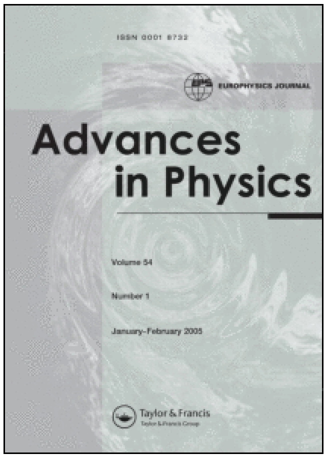

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The thermal conductivity of dielectric solids at low temperatures

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The Thermal Conductivity of Dielectric Solids at Low Temperatures

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CONTENTS

§ 1. INTRODUCTION

THE measurements of thermal conductivity of dielectric solids have not, until recently, been sufficiently extensive for detailed comparison between theory and experiment to be made. In the last few years, however, a considerable amount of work has been carried out in Oxford and it now seems a suitable time to review the present state of knowledge and to describe the types of experiment which are being carried out. From the theoretical point of view the most interesting effects occur at fairly low temperatures; the temperature range of interest is related to the specific heat and to the size of the specimen and in most cases lies below room temperature and extends down to the lowest temperatures attainable.

In this paper the experimental techniques used will not be described; they are usually the same as those mentioned by Olsen and Rosenberg in the companion paper. Reference will only be made to some special methods.

As the work described here will not, on the whole, be discussed in chronological order, an outline will first be given of the actual development of the subject over the last forty years.

§2. HISTORICAL DEVELOPMENT

2.1. *Dielectric Solids in General*

As a result of numerous measurements on dielectric crystals and on amorphous solids, Eucken (1911 a, b) concluded that, in general, the conductivity of single crystals increases with decreasing temperature while that of amorphous solids decreases. Most of the measurements were made at the steam point, ice point and at liquid air temperature, with a few measurements at the boiling point of liquid hydrogen. In this temperature range the conductivity was found to be roughly inversely proportional to the absolute temperature for crystals and in the case of amorphous solids to be roughly proportional to the specific heat.

These different variations with temperature were explained by Debye's theory (1914), according to which the heat is transported by travelling elastic waves which are coupled together on account of their anharmonicity. In crystals the waves are scattered by regions of differing density arising from thermal motion and Debye calculated the attenuation of the waves produced by this scattering. From the dependence of attenuation on temperature he derived a variation of conductivity which is in agreement with Eucken's experiments.

More recent theories lead to the same temperature variation at sufficiently high temperatures but show that at low temperatures the scattering of the waves falls off more rapidly.

2.2. *Crystals*

In Peierls' theory of heat conductivity of crystals (1929) the normal modes of a perfect lattice are quantized ; the quanta of vibrational energy are now called phonons. Thermal resistance is due to a certain type of collision between phonons (Umklapp processes) and Peierls showed that the probability of such collisions falls off exponentially at low temperatures, leading to a corresponding exponential increase in the conductivity. De Haas and Biermasz (1935) carried out experiments designed to test the validity of Peierls' theory. Although they found that the conductivity of quartz in the liquid hydrogen range increases more rapidly than the inverse of the temperature, their most interesting result was that in the helium range the conductivity actually decreases with decreasing temperature and must, therefore, pass through a maximum at about 10° K.

Peierls suggested that this behaviour was due to scattering of the lattice waves at the boundaries of the crystal and the consequences of this suggestion were developed by Casimir (1938). He showed that such a scattering would lead to a conductivity, at sufficiently low temperatures, proportional to the diameter of the crystal and to the cube of the temperature. The later experiments of de Haas and Biermasz were almost entirely confined to the study of this effect and although exact agreement with the theory was not obtained, the results indicated that the size and temperature dependence calculated by Casimir might be accurately obeyed at temperatures considerably lower than those at which measurements had yet been made.

Mean free path treatments of thermal conductivity have been given by Pomeranchuk (1941 a, b ; 1942) and by Klemens (1951). Exact expressions are found for the variation of conductivity with temperature by picking out the processes which are chiefly responsible for limiting the phonon mean free path. It is then possible to calculate the conductivity to be expected when two or more processes combine in limiting the mean free path. (Even in an ideal crystal, there must be at least two such processes in the region of the conductivity maximum.)

Recent experiments (Berman, Simon and Wilks 1951) have shown that the exponential increase in conductivity predicted by Peierls can be observed for sufficiently pure crystals over a relatively small temperature range. There are, nevertheless, considerable discrepancies between the expected variation of conductivity and that found experimentally and experiments now in progress in Oxford are designed to investigate these discrepancies.

The present theories enable us to predict the conductivity as a function of temperature, provided that we know one value at a comparatively high temperature. Figure 1 shows the conductivity of ideal sapphire crystals of two different diameters, calculated according to Klemens' theory ; the conductivity actually found is also shown. It is evident that the greatest discrepancies occur in the region of the conductivity maximum but, even for real crystals, the conductivity reaches values comparable with those of pure metals at their maxima.

2.3. *Amorphous Solids*

Several observers have reported values for the conductivity of glasses which indicate that below liquid air temperatures the conductivity begins to fall off more slowly than the specific heat. The explanation of this was given by Kittel (1949) and the theory was developed in detail by Klemens (1951) who showed that at sufficiently low temperatures the conductivity should be proportional to the absolute temperature although the specific heat is proportional to the cube of the temperature. This temperature variation has been confirmed for several glasses and for some plastics (Bijl 1949, Berman 1951).

Figure 2 shows the measured values of the thermal conductivity of quartz glass together with the curve calculated by Klemens (for which the empirical constants have been found by comparison with experiment) ; except at the very lowest temperatures the specific heat varies as curve II in the figure, so that the difference between the present theory and an extrapolation of Debye's relationship is clearly seen.

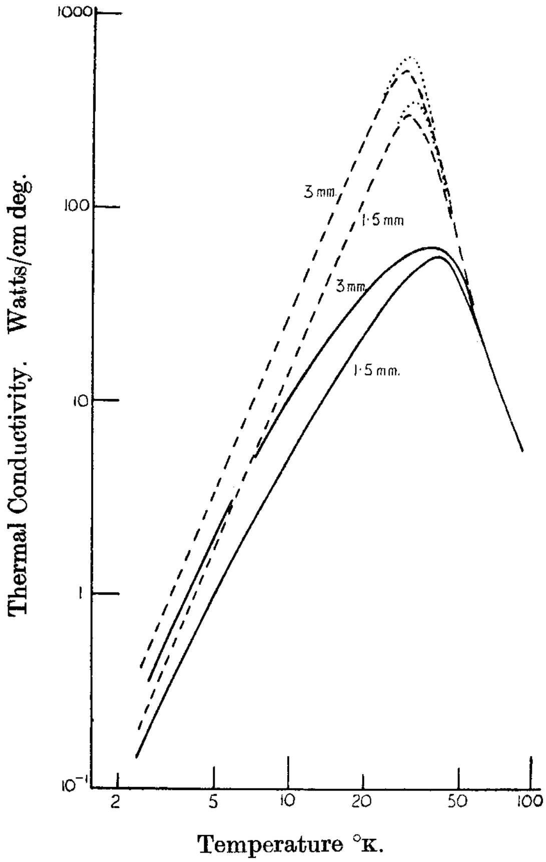
§3. THEORY OF THE CONDUCTIVITY OF IDEAL CRYSTALS

For an ideal crystal we assume there are only two types of process which give rise to thermal resistance : Umklapp processes and boundary scattering. The resistances due to these two causes are only comparable over a small temperature range which, for crystals of a few millimetres diameter, is in the neighbourhood of one thirtieth of the Debye characteristic temperature. At higher temperatures the conductivity is almost entirely determined by Umklapp processes and at lower temperatures by boundary scattering. These three temperature regions will be treated separately in the following discussion.

3.1. *The Region above the Conductivity Maximum*

Although Debye's theory has been superseded, it introduced important concepts which are still valid. Debye treated a crystal as a continuum in which heat is carried by travelling elastic waves of a single frequency. He pointed out that if the waves were purely harmonic there would be no coupling between waves ; consequently attenuation of the waves by

Fig. 1



The thermal conductivity of sapphire single crystals of diameters 1·5 and 3 mm.

Theoretical curves { – – – resistances combined according to Klemens (1951).
. . . simple addition of resistances.

Experimental curves ——— .

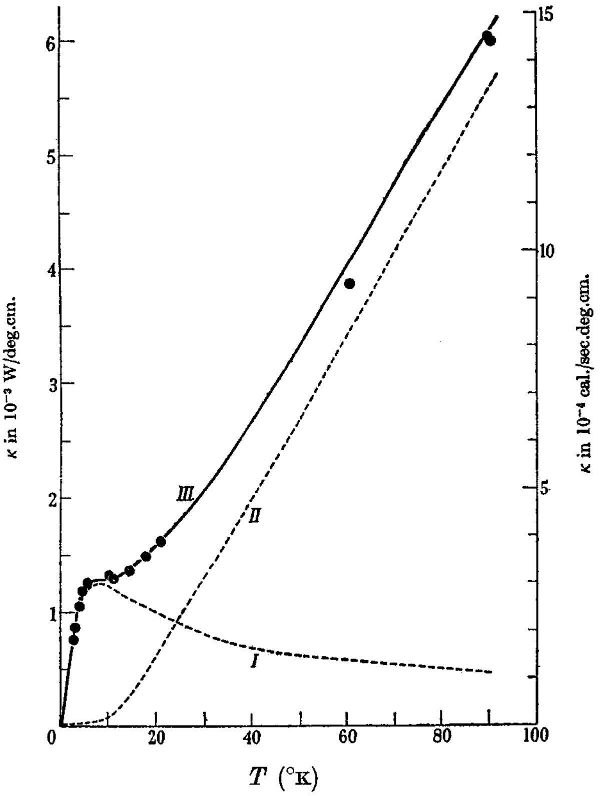
mutual scattering could not occur. It would not, therefore, be possible to set up a temperature gradient within a crystal so that there would be no definable thermal resistance. The lattice vibrations must be assumed to be anharmonic to account for thermal expansion and Debye explained the required coupling between the waves in terms of this anharmonicity.

As a measure of the scattering, Debye defined the mean free path l of a wave as the distance which the wave travels before its intensity is reduced to $1/e$ of its initial value. The thermal conductivity, κ, is then given by the equation :

$$\kappa=\tfrac{1}{4}c\,v\,l \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where c is the specific heat per unit volume and v is the wave velocity.

Fig. 2



Thermal conductivity of quartz glass. Curve *I* denotes κ_{I}, curve *II* κ_{II}, curve *III* $\kappa=\kappa_{\mathrm{I}}+\kappa_{\mathrm{II}}$. Full circles denote experimental points of Berman (1951); measurements of three specimens differing slightly in their absolute value of conductivity are here brought into agreement by multiplication with an appropriate constant (Klemens 1951).

