then should be on a somewhat firmer theoretical basis than normally is the case.

It is convenient to divide the scattering cross section as a function of wavelength into three regions where the wavelength is greater than, roughly equal to, or smaller than the size of the defect. In the first regime the total cross section should follow a Rayleigh law and vary as the fourth power of the frequency. In the second, it is difficult to generalize, but resonance effects may be expected. In the last, the cross section becomes constant. In this region the total cross section as calculated from the partial-wave analysis is twice the geometrical cross section of the sphere. This is the well-known extinction paradox. However, this need not cause any difficulty because the procedure outlined in Ref. 3 replaces the total cross section by the transport cross section which, in this limit, is equal to the geometrical cross section.

The last region has already been studied by Worlock[4]: He has measured the thermal conductivity of NaCl crystals containing silver colloids down to 1.2°K. His results indicate that down to this temperature all the scattering appears to be independent of phonon frequency.

Worlock has kindly made his crystals available and

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[1] C. F. Ying and R. Truell, J. Appl. Phys. **27**, 1086 (1956).

[2] N. G. Einspruch *et al.*, J. Appl. Phys. **31**, 806 (1960).

[3] R. E. Peierls, *Quantum Theory of Solids* (Clarendon Press, Oxford, England, 1955), p. 119.

[4] J. M. Worlock, Phys. Rev. **147**, 636 (1966).

the measurements have been extended to 0.23°K covering the first and second region. Of particular interest, then, are the effects of the transition from a Rayleigh law to a geometrical law and the possible effects of any peaks and valleys in the cross section.

It also develops that the scattering cross section, its dependence on phonon frequency, and the resulting thermal conductivity are a sensitive function of the size of the defect. Clearly, then, it is possible to use measurements of the thermal conductivity as a tool to investigate the sizes of precipitates. This technique is particularly useful since it is most sensitive to radii between about 10 and 100 Å.

II. EXPERIMENTAL

The samples consisted of four NaCl crystals containing various concentrations and sizes of metallic-silver colloids. Their preparation has been described in detail in Ref. 4. Our designation is identical to Worlock's, and we used crystals 6, 7, and 8.

The thermal-conductivity measurements were made in a ^{3}He cryostat capable of temperatures as low as 0.21°K. The cryostat is shown schematically in Fig. 1, and is described in Ref. 5.

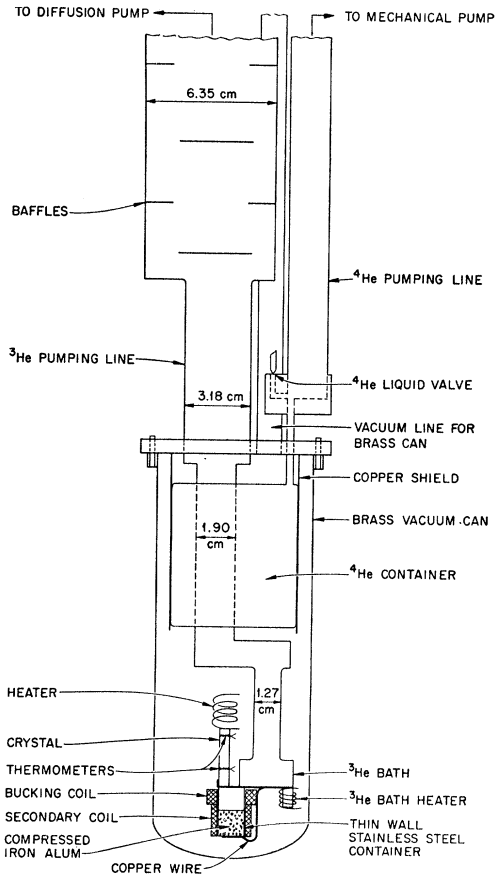

FIG. 1. ^{3}He cryostat.

[5] D. Walton, Rev. Sci. Instr. 37, 734 (1966).