Debye supposed that a wave is scattered when it passes through regions whose density and elastic constants differ from the average value throughout the crystal. These density variations result from the anharmonicities in the thermal motion of the lattice and, for purposes of calculation were considered to be static. This assumption is only justified at high temperatures, when the density variations are not correlated with the scattered waves. The calculation showed that the mean free path is inversely proportional to the absolute temperature and, since the wave velocity is nearly independent of temperature, the thermal conductivity must be inversely proportional to temperature for temperatures where the specific heat is constant.

In Peierls' theory (1929, 1935) a crystal is treated as a lattice of atoms rather than a continuum. The coupling between normal modes of vibration is ascribed to anharmonicities arising from third and higher order terms in the potential energy of a displaced atom. The part played by these terms is analogous to that of collisions in the theory of a perfect gas ; though introducing only a small perturbation of the motion they are responsible for the coupling between the normal modes which is essential in producing thermal equilibrium. In Peierls' theory the normal modes of vibration are quantized and, by analogy with the photons of radiation theory, these quanta are now termed phonons. For a phonon associated with an angular frequency ω and wave number $\mathbf{K}$, $\hbar\omega$ gives the energy while $\hbar\mathbf{K}$ behaves rather like a momentum.

In the presence of a temperature gradient the phonon distribution differs from that corresponding to the equilibrium distribution at uniform temperature—the Planck distribution. Collisions between phonons tend to restore the equilibrium distribution and the rate of the restoring process determines the thermal conductivity. Collisions are possible if the three values of ω and $\mathbf{K}$ obey the equations :

$$\omega_1+\omega_2=\omega_3 \quad \ldots \ldots \ldots \quad (2)$$

and

$$\mathbf{K}_1+\mathbf{K}_2=\mathbf{K}_3 \quad \ldots \ldots \ldots \quad (3)$$

which are conditions corresponding to the conservation of energy and momentum. Equation (2) states that after a collision the resulting wave or waves still carry the same energy as before and eqn. (3) implies that this energy is still flowing in the same direction. Such collisions do not in themselves give rise to a thermal resistance. Peierls also showed that, for a discrete lattice, collisions are possible in which eqn. (3) does not hold but is replaced by

$$\mathbf{K}_1+\mathbf{K}_2=\mathbf{K}_3+\frac{2\pi\boldsymbol{\epsilon}}{a} \quad \ldots \ldots \ldots \quad (4)$$

where a is the lattice constant and $\boldsymbol{\epsilon}$ is a unit vector, the possible directions of which depend on the crystal symmetry. Equation (4) implies that the direction of flow of the energy is changed after a collision and, as $\boldsymbol{\epsilon}$ can take up one of several directions (e.g. six directions parallel to the axes of a cubic crystal), the result of such collisions is much the same as if the waves were scattered at random. This type of collision, which Peierls called an Umklapp process (in the following discussion the abbreviation U-process will be used), gives rise to thermal resistance.

It is convenient to use the concept of mean free path, as in Debye's theory, but since the waves have been replaced by phonons, eqn. (1) is rewritten as

$$\kappa = \tfrac{1}{3}\, c\, v\, l \qquad (5)$$

by analogy with kinetic theory. For the case being considered l is the mean free path for U-processes. It is now necessary to take into account the contributions to the right hand side of (5) from phonons corresponding to waves of all frequencies up to the Debye limit and of three possible polarizations, so that eqn. (5) should be written :

$$\kappa = \tfrac{1}{3} \sum_{Kj} c_{Kj}\, v_{G_{Kj}}\, l_{Kj}, \qquad (6)$$

where j denotes the direction of polarization and v_G is the group velocity. At sufficiently high temperatures the contribution to the specific heat, c_{Kj}, is the same for all waves and is independent of temperature. The mean free path is inversely proportional to the rate of loss of energy of a wave, which Peierls showed to be proportional to its own additional energy and to the intensities of the other waves with which it can interact. The mean free path is thus inversely proportional to the intensity of the other waves taking part and at high temperatures all the intensities are proportional to T, so that $l \propto 1/T$ and the conductivity is inversely proportional to the absolute temperature, which is the relation also deduced by Debye.

For treating the low temperature conductivity Peierls did not use a mean free path method, but pointed out that eqn. (4) implies that the phonons must have a minimum energy for an Umklapp process to occur. He further showed that as a rough criterion we may take this threshold energy as $k\theta/2$, where k is Boltzmann's constant and θ is the Debye characteristic temperature. The intensity of excitation of such phonons is proportional to $1/(e^{\theta/2T}-1)$, which at low temperatures approaches the value $e^{-\theta/2T}$. The probability of U-processes therefore contains the term $e^{-\theta/2T}$ and the thermal resistance is proportional to $f(T)\, e^{-\theta/2T}$, where at sufficiently low temperatures the function $f(T)$ behaves as a power of T.

Experiments confirm the main features of the temperature variation predicted by Peierls, but comparison is difficult when several scattering mechanisms have to be taken into account. Mean free path treatments of thermal conductivity have, however, been given by Pomeranchuk (1941 a, b ; 1942) and Klemens (1951), and these are more easily applied to discussions of experimental results.

The expressions for the conductivity found by Pomeranchuk differ considerably from those of other authors mainly because of the long mean free paths which are assumed for long waves. At high temperatures four phonon processes are considered essential for ensuring a finite conductivity and for $T \gg \theta$ the deduced conductivity is proportional to $T^{-3/2}$. At somewhat lower temperatures the effect of the long free paths of long waves is to make the conductivity weakly size-dependent at temperatures considerably higher than those for which Casimir's relation holds. The conductivity is proportional to $L^{1/4}\ T^{-3/4}$ where L is the smallest dimension of the crystal.

At still lower temperatures Pomeranchuk shows that the form of the conductivity-temperature relation is very sensitive to the concentration of defects in the crystal. There is a range of temperature where there is a true conductivity, independent of size, only for crystals of sufficient purity. For these the conductivity is inversely proportional to the temperature and to the defect concentration. It is not shown whether the conductivity of an ideal crystal would vary exponentionally with the temperature, as predicted by Peierls. For crystals with a defect concentration greater than a certain minimum there should exist a temperature region in which the conductivity is independent of temperature, but is again proportional to $L^{1/4}$. Finally, at sufficiently low temperatures Casimir's relation will hold for all crystals.

There does not seem to be any experimental confirmation of even the more striking of Pomeranchuk's conclusions, such as the size dependence at high temperatures and the temperature independent conductivity. It is probable that the dependence on size at relatively high temperatures has not been looked for under conditions which would enable an exact comparison to be made. Pomeranchuk remarks that a temperature independent conductivity should be observed in diamond ; for an impurity concentration of 4×10^{-4} this would extend from 54 to 380° K. The existence of such a temperature independent conductivity between 24 and 340° K was deduced from the measurements of Eucken (1911 c) and of de Haas and Biermasz (1938 a). These experiments are discussed in § 5.1 where it is pointed out that it does not seem justifiable to draw this conclusion.

Pomeranchuk considers that the chief contribution to the conductivity of crystals comes from longitudinal phonons of long wavelength. In order to obtain numerical agreement with experiment the calculated mean free path has to be divided by a factor of 100. Klemens, however, while he uses Pomeranchuk's expressions for the mean free paths for various scattering processes, considers all processes tending to restore equilibrium, including those in which momentum is conserved. He shows that a longitudinal mode of vibration tends to return to its equilibrium value mainly by means of interactions with transverse waves of about the same frequency and a low frequency transverse mode by interactions with modes of frequency kT/h. It is thus shown that 3-phonon processes are sufficient for producing a finite conductivity and the contribution to the conductivity from longitudinal modes is of similar magnitude to that from transverse modes in the case of crystals. The conductivity is not size-dependent except where Casimir's relation holds. According to Klemens the resistance due to Umklapp processes is proportional to $T^{-1}\ \mathrm{e}^{-\theta/2T}$. As will be discussed in § 5.1, it is difficult to verify this power of temperature by experiment.

It should be realized that it is only the temperature variation of conductivity which has been calculated and not its absolute magnitude. The latter obviously depends on the strength of the coupling between the modes of vibration or on the number of collisions between phonons, which is determined by the anharmonicities of the interatomic forces, and this is difficult to deduce from other data. Van Vleck (1941 a) has treated a similar but somewhat simpler problem in connection with paramagnetic relaxation in the alums ; namely the transfer of energy between lattice oscillators at the same position in space but at different temperatures. The anharmonicity was derived from compressibility data and the temperature was low enough for U-processes to be neglected. In this case thermal equilibrium is restored by processes represented by eqns. (2) and (3) ; as has been mentioned before, however, these processes alone do not lead to a thermal resistance. Even if a similar calculation could be made for thermal conductivity it would be difficult to obtain the necessary experimental data from which the anharmonicity could be derived for crystals as hard as sapphire and diamond but it may be possible in the case of solid helium, which is very compressible.

It will be seen that the absolute value of the conductivity of dielectric crystals can be very high, yet in discussions of the Wiedemann–Franz law it is assumed that the contribution of the lattice conductivity to the measured conductivity of monovalent metals, such as copper and sodium, is negligible. The justification for this is that the presence of free electrons in metals provides an extra mechanism for scattering phonons so that even in a pure metal the lattice conductivity is small at all temperatures, regardless of the degree of anharmonicity of the atomic forces.

3.2. *Boundary Scattering*

In his original paper Peierls drew attention to the conductivity of diamond which according to Eucken's measurements appeared (erroneously) to be almost independent of temperature. Since the characteristic temperature is very high, the measurements extended to lower values of T/θ than for other crystals. Peierls suggested that under these conditions, where U-processes are very rare, reflection of the waves at the crystal boundaries is all-important so that the conductivity, if defined in the usual way, would depend on the crystal size.

In their first experiments to test Peierls' theory at low temperatures, de Haas and Biermasz (1935) found that the thermal resistance of a quartz crystal increased with decreasing temperature in the liquid helium region. It was realized that impurities in the crystal would give rise to a thermal resistance additional to that caused by Umklapp processes, but Peierls had shown that this resistance too should fall off at low temperatures.

Casimir (1938) worked out the consequences of Peierls' suggestion that scattering of the lattice waves at the boundaries of a crystal becomes important at low temperatures. By assuming that the interaction between the waves can be completely neglected Casimir compared a crystal to a hollow space filled with electromagnetic radiation. He calculated the flow of heat in a crystal under these conditions by considering the case to be similar to the flow of radiation down a tube with diffusely reflecting walls. Diffuse reflection was to be expected because in the crystals which had been measured the irregularities of the walls were certainly larger than the wave-lengths of the lattice waves dominant in heat conduction at the temperatures considered. (If the reflection were specular the heat flow would be independent of length, which is not in agreement with experiments.) There will then be a temperature gradient along the walls when there is a flow of heat along the crystal.

On the assumption that all phonons behave in the same way on reflection Casimir deduced that the flow of heat is proportional to the temperature gradient, to the cube of the absolute temperature and to the cube of the radius of the crystal (or to the cube of the length of side for a crystal of square cross-section). If a heat conductivity is defined from this relation it will evidently be proportional to the radius of the crystal, but it must be emphasized that this is not a true conductivity.

On the more exact theory of Klemens account is taken of the interaction between the lattice waves, even when these are not of the Umklapp type. Since such collisions alone do not give rise to thermal resistance the effect of boundary scattering is the same as that calculated by Casimir.

Casimir's result is that the conductivity is given by

$$\kappa = 2{\cdot}31 \times 10^3 R p A^{2/3} T^3 \text{ Watts/cm deg}, \quad . \quad . \quad . \quad . \quad (7)$$

where R is the radius of the crystal and p is a dimensionless quantity equal to the ratio $\left(\Sigma\overline{\frac{1}{v_j^2}}\right)\Big/\left(\Sigma\overline{\frac{1}{v_j^3}}\right)^{2/3}$; $(\overline{})$ denotes the mean value over all directions. A is the constant in the expression $c_v = AT^3$, for the specific heat per unit volume at low temperatures according to Debye's theory. The factor p occurs because different mean velocities are required for evaluating the specific heat and the energy flow. For a crystal of square cross-section of side d, R is replaced by $0{\cdot}56d$.

It is very convenient to discuss the effect of boundary scattering by expressing the conductivity in terms of the phonon mean free paths, as has been done previously. If the conductivity is equated to $\frac{1}{3}cvl$, then it is possible to calculate the value of l which will give the same conductivity as that derived by Casimir and given by eqn. (7). From Debye's theory both the specific heat and, therefore, the mean wave velocity can be expressed in terms of θ, M and ρ, where M is the mean atomic weight in the crystal and ρ is the density. If p is taken as $1{\cdot}4$ (which, as Casimir shows, is about the value it has for most crystals) then l is almost exactly equal to $2R$, the diameter of the crystal.

It will be noticed that for boundary scattering, acting alone, it is possible to calculate the absolute magnitude of the conductivity since, unlike Umklapp processes, the strength of coupling between the waves is not involved.

3.3. *The Combined Effect of Umklapp Processes and Boundary Scattering*

For an ideal crystal Umklapp processes are dominant in determining the conductivity at high temperatures and boundary scattering is dominant at low temperatures. Over a certain range of temperature both processes must be considered, but this range is small as both types of resistance vary rapidly with temperature. In order to calculate the conductivity when more than one scattering process is important it is necessary to insert into eqn. (6) the value of the mean free path l_{Kj} (for phonons Kj) resulting from the combined scattering processes, and then to carry out the summation, over all values of K and j. Simple addition of the thermal resistances due to each scattering process, considered as acting separately, will in general only lead to the same result if all scattering processes are independent of K and j.

Klemens has in this way derived a combination formula which gives the conductivity when Umklapp processes and boundary scattering are both important. The results calculated for ideal sapphire crystals are shown in fig. 1, together with the values which would be obtained by adding the resistances which the two processes would produce if they acted separately. In the neighbourhood of the maximum the difference can amount to about 30%.

3.4. *Other Factors which may affect the Conductivity*

Measurements have been made of the thermal conductivity of some dielectric solids in the region of specific heat anomalies. Eucken and Schröder (1939), Gerritsen and van der Star (1942) and v. Simson (1951) have measured HBr, CH_4 and NH_4Cl respectively, in each of which the anomalies in the solid state are associated with the rotational energies of the molecule or parts of the molecule. Corresponding anomalous increases in the measured heat conductivities have been found, but no detailed theoretical work has been carried out on this subject.

The contribution of the spins in a paramagnetic salt to heat conductivity has been treated theoretically by Fröhlich and Heitler (1936) and by Akhieser and Pomeranchuk (1944). Pomeranchuk (1941 c) has also discussed the effect of the magnetic spectrum on the phonon conductivity. An excited ionic level is considered not localized in the lattice but the excitation energy is exchanged with other ions. The thermal conductivity associated with the motion of the excitations is determined at low temperatures by their mutual scattering and also by the effect of impurities. Both calculations show that if only mutual scattering is important this ‘ exciton ’ conductivity increases with decreasing temperature. At sufficiently low temperatures it should therefore become greater than the phonon conductivity which decreases as the cube of the temperature. Akhieser and Pomeranchuk estimate that in potassium chrome alum the two contributions would be about equal at 0·02° K. The calculation only gives the order of magnitude of the ratio of the two contributions (e.g., in the expression for the lattice specific heat

$C_v = 464(T/\theta)^3$ cal/mole the numerical factor is omitted) but as the ratio varies as T^4 the calculation will certainly give the order of magnitude of the temperature at which they become equal.

The only experiments in which the contribution of the spins might have been noticeable are those of Garrett (1950) on potassium chrome alum. Even here, however, the lowest temperature at which measurements were made is about ten times larger than that at which Akhieser and Pomeranchuk estimate that this contribution would be equal to the phonon conductivity, and, indeed, no effect was found.

§4. THE THEORY OF IMPERFECT CRYSTALS

As can be seen from fig. 1, even the dielectric crystal with the highest conductivity so far measured, synthetic sapphire, has a conductivity which, near the maximum, is only about one eighth of that to be expected for a perfect crystal. This can be attributed to imperfections in the crystal, which will produce extra scattering of the phonons. Various types of imperfections may occur and mention will be made here of the effects of mosaic structure and of small scale defects, such as impurity atoms or displaced atoms.

4.1. *Small Scale Defects*

A single defect alters the elastic properties of the crystal over a region of the order of size of a unit cell; for long waves the scattering will obey Rayleigh's law and the mean free path of a phonon is proportional to $1/K^4$. If there were no coupling between waves the mean free path of the longest waves would tend to infinity, giving rise to an infinite conductivity. Peierls showed that the anharmonic coupling leads to a finite conductivity because it effects the transfer of energy away from these long waves by processes represented by eqns. (2) and (3). As a result, the thermal resistance due to small defects is proportional to the absolute temperature at low temperatures. This result is also obtained by Klemens.

For short waves or for defects of large extent Rayleigh's law is not applicable; the scattering is less frequency dependent and becomes almost frequency independent at the highest frequencies. Hence the resistance due to defects is proportional to the temperature only at low temperatures.

4.2. *Mosaic Structure*

From x-ray observations it is evident that the alignment of the atomic planes is not perfect even in single crystals. A broadening of the diffraction pattern indicates that the crystal is divided into small regions which are inclined at very small angles (of the order of seconds) to neighbouring regions. Pomeranchuk (1942) has calculated the phonon mean free path when it is limited by such disorientations and has shown that it is proportional to $1/K^2$. At low temperatures the thermal resistance due to this cause is proportional to $1/T$.

§5. EXPERIMENTAL WORK ON THERMAL CONDUCTIVITY OF PURE CRYSTALS

Many authors have reported measurements on particular crystals at various temperatures and instead of discussing these in chronological order it would seem to be more useful to describe them according to the information they yield when considered in the light of present knowledge about thermal conductivity.

5.1. *The Umklapp Process*

It is now known that it is necessary to measure thermal conductivity at temperatures between $\theta/20$ and $\theta/10$ in order to observe the exponential variation of conductivity predicted by Peierls for low temperatures. This exponential rise should be observable at still lower temperatures in ideal crystals with diameters of the order of a millimetre, but seems to be masked by lattice imperfections at temperatures somewhat higher than those at which boundary scattering should be appreciable.

For the crystals measured by Eucken the temperature of liquid air is too high for the conductivity to deviate appreciably from the $1/T$ law, except for diamond. Although the values differed considerably from crystal to crystal Eucken found the average value of κ_{83}/κ_{273} to be of the order of 3–4. A few measurements were made at the boiling point of liquid hydrogen and for rock salt and for quartz the ratio κ_{22}/κ_{88} was greater than 10, but was only about 3 for sylvin.

The diamond specimen which Eucken used in his experiments (1911 c) was not large enough for the temperature gradient to be determined in the usual way and the overall resistance which was measured included some contact resistance at either end of the crystal. He showed that this could lead to considerable error in the conductivity at low temperatures by measuring a rock-salt crystal in the same way and comparing the values found with the results of his more accurate method. Although it could be seen that the conductivity of diamond must be very great at room temperature it was not evident how the conductivity varied with temperature.

Although some of the results obtained by Eucken provided data for comparison with Peierls' theory, systematic measurements at low temperatures were very necessary. De Haas and Biermasz started their series of experiments in 1935 by measuring the conductivity of a quartz crystal. Although they verified Eucken's ratio of κ_{22}/κ_{88} and found that the rise in conductivity continued certainly down to 15° K, they subsequently concentrated their attention on the unexpected variation of conductivity which they found to occur at liquid helium temperatures. For the alkali halides which de Haas and Biermasz measured (1937) the conductivity did not increase faster than inversely proportional to the temperature down to 15° K but they again found that the conductivity decreased in the liquid helium region.

It is probable that the conductivity of the alkali halide crystals does not rise rapidly with decreasing temperature in a way similar to quartz because of the effect of small quantities of impurities. In view of the recent papers of Krishnan and Roy (1951, 1952), in which it is shown that the cubic anharmonicities in these crystals are absent, owing to the symmetry of the lattice, it would be very interesting if measurements were made on crystals sufficiently pure for the conductivity to be limited only by mutual scattering of the phonons at temperatures where the exponential rise of conductivity would be expected. The relatively large thermal conductivity of KCl at room temperature, where the effect of impurities is small, also suggests a small anharmonicity ; the phonon mean free path, calculated from eqn. (5) is several times greater than in quartz at the same temperature.

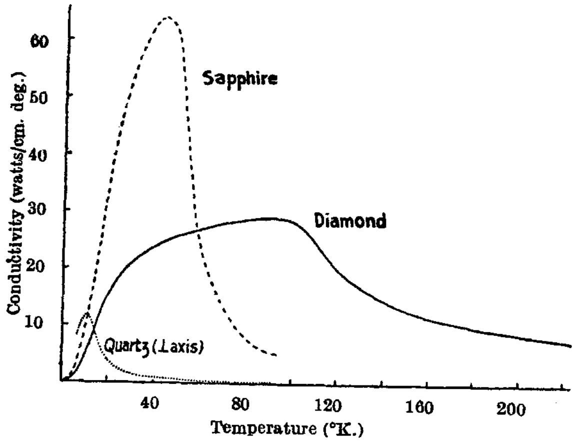
De Haas and Biermasz also measured the conductivity of diamond (1938 a) ; most of the measurements were at temperatures below 20° K, but they also measured one crystal at liquid air temperature to see whether the apparent temperature independence suggested by Eucken's results held. Below 20° K the variation of conductivity showed that boundary scattering was the chief cause of thermal resistance but the value at 89° K was the same as the extrapolated value at 24° K. This value was nearly ten times greater than Eucken's and de Haas and Biermasz attributed this to a difference in the quality of the stones. They concluded that between 24 and 90° K the conductivity is independent of temperature. Although the values of de Haas and Biermasz and of Eucken differed by a large factor, so that the two sets of results could not be combined, the impression left by these experiments seems to have been that the thermal conductivity of diamond is independent of temperature between 24 and 340° K. Recently measurements have been made on a specimen of gem quality between 2° K and room temperature (Berman, Simon and Wilks 1951) and it has been found that the conductivity is not independent of temperature over the large range of temperature, as previously assumed. There is certainly a smaller variation, over a much narrower temperature range (20–100° K), than would be expected for an ideal crystal and this can be explained in terms of the effect of a very small concentration of clusters of impurities or other defects (Klemens 1952).