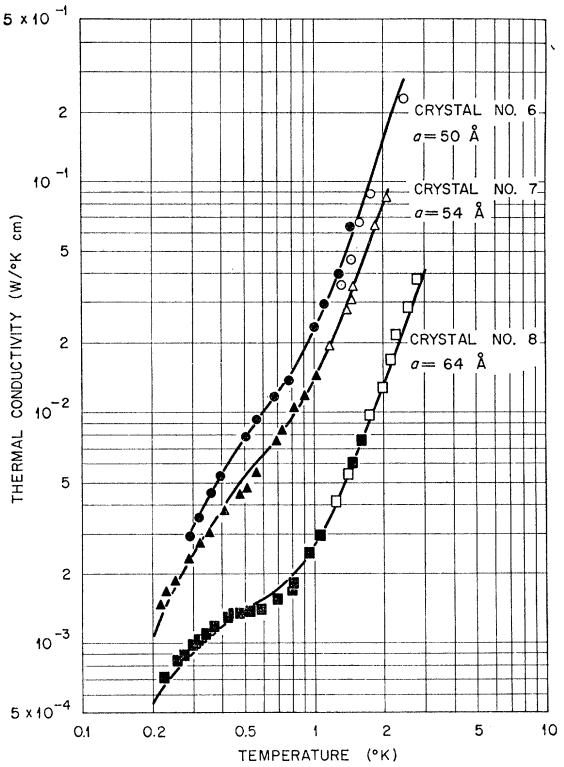

FIG. 2. Thermal conductivity of sodium chloride containing silver colloids.

The conductivities were measured by the conventional potentiometric techniques (see Fig. 2). Pairs of Speer carbon resistors, matched at an He temperature whose nominal room-temperature resistance was 510 Ω, served as thermometers. The resistors were mounted by wrapping them in a copper-foil strip coated with G.E. 7031 cement. The copper strip had previously been soldered to a copper clamp. After the cement had dried, the thermometer and clamp assemblies were attached to the thermal conductivity specimen by means of an indium-faced spring. The resistances were measured by a dc technique rather than by using an ac bridge. Thermal emf's in the dc circuitry were reduced to unimportant values by using copper-to-copper junctions where necessary. The power dissipated in the resistors was about 5×10^{-10} W, and frequent checks revealed that this power was about a factor of four less than that at which self-heating effects became measurable.

Rather than measure the resistances of each thermometer independently, the resistance of one, and the difference in resistance between it and its mate were monitored. In making a measurement the following procedure was used: The crystal heater was turned on, and the pumping rate on the ^{3}He adjusted until the desired temperature was reached. The value of the monitoring resistor and ΔR were noted. Then the crystal heater was turned off and the bath heater turned on

and adjusted until the monitoring resistor had reached its previous value, and ΔR was again measured. The difference between the two values of ΔR is then the desired measure of ΔT, the temperature difference due to the heat flow when the crystal heater was turned on. The advantage in following this procedure is twofold: (1) The difference in resistance can be measured more accurately than would be the case if two values of resistance were subtracted; (2) the difference in resistance is sufficiently insensitive to temperature that the value of the monitoring resistor is normally only needed to three figures. A third advantage is that ΔR can be recorded and any delays in coming to equilibrium can be observed and allowed for. Delays of this nature were never observed. Had they existed, they would have been shorter than the time constant involved in adjusting the bath temperature to its required value, i.e., shorter than about a minute.

The resistance thermometers were calibrated during each run against the vapor pressure of ^{3}He down to 0.5°K, and against the magnetic susceptibility of iron alum at lower temperatures.

III. RESULTS

The experimental results are shown in Fig. 2. The solid points represent data obtained here, whereas the open circles refer to data obtained by Worlock. The good agreement between the data obtained on two different systems many months apart is noteworthy.

The solid lines were calculated according to a procedure outlined in the next section.

IV. DISCUSSION

The most striking feature of these results is their qualitative similarity to those obtained by Seward and Narayanamurti[6] and Narayanamurti *et al.*[7] for resonant scattering by a localized mode. Careful observation, however, reveals the following important difference: The temperature at which the break occurs is variable with concentration of impurity in these data. For a resonant-scattering process this temperature should be invariant on changing the defect concentration. Reference to the results obtained by Seward and Narayanamurti and Narayanamurti *et al.* reveal that this is in fact the case. Table I shows the temperature of the break, determined by drawing the two best straight lines through the data points above and below the break, for the different concentrations.

The solid lines in Fig. 2 are the result of a numerical computation of the thermal conductivity. In Sec. I it was pointed out that three pieces of information are required to do this: (a) a knowledge of the intrinsic scattering in the pure crystal, (b) a solution to the Boltzmann equation, and (c) the scattering cross section of the defect.

TABLE I. Temperature of the break in a plot of the thermal conductivity against temperature for different defect concentrations.

Temperature of break (°K)	Defect concentration (cm^{-3})
KCl-KCN	
5.6	9×10^{17}
5.1	8.4×10^{18}
5.2	4.9×10^{19}
NaCl-Ag	
1.2	1.4×10^{17}
1.1	2.8×10^{17}
0.9	2.4×10^{18}

For the intrinsic scattering it is only necessary to consider boundary scattering at these temperatures. The only uncertainty will be the degree of specularity in the boundary term. Rather than treat this as an adjustable parameter, an effective scattering length was obtained from the lowest temperature data for crystal 6. This length was then divided by the Casimir length. The effective scattering length for crystals 7 and 8 was then taken to be the product of this ratio and the Casimir length for the respective crystals.