As all the earlier measurements of thermal conductivity had only been made at fairly widely spaced temperatures or over small temperature ranges and had in many cases led to inconclusive results, it was considered necessary to make measurements over a considerably larger range. For this purpose an apparatus was designed (Berman 1951) to cover the temperature range from 2 to 90° K. For some substances the measurements have also been extended up to room temperature. Measurements have been made on single crystals of quartz, synthetic sapphire and diamond of various cross-sections ; the conductivities of the largest crystal measured in each case are shown in fig. 3.

Recently extensive measurements have been carried out on the thermal conductivity of solid helium at different pressures (Wilkinson and Wilks 1951, Webb, Wilkinson and Wilks, 1952) and some of the results are shown in fig. 4. Solid helium is very compressible and, unlike other substances, lends itself to the formation of crystals of substantially different density and θ values by using quite moderate pressures.

As has been discussed previously, the variation of conductivity with temperature is determined by the ratio T/θ. The crystals which have been measured represent a wide range of θ values, varying from about 25° for solid helium at the lowest pressures to over 2000° K for diamond, so that the measurements provide a considerable amount of data for comparison with Peierls' theory. This comparison has recently been made (Berman, Simon and Wilks 1951) and figs. 3 and 4 are taken from the paper. It can be seen that the thermal conductivities of these pure crystals behave in the same general way. Between temperatures equivalent to roughly $\theta/20$ and $\theta/10$ the conductivity fits a relation of the form $\kappa \propto T^{\nu} \exp(\theta/bT)$. If θ is taken as the Debye characteristic temperature corresponding to the specific heat per mean gram atomic weight then b has a value close to 2 for each crystal. Since the exponential factor is so strong it is not possible to decide the power of T from the experiments. Over the relatively small temperature ranges for which this relation holds, the experimental results can be fitted equally well by different values of ν and corresponding values of b not very different from 2. Since it was only shown by Peierls that b should be of the order of 2 and since none of the crystals has a specific heat which exactly follows

Fig. 3



Thermal conductivities of quartz, synthetic sapphire and diamond. (Berman, Simon and Wilks 1951.)

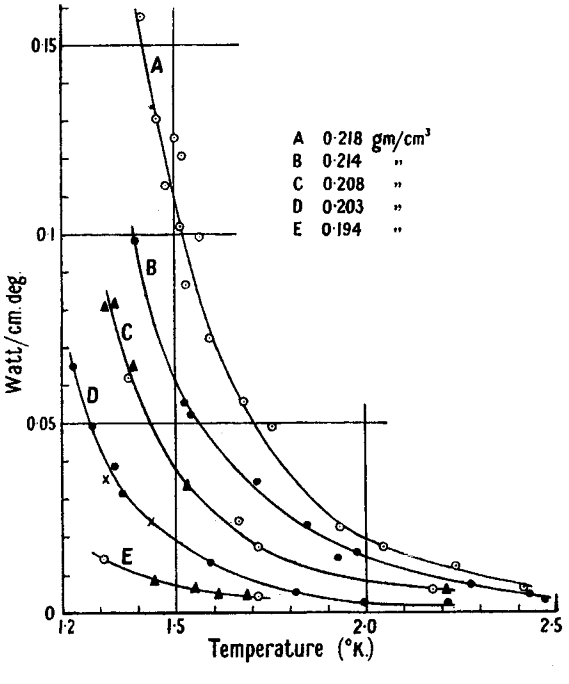
Debye's law, the precise value of θ/b which is found to give the best fit with the conductivity measurements is not a crucial test of Peierls' theory.

The mean free paths for U-processes have been calculated from the relation $\kappa=\frac{1}{3}cvl$ and are shown in fig. 5. The mean free paths can be expressed by relations of the form

$$l=A\exp(\theta/b'T) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where the values of b' are 2·3 for solid helium, 2·7 for diamond and 2·1 for sapphire and A varies from 6×10^{-8} cm for helium to $1{\cdot}4\times10^{-6}$ cm for diamond. Values for quartz have not been derived as the crystal is strongly anisotropic and the conductivity is difficult to treat theoretically.

Fig. 4

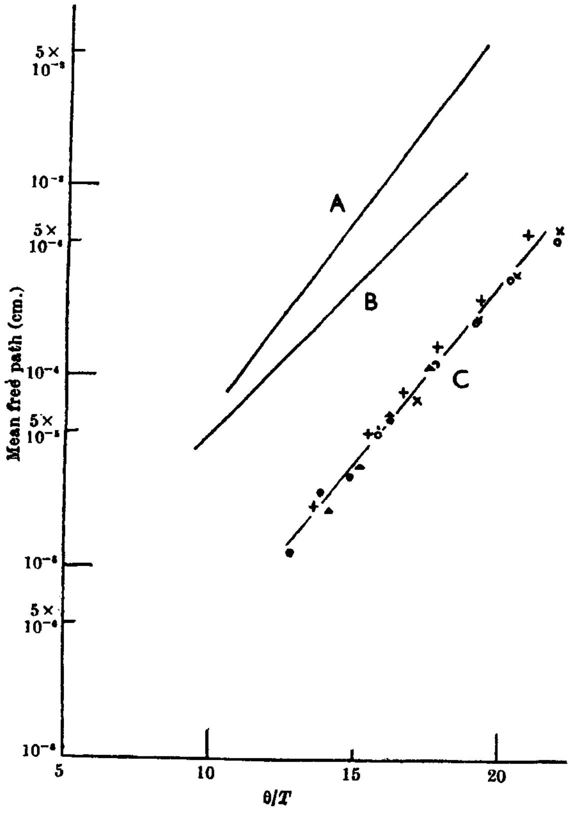


Thermal conductivity of solid helium at constant density.
(Berman, Simon and Wilks 1951.)

For each crystal the probability of a U-process, as measured by the mean free path, is a function of θ/T, but the absolute number of collisions depends on the values of A, which must therefore be a measure of the anharmonicity of the inter-atomic forces. It is interesting to observe that the value of A is the same for solid helium crystals having the wide range of density and conductivity shown in fig. 4.

It can be seen from fig. 3 that the maximum conductivity occurs for each crystal for a value of θ/T of about 20–25. If the conductivity maximum were determined by the onset of appreciable boundary scattering alone then at the maximum the mean free path due to U-processes should be of the order of the crystal diameter. However, for all the crystals so far measured the mean free path at the maximum is an order of magnitude lower than this and possible explanations of the discrepancy will be discussed in § 5.3. Efforts are being made to obtain crystals of other substances in order to make further measurements in the temperature range where the exponential variations of conductivity should be found. The combination of requirements is however rather exacting : great purity, freedom from strains, simple structure and sufficient size (particularly length) for accurate measurements.

Fig. 5



Mean free path for U-collisions as a function of θ/T. A : synthetic sapphire ($\theta \simeq 980$) ; B : diamond ($\theta \simeq 1{,}840$) ; C : solid helium (θ, 22–35). For solid helium the densities are : 0·218 (×) ; 0·214 (○) ; 0·208 (+) ; 0·203 (▲) ; 0·194 (●) g/cm^3. (Berman, Simon and Wilks 1951.)

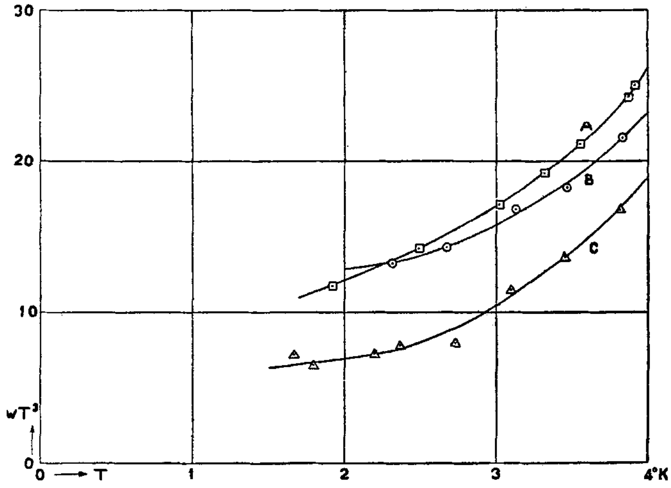
The simple expression (8) for the mean free path does not hold at temperatures greater than about $\theta/10$ since the other temperature dependent terms become important. It is evident however that the mean free path continues to decrease and measurements at high temperatures suggest that it would eventually reach the order of atomic dimensions. In potassium chloride, for example, at 0° C, ($\theta/T=0{\cdot}8$) the value of the mean free path calculated from the thermal conductivity is only of the order of twenty lattice spacings.

5.2. *Boundary Scattering*

5.2.1. *Single Crystals*

De Haas and Biermasz carried out many experiments on the size effect at liquid helium temperatures but did not find for any crystal even at the lowest temperatures (2° K) that the conductivity is proportional to T^3, as given by Casimir's formula. For diamond and quartz the highest power of T reached was about 2·5 while for KCl and KBr the power of T was less than 2. The deviation from the expected relation can be clearly seen by plotting T^3/κ against T, when a horizontal line should be obtained. Figure 6 shows such a plot made by Casimir. (In the figure $W=1/\kappa$.) This behaviour can be explained by assuming that there is present in all these crystals some additional source of scattering and that the resistance due to it does not vary rapidly with temperature, so that it is still important down to the lowest temperatures of the measurements.

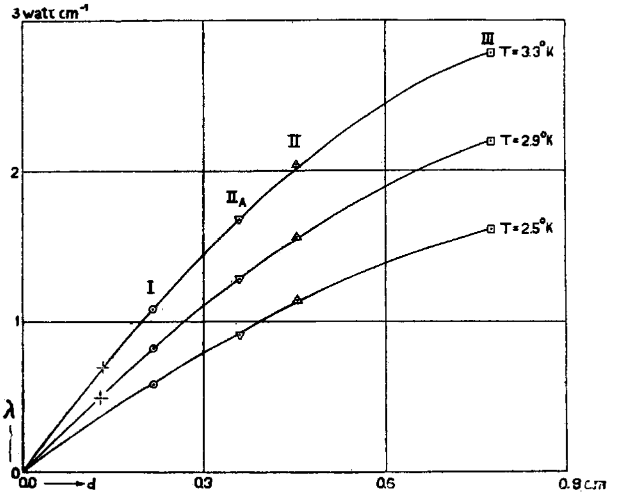
Fig. 6



WT^3 versus T. A: KCl, $d=0{\cdot}252$ cm; B: SiO_2, $R=0{\cdot}227$ cm; C: SiO_2, $R=0{\cdot}108$ cm; (the ordinates of C have been diminished by 20). (Casimir 1938.)

In accord with the idea that deviations from the T^3 law are caused by imperfections in the crystals, de Haas and Biermasz found that at a given temperature the conductivity is not strictly proportional to the diameter of the crystal and, in fact, seems to approach a limiting value for large diameters. This is shown by plotting the conductivity at constant temperature against the diameter and fig. 7 is taken from the work of de Haas and Biermasz. They suggest that the deviations from the T^3 law are due to a mosaic structure in the crystals ; this has also been suggested by Klemens (1951) for quartz. As has been discussed earlier, scattering by a mosaic structure would lead to a thermal resistance inversely proportional to the temperature, so that if mosaic scattering alone were important the conductivity would be proportional to the temperature. At liquid helium temperatures the resistance due to U-processes in quartz is extremely small, so that for an infinitely large crystal the conductivity would only be limited by mosaic scattering. From fig. 7 it can be seen that the limiting values of the conductivities for large diameters are roughly proportional to the temperature, in agreement with the relation which should hold for mosaic scattering.

Fig. 7



Thermal conductivity of SiO_2 ⊥ as a function of the thickness. (de Haas and Biermasz 1938 b.)

Klemens suggests that the departures from ideal behaviour in the alkali halides, both above and below the temperature of the conductivity maximum, are due to impurities and has shown that very small concentrations can explain the results (as will be discussed in § 6.1).

If this explanation of deviations from Casimir's formula is correct, then at sufficiently low temperatures boundary scattering would be the only important cause of thermal resistance and the T^3 law would be obeyed. Few measurements on single crystals have been made, however, at lower temperatures. From the rate of temperature equalization of the ends of paramagnetic crystals demagnetized from inhomogeneous fields, Kurti, Rollin and Simon (1936) deduced values for the conductivity of potassium chrome alum at 0·18° K and of iron ammonium alum at

0·07 and 0·10° K. Although the accuracy of the experiments was not sufficient for the temperature variation of the conductivity to be deduced with great certainty, the ratio between the values of the conductivities of iron ammonium alum was about 3, while the cubes of the temperatures are in the ratio of about 3 too. If we take Duyckaerts' values of the lattice specific heat (1942) and assume a value of 2×10^5 cm/sec for the phonon velocity (see van Vleck 1941 b), then the mean free path calculated from eqn. (5) is about quarter of a millimetre, which is less than one twentieth of the crystal diameter.

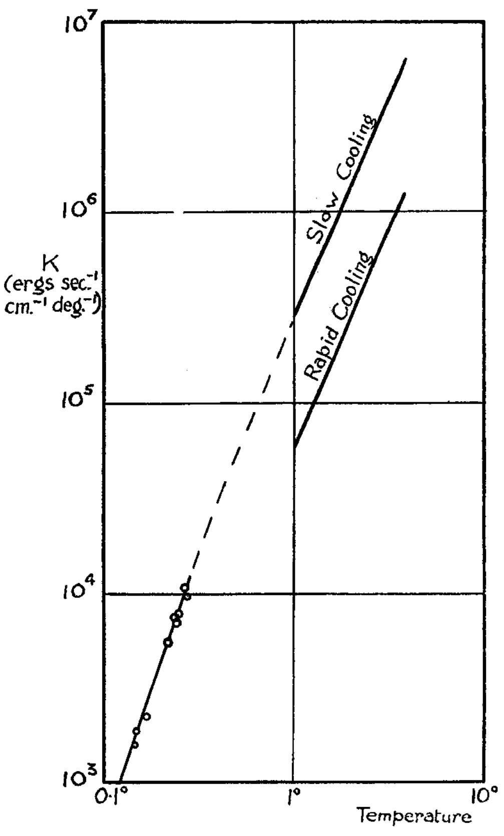
Potassium chrome alum has also been measured by Bijl (1949) and by Garrett (1950). Bijl used a conventional heating method and determined the temperature gradient, when a steady state had been reached, by measuring the mutual inductance between a primary coil and two secondary coils wound round the ends of the specimen. The measurements were made between 1·4 and 3·9° K and in this region the conductivity was found to be proportional to a power of the temperature of about 2·3. Bijl found that the conductivity depended on the rate at which the specimen was cooled below 70° K, an effect which has not yet been fully explained (see Eisenstein 1952).

Garrett used a method similar to that of Kurti *et al.*, but a temperature gradient was produced in the crystal by magnetizing the specimen non-uniformly after the adiabatic demagnetization. The conductivity was measured at temperatures between 0·16 and 0·29° K and in this range the conductivity was found to be proportional to the cube of the temperature within the experimental accuracy and seems to fit on to the 'slow cooling' curve of Bijl, as shown in fig. 8. The phonon mean free path calculated from Garrett's measurements, taking the value of the lattice specific heat given by Casimir (1940) and a value of 2×10^5 cm/sec for the phonon velocity, is about $\frac{1}{2}$ mm while the diameter of the crystal was 15 mm. Such a large discrepancy suggests that there are boundaries within the crystal sufficiently definite to scatter phonons independently of their wave-number and so to limit the mean free path to $\frac{1}{2}$ mm even at these low temperatures.

It is evident that in order to find whether Casimir's formula is correct for the case where only boundary scattering is important, it is necessary to measure the conductivity at temperatures which are only a small fraction of the temperature at which the conductivity maximum occurs. Except for diamond, for which the limitation has been the size of crystals available, the measurements have not been carried out at low enough temperatures by conventional methods and the methods relying on temperature equalization in a paramagnetic salt are too difficult to carry out for many experiments to have been made at sufficiently low temperatures. Recently artificial sapphire crystals (θ 900° K) of great purity have become available in suitable sizes for measurement. Also a diamond of sufficient length and of regular cross-section has been obtained. For these two crystals the conductivity maxima occur at temperatures approximately 4 and 10 times that of quartz, so that measurements down to liquid helium temperatures extend correspondingly further into the region where boundary scattering is the dominant factor in determining the conductivity.

The measurements on diamond have not yet been made on specimens of sufficiently different cross-section, but the results obtained so far seem to agree with those on artificial sapphire. For both crystals the conductivity does not vary with a power of T greater than 2·7 to 2·8, although the lowest temperature of the measurements, 2° K, corresponds to about 1/50 of the temperature of the maximum for diamond. At 2° K, however, the phonon mean free path in diamond, calculated from eqn. (5), is slightly greater than the length of side of the square cross-section. According to Casimir's theory, the conductivity for a crystal of square cross-section, should correspond to a mean free path 1·1 times the length of the side.

Fig. 8



The thermal conductivity of Potassium Chrome Alum. (Garrett 1950.)

The values found for the conductivity of diamond at helium temperatures are about three times as great as those found by de Haas and Biermasz.

They used crystals of triangular cross-section, the linear dimensions of which must have been of the order of one millimetre ; the original side of the crystal now measured was 4 mm.

The measurements on sapphire have so far been made on a crystal 3 mm diameter, which was later ground to a diameter of 1·5 mm ; measurements on specimens of both larger and smaller diameter will also be made. The results are shown in fig. 1. The main features are in agreement with theory, namely that at high temperatures the conductivity is independent of the diameter but that at the lowest temperatures, below 10° K, the conductivity is proportional to the diameter. However the mean free path at 10° K is only one third of the diameter of each specimen and increases with decreasing temperature, reaching 0·8 of the diameter at 2° K. Strict proportionality of conductivity to diameter suggests that only boundary scattering is important, but in that case Casimir's theory leads to a conductivity proportional to T^3 and a mean free path equal to the diameter of the crystal. There does not seem to be a simple explanation of these results and the measurements made so far on diamond indicate a similar behaviour.

One explanation would be that, although the evidence suggests that at sufficiently low temperatures Casimir's relation would be valid, at the temperatures of the present measurements the resistance due to boundary scattering is not proportional to T^3. If the power of the temperature is considered to be an unknown factor to be derived from experiments of the type discussed, then if boundary resistance is taken as being inversely proportional to the diameter, the total resistance at low temperatures due to imperfections as well as boundary scattering can be represented by $x/R+B$, where x and B are functions of the temperature and the two terms represent boundary scattering and the size-independent defect- or Umklapp-resistance. For crystals of two different diameters we have then the equations

$$x/R_1+B=1/\kappa_1 \quad \text{and} \quad x/R_2+B=1/\kappa_2$$

at a given temperature. If these simultaneous equations are solved for the conductivities of the two sapphire specimens for temperatures between 2 and 45° K, then it is found that x is proportional to $T^{2\cdot6}$ and B is nearly independent of temperature. This cannot be considered as a proof that boundary resistance departs from a T^{-3} variation and it is clear that further experiments are necessary.*

5.2.2. *Polycrystalline Solids*

It is evident that at low temperatures a crystal of very small diameter would have a very low thermal conductivity but measurements have not been made on single crystals with a diameter less than the order of a millimetre. Several authors have, however, reported values for the

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* More recent experiments on still thinner diamond and sapphire crystals show conductivities departing only very little from the T^3 law below 4° K.

conductivity of compressed powders of paramagnetic salts, composed of grains from 10^{-3} cm upwards. Kurti, Rollin and Simon (1936) mentioned that the conductivity of a compressed powder of iron ammonium alum was about 1/10 of the conductivity of a single crystal of 7 mm diameter. The dependence of conductivity on size was not known at the time and there was therefore no reason to think that the difference was due to a cause other than the porosity ; neither the density of the specimen nor the grain size were stated.

Van Dijk and Keesom (1940) deduced the relation $\kappa = 0{\cdot}00312\ T_m{}^3$ calories/cm sec deg for the conductivity of a compressed powder of the same salt in the temperature range 0·04 to 0·3° K (T_m being the magnetic temperature). This would give a value at 0·1° about one sixth of the single crystal value of Kurti *et al.* Again the grain size is not given, but the density is stated to be very close to the single crystal value.

Hudson (1949) obtained some mean conductivity values between 0·10 and 0·22° K for a compressed powder of iron ammonium alum of nearly single crystal density, consisting of crystallites estimated to be between 10^{-3} and 10^{-2} cm in size. At 0·10° K the conductivity was about fifty times less than the single crystal value of Kurti *et al.* although from the relative diameters alone the ratio would be expected to be several hundred. Hudson attributes this discrepancy to an increase of the phonon mean free path above the size of the crystallites, which is made possible by the good contact between the crystallites. However, as has been pointed out above, the mean free path calculated from the single crystal conductivity is about one twentieth of the crystal diameter, so that Hudson's results actually suggest that the mean free path in the polycrystalline material is of the order of size of the crystallites.