Another effect was also allowed for—the change in the effective boundary scattering in the presence of other scattering processes. If the scattering by other processes in the crystal is strong, the effect of the boundary is reduced. In effect, phonons in the center of the specimen are less affected by the presence of the boundaries than phonons near the surface. It was found that taking this into account made a difference of about 7% in the calculated conductivity. It should be emphasized that this contribution will be important at temperatures where the boundary scattering is relatively weak in comparison to the rest. In particular, if the defect scattering follows a Rayleigh law, the fractional change in the conductivity, which results upon taking this effect into account, appears to be roughly independent of temperature.

The relaxation-time approximation to the solution of the Boltzmann equation becomes exact if the phonons are only scattered elastically and by the boundaries of the crystal. However, the transport cross section must be used to compute the thermal conductivity. The transport cross section is

$$\sigma_T = \int d\sigma (1-\cos\theta) d\theta ,$$

where $d\sigma$ is the differential cross section and θ is the angle between the incident and scattered wave packets. This procedure effectively removes the forward-scattering peak at high energies, with the result that in the high-energy limit the transport cross section

[6] W. D. Seward and V. Narayanamurti, Phys. Rev. 148, 463 (1966).
[7] V. Narayanamurti *et al.*, Phys. Rev. 148, 481 (1966).

becomes equal to the geometrical cross section of the sphere.

The transport cross sections were obtained numerically from a partial-wave analysis. The details of this calculation are outlined in the next paper. The thermal conductivity was then obtained, also numerically, by taking the cross sections and using them to evaluate the following integral:

$$K=A\int_0^\infty \frac{e^y}{(e^y-1)^2}\frac{v^4}{C(B+n\sigma)_T},$$

where

$$A=k^4T^3/2\pi^2C\hbar^3,$$
$$y=\hbar\omega/kT.$$

Here, C is an average sound velocity, B is the reciprocal of the boundary scattering length, n is the concentration of defects, σ_T is the transport cross section, and the other quantities have their usual meaning.

The cross section was calculated for a longitudinal incident wave using the particle radius as an adjustable parameter to obtain the best agreement between theory and experiment. The fit was very sensitive to the radius since σ_T is proportional to the radius cubed for Rayleigh scattering if the total amount of silver is held constant. Although a greater degree of precision would have been attained by separately computing the cross sections for the transverse waves, it was felt that the additional labor involved was unwarranted. Furthermore, it was assumed that all the particles were spheres of the same radius, and that they all had the elastic constants and density appropriate to bulk silver. The density of colloids was taken to be such that it would account for all the silver contained in the crystal. The assumption of an identical size for the colloids is realistic to some extent: As Worlock[4] points out, the fact that they are nucleated at random in the crystal means that most of them should be within about 10% of their mean radius. The elastic properties of the colloids must be treated to some extent as an adjustable parameter. However, the cross section is not as sensitive to the elastic properties as it is to the size of the colloids. Thus, the use of the properties of the bulk will probably not introduce an appreciable error. It is also unlikely that the presence of an elastic strain field will contribute appreciably to the scattering cross section. Carruthers[8] has estimated the scattering due to a spherically symmetric displacement field. Using his results, it can be shown that the strain at the colloid surface would have to be of the order of 10%. Since these are large particles, it is unlikely that such a large strain could exist without being relieved by plastic flow in the matrix.

Figure 3 is a plot of the cross section and the integrand as a function of x for a temperature of 3°K and a radius of 64 Å. The following features of the results are noteworthy: As expected, the cross section follows a Rayleigh law at the lower values of x, becoming essentially constant at the higher values with a transition region between. It can be observed that even at 3°K the conductivity is largely determined by this transition region, and a truly geometrical scattering law is not operative yet. In fact it appears that geometrical scattering will never really be observed at temperatures below the conductivity maximum. Thus it can be concluded that the transition region has a profound effect and determines the conductivity at temperatures well above that of the break. The transition region shows considerable structure which is reflected in the integrand. This structure, of course, is too fine to affect the thermal conductivity. However, there is a broad maximum in the transition region which can affect the conductivity. For this system the maximum is so broad and shallow that it can simply be considered a geometrical cross section which is roughly 70% higher than the true cross section. This is not true in general, and, as shown in the following paper, there are many cases, notably when the density of the scattering center is very much greater than that of the matrix, where, because of a resonance, the maximum in the transition region is much higher.

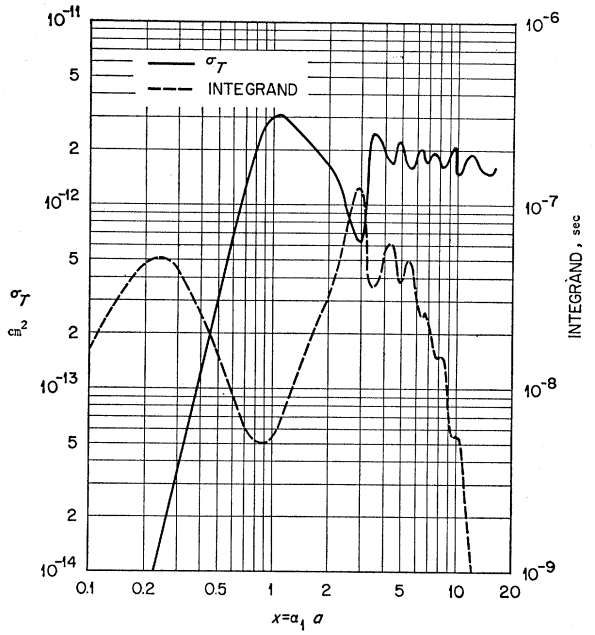

FIG. 3. Scattering cross section and integrand in the thermal-conductivity integral as a function of $x=\hbar\omega_0/kT$ for a temperature such that $x=\alpha_1 a$, where $a=64$ Å, and α_1 is the phonon wave vector.

The agreement between the calculated data and the experimental results which has been obtained is subject to only one adjustable parameter, the size of the colloids. Since the agreement is good, this would suggest that the lattice thermal conductivity can be used to measure the sizes of inclusions in crystals. The technique

[8] P. Carruthers, Rev. Mod. Phys. 33, 126 (1961).

would consist of measuring the thermal conductivity over a sufficiently wide temperature range that regions both above and below the break are covered. If a reasonable estimate of the elastic properties of the colloids can be made, and if the total amount of material incorporated in them is known, the fit of a calculated curve to the data is very sensitive to the mean size. In fact, at temperatures below the break such that Rayleigh scattering is dominant, the cross section varies as the radius to the sixth power.

V. SUMMARY

The purpose of this investigation has been to study the scattering of phonons by an elastic sphere through its effect on the thermal conductivity. In particular, the effect of a transition from a Rayleigh to a geometrical scattering law was required. In general, the following effects have been observed:

(i) Goemetrical scattering is never truly operative.

(ii) Although the resonances in the transition region can never be observed through their effect on the conductivity, there is a broad maximum which is important.

(iii) The fit of the experimental data is extremely sensitive to the assumed mean particle radius. It is less sensitive to the assumed properties of the particle. Thus, if it is possible to make a reasonable estimate of the elastic properties of inclusion in crystals, it is possible to use the thermal conductivity as a means of measuring their mean size.

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Scattering of Phonons by a Square-Well Potential and the Effect of Colloids on the Thermal Conductivity. II. Theoretical*

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The scattering cross section of an elastic sphere as a function of frequency has been obtained for a number of representative combinations of the properties of the sphere and the matrix. These are obtained from a partial-wave analysis and are intended to be used primarily in the computation of thermal conductivity. To simplify the problem, it has been assumed that both the sphere and the matrix are isotropic and that they obey the Cauchy relations. From the exact results, suitable procedures for obtaining analytic approximations are discussed.

I. INTRODUCTION

IT is the purpose of this paper to investigate the effect of the elastic properties of an elastic sphere on its scattering cross section for an incident longitudinal acoustic wave. These results are intended to be used primarily in understanding the effects of a macroscopic scattering center on the thermal conductivity.

Although it is possible to calculate exact numerical values of scattering cross sections using a partial-wave analysis, this is a cumbersome procedure, and it is desirable to find sufficiently general analytic approximations. Our objective will be to search for those approximations which would be most useful in calculating the thermal conductivity. In this respect our task is simplified because an integral over the phonon spectrum is involved.

An obvious approximation would be to assume a Rayleigh law, calculated using Born approximation for long wavelengths. For short wavelengths a constant cross section would be used. The transition from one to the other would occur when the incident wave vector equalled the radius of the sphere. The transport cross section as defined below is of interest here, so the high-frequency limiting cross section will be the geometrical cross section of the sphere.

Our objective has been to compare the complete numerical solutions with the above approximation, and to investigate the possibility of broadening it to include those cases where it proves inadequate. It is obvious at the outset that it will be impossible to adequately represent the fluctuations in the cross section which usually occur in the transition region from a Rayleigh to a constant scattering law. However, the thermal conductivity involves an average over the phonon spectrum, and it is insensitive to this fine structure. In this case, where these results should be most applicable, we may neglect the fine structure.

The problem of scattering of a plane longitudinal wave by an isotropic elastic sphere in an isotropic solid

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