Recently some other polycrystalline solids have been measured (Berman 1952) and for specimens of alumina and beryllia which had nearly the single crystal density the calculated mean free path becomes slightly greater than the estimated crystallite size at low temperatures. For graphite specimens with a density of about 70% of the single crystal there is no evidence that the phonon mean free path does increase above the crystallite size. The interpretation of the results is made difficult by the absence of measurements on the corresponding single crystals, except in the case of alumina, although even for this it is not certain that the crystal form was exactly the same as the artificial sapphires which have been measured.

The sintered alumina had a density equivalent to 95% of the single crystal value and at temperatures above the conductivity maximum had a conductivity about half that of a single crystal. This difference can be ascribed to the fact that the crystallites do not touch over their whole surface, so that even if there is no actual contact resistance the overall conductivity is less than that of the individual crystallites. Below the maximum the conductivity decreases proportionally to $T^{2{\cdot}7}$, which indicates that the mean free path is still increasing slowly, and is about

20 μ at 3° K, compared with direct measurements of the crystallite size from a photomicrograph which showed crystallites ranging in size from about 5 to 30 μ. This suggests that the mean free path does increase slightly above the crystallite size and it is interesting to estimate the crystallite size from the position and value of the conductivity maximum. The maximum conductivity occurs at 75° K and the mean free path due to Umklapp processes at this temperature can be obtained from the single crystal measurements, and is about 3 μ. As the maximum would be expected to occur at a temperature such that the Umklapp mean free path is of the order of size of the crystallites, this gives a value for the crystallite size. The actual value of the conductivity at the maximum also suggests this order of size of the crystallites.

The sintered beryllia was only measured up to about 90° K and over this whole range the conductivity increases with temperature so that the maximum must occur at a considerably higher temperature than for alumina. Although the boundary resistance is about the same for the two substances, much higher values of conductivity at room temperature and above have been reported for sintered beryllia (e.g. Norton and Kingery 1952) so that its resistance due to Umklapp processes must be lower and the maximum conductivity should occur at a higher temperature than for alumina.

Many samples of graphite have been measured above room temperature by Powell and Schofield (1939) who found that some specimens at room temperature had very high conductivities. For example, some samples had conductivities similar to that of copper, even though measurements of the electrical conductivity show that less than 1% of the heat conductivity can be ascribed to free electrons.

Samples having mean crystallite sizes of 300, 1000 and 2000 Å have now been measured (Berman 1952) from 2° K up to room temperature and the general behaviour is similar to that of the sintered alumina. However, the conductivity is much lower at low temperatures, corresponding to the much smaller crystallite size, and for the specimen with the smallest crystallite size the mean free path seems to be restricted to about 300 Å even at the lowest temperatures. Graphite is an extremely anisotropic solid and has a specific heat which departs considerably from Debye's theory, being proportional to a power of T between 2 and 2·5 at low temperatures, so that the interpretation of the conductivity results is uncertain. It may be significant that the conductivity at low temperatures varies as a power of T which is about 2·2 for the specimen of smallest crystallite size and is about 2·7 in the largest case.

These graphite specimens are very good heat insulators at low temperatures; at 2° K, for example, the thermal conductivity of the 300 Å graphite is one twelfth of that of ordinary glass, which would generally be considered a good heat insulator. It is not certain how the conductivities would compare at lower temperatures, since the conductivity even of glass would eventually be limited by boundary scattering, while the conductivity of graphite might not continue to fall off so rapidly below 1° K if the electronic heat conductivity becomes more important than the lattice contribution.

Although the results on microcrystals are, in general, more difficult to interpret than those in single crystals it does appear that they conform more closely to the simple theoretical picture of an ideal crystal with only two causes of thermal resistance, Umklapp processes and boundary scattering. Presumably as the phonon mean free path is always restricted to a very small length by these two processes the effect of imperfections in the crystal lattice is not noticeable at any temperature.

5.3. *The Conductivity near the Maximum*

The conductivity to be expected when both boundary scattering and U-processes are important has been discussed in § 3.3. For single crystals of the size usually measured, the conductivity at the maximum should be about 20–30% less than would be given by simple addition of the resistances due to the two processes, considered to act separately. Since the resistances due to both processes vary rapidly with temperature the conductivity on either side of the maximum should very soon be determined by one process alone.

For all the pure single crystals which have so far been measured the maximum conductivity is less than the value calculated for an ideal crystal, even when this is calculated according to the combination formula given by Klemens. The absolute value of the Umklapp resistance in the neighbourhood of the maximum cannot at present be calculated from other properties of the crystal, but it can be estimated by extrapolation from higher temperatures where it is the dominant factor.

A small difference between the calculated and experimental values of the maximum conductivity could be ascribed to uncertainty as to the dependence of Umklapp scattering on temperature at temperatures below those at which its effects alone are important. However, for solid helium in a tube of $\frac{1}{2}$ mm diameter the discrepancy is about a factor 2, for the 3 mm diameter sapphire it is a factor 8 and for a diamond of 4 mm square cross-section it is a factor of over 20.

The simplest explanation is to postulate a sufficient number of defects to account for the discrepancies ; it is then necessary to decide the type of defect which would give the extra thermal resistance observed. For both sapphire and diamond the differences between the calculated and observed thermal resistances increase with decreasing temperature ; in the case of sapphire the extra resistance is roughly inversely proportional to the temperature, while for diamond the variation with temperature is much less. For the two sizes of sapphire the extra resistance is the same at the conductivity maximum, but increases more rapidly with decreasing temperature for the smaller crystal, a fact which is connected with the departures from Casimir's law discussed earlier. The equality of the extra resistances at the maxima confirms the belief that these are due to some defect in the crystal and not merely to an error in the theory and the experiments made so far on diamond also suggest that the extra resistance at the maximum does not depend on the size. As the extra resistance must actually be the main resistance at the maximum the value of the maximum itself should be little changed by altering the diameter of the crystal, which only alters a small component of the total resistance. From fig. 1 it can be seen that the maximum conductivities for the two sapphires should occur at about 30° K and should be about 500 and 300 watt units, whereas the actual maxima are at a higher temperature, of much smaller magnitude and are only about 12% different from each other. Experiments will be made when the crystal is further reduced in diameter.

An extra thermal resistance which increases slowly with decreasing temperature could be due either to the effect of a mosaic structure or to impurities (or other small scale defects). Impurities would have to be grouped together in clusters which are of such a size that Rayleigh scattering does not occur for the wavelengths which are important at the temperatures concerned. At lower temperatures Rayleigh scattering might occur, but here the boundary resistance is great enough to mask the effect of defects.

Only one experiment has been made to find the effect of a mosaic structure : this was performed on an artificial sapphire selected, by x-ray examination, to have a mosaic structure much more pronounced than in most specimens. Although this structure was certainly more marked than in the sapphire on which the other experiments have been carried out, the thermal conductivity was no different even in the region of the conductivity maximum, where any extra source of resistance would be most noticeable (Berman, to be published).

Klemens (1952) has pointed out that Ahearn (1951) postulates the presence of clusters of defects in diamond to explain the electrical properties which he has measured. Such clusters could also account for a thermal resistance which is nearly independent of temperature. The strong effect of defects in diamond would also explain the differences between the values measured by de Haas and Biermasz and those shown in fig. 3. At liquid helium temperatures the two sets of measurements are in agreement when account is taken of the different cross-sectional areas used, but at liquid air temperature the single measurement of de Haas and Biermasz gives a value of the conductivity one half of the recent value. As has been explained, reduction of the cross-section has very little effect on the conductivity in this temperature region, so that the difference in conductivities here can be ascribed to the different qualities of the stones.

The purity of the diamond which is being used for the present measurements will be determined at the end of the experiments and it is hoped that it will be possible to obtain a stone of different purity. Artificial sapphires can be prepared with a wide range of suitable impurities and one series of measurements on an impure crystal will be described in the next section.

The relative smallness of the discrepancy between the calculated and measured conductivity maximum for solid helium would be expected both from the purity of the crystal, which must result from the way in which it is formed in the apparatus (Webb *et al.* 1952) and also from the small diameter of the crystal measured. It would be interesting to find whether the discrepancy increases with increasing diameter as for diamond and sapphire.

§ 6. MEASUREMENTS OF THE EFFECTS OF LATTICE IMPERFECTIONS

6.1. *Impurities*

There have not been many measurements designed to determine the effect of lattice imperfections on thermal conductivity. Eucken and Kuhn (1928) measured a series of mixed crystals of KCl–KBr at room temperature and at liquid air temperature. The thermal conductivity was greatest for crystals of either of the pure components and for any intermediate concentrations the relative decrease in conductivity was greater at the lower temperature. This occurs because the resistance due to impurities is weakly dependent on temperature at these temperatures while the Umklapp resistance is roughly proportional to the temperature in this range. The importance of these experiments is that quantitative deductions can be made as to the effect of impurities, whereas in later experiments the impurity concentration is not known so accurately.

De Haas and Biermasz found that above the conductivity maximum the thermal conductivities of KCl and KBr crystals are inversely proportional to the temperature and the absolute values are smaller than those for quartz. The conductivity of KCl is about one quarter of that of quartz in the region of the maxima but becomes greater at temperatures above about 60° K. The values for KBr are smaller at all temperatures at which measurements were made. This strongly suggests that the absence of the exponential variation of conductivity at low temperatures is not observed for the alkali halides on account of impurity scattering. For these ionic crystals there is a simple mechanism by which impurity atoms can enter the lattice, whether they are of the same or different valency from the other atoms. The scattering can then be due either to the effect of the presence of an atom of different atomic weight or to the combined effect of an impurity atom and the corresponding hole created to preserve the electrical neutrality of the crystal as a whole. The latter cause would be expected to give the greater scattering.

In the KCl crystal measured by de Haas and Biermasz the concentration of sodium and magnesium impurities were both estimated to be less than 10^{-4}. Since magnesium is divalent there must be a potassium atom missing from the lattice for each magnesium atom present. Klemens (1951) has calculated the thermal resistance to be expected on the assumption that the effect of an impurity atom and the associated vacant site is the same as would be produced by the presence in the crystal of a spherical hole of radius equal to X times the lattice constant. If ϵ is the impurity concentration then he shows that for KCl $\epsilon X^6 = 6{\cdot}4 \times 10^{-5}$. If X is of the order of unity, then the impurity concentration calculated this way is not inconsistent with the estimated purity of the crystal. Comparison at liquid air temperature of the resistance of the crystal measured by de Haas and Biermasz with that of a mixed crystal containing 10% KBr shows that the scattering caused by an atom of wrong valency is at least 100 times greater than the scattering produced by an atom of different mass but of the same valency.

In the case of KCl and KBr Klemens has also accounted for the low power of the temperature variation of the conductivity below the maxima by the presence of impurites. The resistance due to impurities is proportional to the temperature and therefore dies away much more slowly than that due to Umklapp processes. Measurements would have to be made at much lower temperatures for boundary scattering alone to be important.

An experiment has been made to determine the effect of impurities directly, as a function of temperature (Berman, to be published). Measurements were made on an artificial ruby, which is an artificial sapphire with chromium impurity. Scattering is caused by the replacement of a few aluminium atoms by chromium atoms, which have the same valency but double the atomic weight. The thermal resistance of a pure sapphire of the same diameter has been subtracted from the resistance of the ruby and the resulting resistance is practically independent of temperature between about 20 and 70° K.

This indicates that it is possible for impurities to give an extra thermal resistance which varies with temperature in a way similar to the variation of extra resistance calculated in diamond and sapphire. From this experiment it would be assumed that in the ruby the impurity atoms are to a certain extent clustered together so that the scattering deviates from Rayleigh's law. It is not certain how significant it is that at the surface there was a concentration of chromium atoms not in homogeneous solution in the crystal.

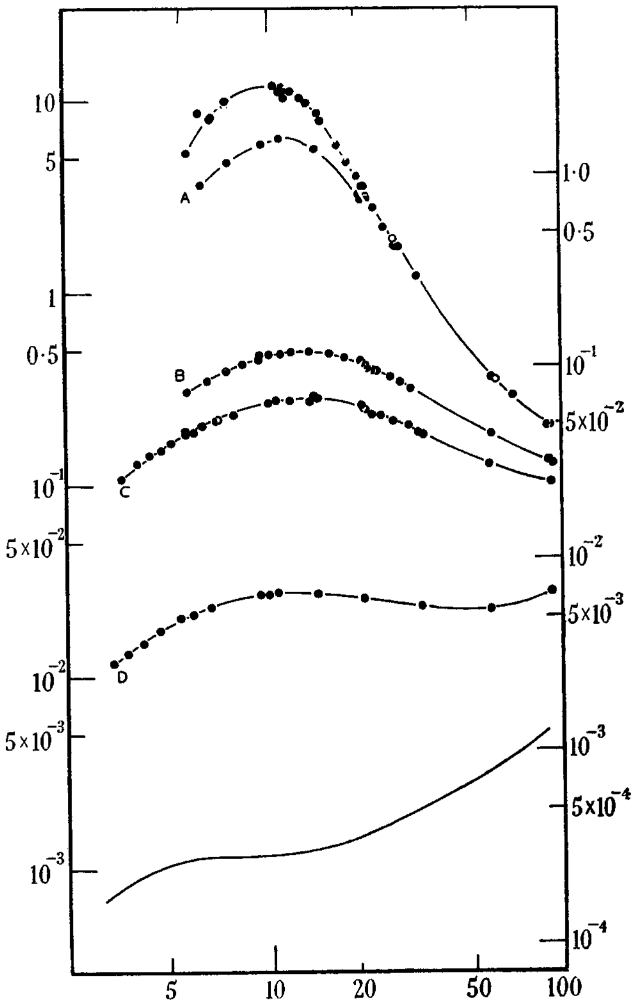
The exact concentration of chromium is not yet known as this can only be determined by analysis of the crystal, being less than the concentration of chromium in the powder from which the crystal is made. It is estimated to be of the order of ½%, which is considerably more than the maximum divalent impurity which could have been present in the KCl crystal measured by de Haas and Biermasz. The relative increase in resistance is, however, small, in agreement with the small increase of thermal resistance found, by Eucken and Kuhn, to result from impurities of the correct valency.

It is not certain how the results of Estermann and Zimmerman (1951) on the conductivity of pure and impure germanium should be interpreted. There are no measurements in the neighbourhood of the conductivity maximum and also the two specimens had very different diameters.

6.2. *Displaced Atoms*

Experiments have been made to determine the effect of displaced atoms on the thermal conductivity of a quartz crystal (Berman, Klemens, Simon and Fry 1950, Berman 1951). One crystal was given three successive periods of neutron irradiation in the Harwell pile and a second crystal, which originally had the same conductivity, was later given a very small irradiation. As the conductivities of the two original crystals

Fig. 9

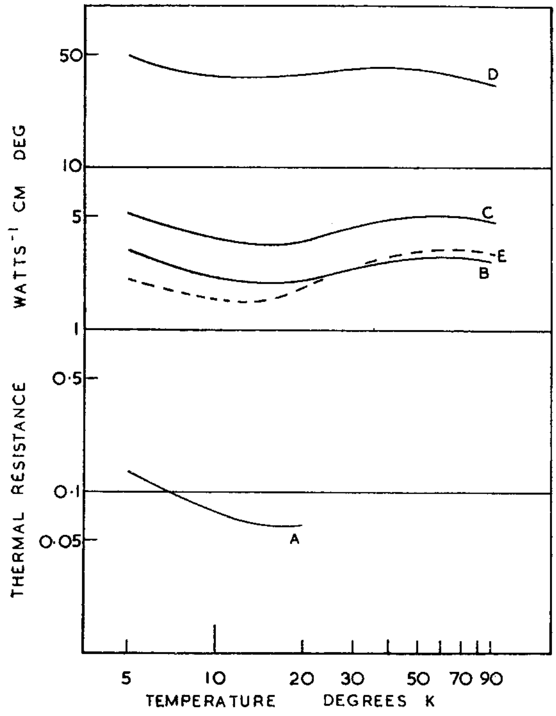


Thermal conductivity of quartz crystal ⊥ axis, irradiated quartz crystal and quartz glass. Approximate cumulative irradiation doses :—A : 0·03 units; B : 1 unit ; C : 2·4 units ; D : 19 units.
Thermal neutron dose for 1 unit : $1{\cdot}8\times10^{18}/\mathrm{cm}^2$.

were the same we may consider the series as four successive irradiations of one crystal.

The conductivity–temperature curves after each irradiation are shown in fig. 9, but in order to interpret the results it is simpler to consider the extra thermal resistance induced. The thermal resistance of the original crystal has been subtracted from the resistance of the crystal subsequently, to give the resistance–temperature curves shown in fig. 10. It is justifiable to assume that the thermal resistance is additive in a simple way as the resistance of the crystal after the irradiation is always considerably greater than the original resistance. This assumption is also confirmed by the fact that all the extra resistance–temperature curves have a similar shape.

Fig. 10



THERMAL RESISTANCE INDUCED IN QUARTZ CRYSTAL BY NEUTRON IRRADIATION

For irradiation doses see fig. 9.

Above 15° K the resistance varies in the manner to be expected for small defects and by comparison with the calculations made for the alkali halides it is possible to estimate the defect concentration ; this agrees with the order of magnitude estimated from the irradiation doses. It is necessary, however, to assume that large defects are also present to explain the increasing resistance at lower temperatures. These could be clusters of interstitial atoms and vacant sites, formed in accordance with the processes discussed by Seitz (1949). The scattering by clusters of defects would be less dependent on the phonon frequency than the scattering by single defects and if they were large enough would act in a similar way to boundary scattering but with a much smaller mean free path.

Some support for the conclusion that there are clusters of defects present is provided by the measurements of conductivity made after various periods of heating following the last irradiation. The crystal was heated for periods usually of about 6 hours, and the thermal resistance extra to that of the original crystal again determined. The simplest comparison between the resistance left after any of these heatings and the resistance induced by irradiation can be made for treatments which resulted in nearly the same resistance. After the crystal had been heated at 700° c the conductivity was restored to roughly the value it had after the second irradiation, as can be seen by comparing curves E and B of fig. 10. The shapes of the curves of extra resistance against temperature are, however, different ; the similarity of the two curves at the higher temperatures suggests that after this particular heating there were present about as many defects as were produced after the second irradiation, but the difference at the lower temperatures suggests that the scattering by the clusters is less for the defects left after heating. As the irradiation effects are cumulative the size of the clusters and the ratio of their number to the total number of defects remains the same for any period of irradiation. On heating, however, the size or density of the clusters must decrease so that when the total number of defects has been reduced to a given amount the relative effect of clusters is less.

An unirradiated crystal, which originally had the same conductivity as the crystals which were later irradiated, was given the same heating as the irradiated crystal in order to find whether heat treatment alone had any effect on the conductivity. De Haas and Biermasz (1935) carried out a similar experiment and found that the conductivity at liquid hydrogen temperatures was reduced by 10–15% after the crystal had been heated to 570° c and then allowed to cool slowly. In the present experiments no difference was found even after heating a crystal to 800° c. It is possible that this difference of behaviour can be explained by the difference between the rates of heating and cooling ; on the other hand, de Haas and Biermasz do not give any indication of the reproducibility of their results if a specimen is merely removed from the apparatus and then set up again. However, after this present crystal had been heated to 850° c its conductivity was considerably reduced and turned out to be almost the same as that produced in the other crystal by the first irradiation. A comparison of the extra resistances suggests that heating produces fewer clusters than irradiation.

The main purpose of the annealing experiments was to find whether the irradiation effects are reversible. They were not complete enough, as regards the influence of both time and temperature for a value of the activation energy of the recovery process to be derived. It is evident, however, that measurements of the thermal conductivity could be used for this purpose, although the effort involved in making measurements at the low temperatures which are necessary for appreciable sensitivity would be considerable.

6.3. *Mosaic Structure*

There have been several suggestions that comparatively low values of thermal conductivity, at temperatures where boundary scattering might be expected to be the chief cause of resistance, can be attributed to scattering due to a mosaic structure (de Haas and Biermasz 1938 b, Garrett 1950, Klemens 1951). It has already been mentioned that de Haas and Biermasz' results for quartz do suggest that for a crystal of sufficiently large diameter the conductivity would be limited by mosaic scattering. It is to be noted, however, that Klemens has shown that for the KCl crystal measured by these workers the observed conductivity can be explained without assuming mosaic scattering.

Garrett found that the conductivity of potassium chrome alum between 0·16 and 0·29° K is proportional to T^3 but that the phonon mean free path calculated from the conductivity is only about 1/10 of the crystal diameter. Although Garrett suggests that this can be ascribed to a mosaic structure Pomeranchuk's treatment leads to scattering by mosaic structure which is frequency dependent, resulting in a conductivity proportional to the temperature. The boundaries within the crystal must therefore be more definite in order to give a scattering which is independent of frequency and a conductivity proportional to the cube of the temperature.

The measurements on artificial sapphire could also possibly be explained by the effect of a mosaic structure but, as has been mentioned, a crystal which was found to have a more marked mosaic character showed no difference in its thermal conductivity. This would seem to be the only set of measurements intended to test the effect of mosaic scattering directly. It cannot be considered conclusive as to the effect of a mosaic structure as this crystal was very short and the accuracy of the measurements was not as high as for other crystals. Any effect could not, however, be greater than 2–3%, so that if a mosaic structure accounts for the great reduction found in the maximum thermal conductivity of the crystals so far measured, it must be at its maximum effectiveness even in crystals of good quality. It is clearly desirable that further experiments should be made on this effect.

§ 7. AMORPHOUS SOLIDS

7.1. *Theoretical*

In his original paper Debye (1914) explained the great difference between the thermal conductivities of crystals and of amorphous solids in terms of the difference in the mean free paths of the lattice waves. In a crystal the scattering arises from the density fluctuations associated with the thermal vibrations and these fluctuations decrease with the temperature, so that the mean free path increases with decreasing temperature. In an amorphous solid, however, the mean free path is restricted by the disordered structure to a length of the order of the interatomic distance and Debye assumed that it would be independent of temperature. Using eqn. (1) it is evident that the thermal conductivity should be proportional to the specific heat.

It was pointed out by Kittel (1949) that it could be deduced from several measurements which had been made below liquid air temperatures that the phonon mean free path in various glasses does increase with decreasing temperature at sufficiently low temperatures. He suggested that this would be expected to occur for temperatures such that the dominant phonons correspond to wavelengths greater than the size of the ‘ unit cell ’ in the glass ; for such phonons the scattering by the disorder in structure decreases with increasing wavelength. For quartz glass, in which the unit cell may be taken to be 7 Å (the size of the oxygen tetrahedron surrounding each silicon atom) the temperature below which the mean free path should increase is about 200° K.

Klemens (1951) has developed a detailed theory of heat conduction in glass. As for a crystal, the thermal motion can be resolved into normal modes of vibration, but as the structure is irregular these normal modes are not plane waves. The instantaneous displacements can still be resolved into plane waves but there is now an interchange of energy between them leading to ‘ structure scattering ’. Klemens assumes that short waves are attenuated by this process with a constant mean free path. In order to find the mean free path of long waves he considers their energy in two parts : the energy pertaining to the overall motion of a large region and the energy pertaining to relative motion of neighbouring atoms. The energy of overall motion is assumed to belong to a normal mode which is almost identical to the plane wave and this energy is retained by the wave. The energy of relative motion belongs to high frequency modes and is attenuated in the same way as high frequency plane waves. It is thus shown that the mean free path of long waves is inversely proportional to the square of the wave-number.

As in the treatment of crystals, it is necessary to consider the effect of processes in which momentum is conserved, represented by eqn. (2) and (3), and the mean free path for such processes is assumed to be the same as in crystals, as has been calculated by Pomeranchuk (1941) and by Landau and Rumer (1937).

Klemens obtains the thermal conductivity in terms of three empirical constants which can be found by comparison with the experimental results. At high temperatures the conductivity is mainly determined by the mean free path of transverse waves and is proportional to the specific heat, but at low temperatures the conductivity is determined by longitudinal waves and is proportional to the absolute temperature. The contributions of the two types of waves is equal, for quartz glass, at about 25° K. The comparison between theory and experiment is shown in fig. 2; κ_{I} and κ_{II} denote the contributions of the longitudinal and transverse phonons respectively. It can be seen that the main features of the theoretical curve which are not dependent on the determination of the constants are in agreement with experiment and by choosing the constants suitably very close quantitative agreement is obtainable over the whole range of temperature.

7.2. *Experimental*

The measurements by Eucken (1911 a) on quartz glass and by Stephens (1932) on Pyrex glass showed that the conductivity varies roughly as the specific heat down to liquid air temperature. Measurements have been made at lower temperatures by Bijl (1949) Wilkinson and Wilks (1949) and Berman (1951) and there is an isolated measurement at 1·3° K by Keesom (1944).

Bijl measured four types of glass between 1·5 and 3·0° K, using a method similar to that which he used for potassium chrome alum. The temperature gradient along the rods was measured by measuring the temperature of two specimens of a paramagnetic salt which were enclosed in glass vessels attached to the glass rod. The geometrical factor for calculating the conductivity could not be determined to better than about 30% but, by making all the specimens of the same size, Bijl was able to compare the conductivity of the various types of glass. It was found that the conductivities of all four glasses were of the same order of magnitude and varied approximately as $T^{1\cdot 3}$.

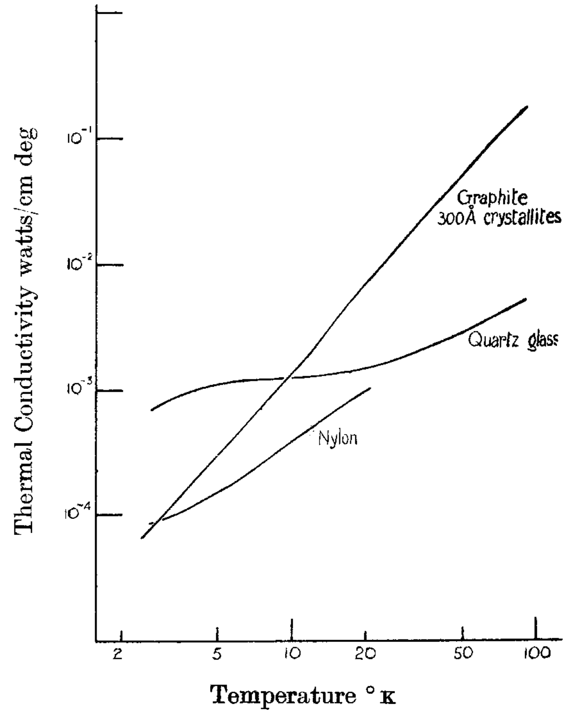
Wilkinson and Wilks measured the conductivity of Phoenix glass by determining the rate at which a rod conducted heat into a vessel of liquid helium. By varying the temperature of the 'warm' end of the rod, it was shown that the conductivity is nearly independent of the temperature between 10 and 20° K.

Quartz glass and Phoenix glass were measured between 2 and 90° K by Berman and a soft glass was measured between 2 and 5° K. The absolute values are in agreement with those of Wilkinson and Wilks for Phoenix glass and the variation with temperature at liquid helium temperatures is similar to that found by Bijl. Comparison with the absolute values found by Bijl cannot be made for any one glass, but the most similar in composition are the Thuringian glass measured by Keesom and Bijl and the G. E. C. Wembley X 8 glass measured by Berman. An extrapolation of Bijl's curve gives a value 30% higher than that found by Keesom at 1·3° K and at liquid helium temperatures his results are also about 30% higher than those of Berman. This difference is the same as the uncertainty in absolute values which Bijl states is due to the difficulty in determining the geometrical factor necessary in calculating the conductivity in his experiments.

Some work has been carried out on plastics: a temperature variation of conductivity similar to that of glass has been found for Perspex (Berman

1951), which was measured between 2 and 20° K. Also an attempt was made to find whether there is any difference in conductivity between stretched and unstretched Nylon threads, associated with the different degree of crystallinity. Up to now only some preliminary measurements have been made on a stretched sample below 20° K. The conductivity can be represented roughly by $\kappa = 2{\cdot}5 \times 10^{-5}\, T^{1{\cdot}2}$ watt units. Until further measurements are made it is not certain whether this temperature variation is related to the similar variation found in glasses below about 4° and which may also hold for Perspex below 2° K.

Fig. 11



Thermal conductivity of graphite (300 Å), quartz glass and nylon.

It has been pointed out in § 5.2.2, that although glasses are poor heat conductors at normal temperatures, microcrystalline solids may have much lower conductivities at low temperatures. In fig. 11 are shown, for comparison, the conductivities of quartz glass, Nylon and of the graphite specimen with the smallest crystallite size which was measured.

§ 8. SUMMARY

The main features of the conductivity-temperature relation for pure dielectric crystals can be explained in terms of Peierls' theory, supplemented by the calculation by Casimir of the influence of the crystal size at low temperatures. The Umklapp processes postulated by Peierls give rise to a thermal resistance which decreases with decreasing temperature at low enough temperatures the decrease follows an exponential law. The thermal resistance remains finite, however, and, in fact, increases again owing to scattering of the phonons at the boundaries of the crystal; this increasing resistance is no longer an intrinsic property of the crystalline material but depends on the diameter of the crystal measured.

The exponential rise in conductivity has recently been observed for several crystals and boundary scattering has been studied for a considerable time, but there are considerable difficulties in explaining the details of the temperature variation of conductivity actually found for single crystals. The greatest discrepancy between the theoretical values, based on the two sources of resistance mentioned, and the experiments is found in the neighbourhood of the conductivity maximum. Here the resistance of the ideal crystal would be very small, so that any extra source of resistance would be shown up most clearly.

Experiments on the dependence of the maximum conductivity on crystal diameter suggest that the discrepancy is due to defects in the crystals, since it is found that the discrepancies are smaller for crystals of smaller diameter; for sufficiently small crystals, such as exist in some polycrystalline solids, the resistances due to Umklapp processes and to boundary scattering are at all temperatures large enough to mask the effect of imperfections.

It was found that only about 3 displaced atoms per million (produced by neutron bombardment) in a quartz crystal halved the value of the maximum conductivity, so that it might be expected that crystals of high purity, having the same diameter, would accidentally have sufficiently different imperfections to show differences in their maxima. However, three natural quartz crystals were measured in the course of the experiments and there was no difference between the values of the maxima (the experimental accuracy was 1–2%). Also, no difference was found between two artificial sapphire crystals, one of which had a much more pronounced mosaic structure than the other. Only in the case of diamond is there some evidence that the maxima may be different for different crystals, and further measurements will be made on pure crystals near the maxima to look for small differences.

From the temperature dependence of the extra thermal resistance which is present near the maximum it is possible to deduce the grouping of imperfections which would give rise to it. Single defects, defects grouped together in either clusters or linear arrays (such that all dimensions are not small compared with the dominant lattice wavelengths) and a mosaic structure have been suggested to explain the results for various crystals. There is, however, only meagre experimental evidence as to the temperature variation of the resistance which each of these groupings of imperfections actually produces.

There are discrepancies between theory and experiment at lower temperatures which cannot be explained simply in terms of imperfections:

these are observed in the region where only boundary scattering would be expected to be important. The conductivity should be proportional to T^3 and should correspond to a phonon mean free path equal to the diameter of the crystal. These two characteristics of boundary scattering have not been found together for the conductivity of any crystal. The T^3 variation of conductivity has only been observed in measurements of potassium chrome alum below 0·3° K and a phonon mean free path equal to the theoretical value has been derived only from measurements on diamond at about 2° K. In both cases the temperatures correspond to about $\theta/1000$. At higher temperatures the conductivity is still found to be proportional to the crystal diameter, which suggests that only boundary scattering is important, but it is proportional to a smaller power of the temperature than 3 and the mean free path is less than the diameter.

Although the thermal conductivities of dielectric crystals do not reach the very high values calculated for the ideal case, the values can be of the order of magnitude associated with metallic conductors. It is commonly stated that metals are better conductors than dielectrics on account of the electronic conductivity. The conductivity of dielectrics is much more temperature dependent than that of metals and it happens that at room temperature the conductivities are generally well below the maximum and are, consequently, lower than the good metallic conductors. For diamond, however, room temperature is still a relatively low temperature and the thermal conductivity is higher than that of any metal yet measured. At the other extreme it has been shown that, as a result of boundary scattering, dielectric solids with sufficiently small crystallites can have conductivities much smaller than amorphous solids, such as glass.

It is hoped that some of the experiments which are planned, particularly those on the ‘ size effect ’, will throw more light on the discrepancies still existing between theory and experiment ; they should suggest ways in which the theory needs further development.

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