

---

# The Thermal Conductivities of Some Dielectric Solids at Low Temperatures (Experimental)

R. Berman

*Proc. R. Soc. Lond. A* 1951 **208**, 90-108

doi: 10.1098/rspa.1951.0146

---

## Email alerting service

Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click [here](#)

---

To subscribe to *Proc. R. Soc. Lond. A* go to:  
<http://rspa.royalsocietypublishing.org/subscriptions>

---

- Bamford, C. H., Hanby, W. E. & Happey, F. 1949*a* *Nature*, **164**, 138.  
 Bamford, C. H., Hanby, W. E. & Happey, F. 1949*b* *Nature*, **164**, 751.  
 Bamford, C. H., Hanby, W. E. & Happey, F. 1951 *Proc. Roy. Soc. A*, **205**, 30.  
 Boyes-Watson, J., Davidson, E. & Perutz, M. F. 1947 *Proc. Roy. Soc. A*, **191**, 83.  
 Bunn, C. W. & Garner, E. V. 1947 *Proc. Roy. Soc. A*, **189**, 39.  
 Crowfoot, D. 1938 *Proc. Roy. Soc. A*, **164**, 580.  
 Elliott, A. & Ambrose, E. J. 1950*a* *Nature*, **165**, 921.  
 Elliott, A. & Ambrose, E. J. 1950*b* *Disc. Faraday Soc.* Cambridge, **9**, 246.  
 Elliott, A., Ambrose, E. J. & Robinson, Conmar 1950 *Nature*, **166**, 194.  
 Elliott, A., Ambrose, E. J. & Temple, R. B. 1948 *J. Chem. Phys.* **16**, 877.  
 Huggins, M. L. 1943 *Chem. Rev.* **32**, 195.  
 Kendrew, J. C. 1950 *Proc. Roy. Soc. A*, **201**, 62.  
 Lens, J. 1947 *J. Biol. Chem.* **169**, 313.  
 Lundgren, H. P. 1941 *J. Amer. Chem. Soc.* **63**, 2854.  
 Palmer, K. J. & Galvin, J. A. 1943 *J. Amer. Chem. Soc.* **65**, 2187.  
 Perutz, M. F. 1949 *Proc. Roy. Soc. A*, **195**, 474.  
 Richards, R. E. & Thompson, H. W. 1947 *J. Chem. Soc.* p. 1248.  
 Rudall, K. M. 1950 *Progress in Biophysics* (1), 39. Edited J. A. V. Butler and J. T. Randall, Butterworth-Springer, London.  
 Svedberg, T. & Pedersen, K. O. 1940 *The ultra-centrifuge*. Oxford University Press.  
 Taylor, H. S. 1941 *Proc. Amer. Phil. Soc.* **85**, 1.  
 Waugh, D. F. 1946 *J. Amer. Chem. Soc.* **68**, 247.  
 Waugh, D. F. 1948 *J. Amer. Chem. Soc.* **70**, 1850.

## The thermal conductivities of some dielectric solids at low temperatures

(Experimental)

BY R. BERMAN, *The Clarendon Laboratory, University of Oxford*

(Communicated by F. E. Simon, F.R.S.—Received 18 January 1951)

An apparatus is described in which the thermal conductivity of solids can be determined at any temperature between 2 and 90°K. Several glasses and dielectric crystals have been measured. It had previously been found that at high temperatures the conductivity of glasses is proportional to the specific heat, but at low temperatures it falls off more slowly than the specific heat. The present experiments show that there is a temperature region in which the conductivity is nearly independent of temperature. A similar variation of conductivity is found for the thermo-plastic Perspex.

The effect of lattice defects in crystals was studied by measuring the thermal conductivity of a quartz crystal before and after successive periods of neutron irradiation. After prolonged irradiation the conductivity approached, in both magnitude and temperature variation, that of quartz glass. Subsequent heating produced a substantial recovery in the conductivity.

The results on both glasses and on crystals can be explained by the theory developed by Klemens (1951). Further measurements made on a corundum crystal confirm the importance of the 'Umklapp' processes, postulated by Peierls, in causing thermal resistance.

### INTRODUCTION

The study of thermal conductivity of solids at low temperatures suffers from a lack of measurements made over a sufficiently wide range of temperature. The existing measurements have been made either at fairly widely separated temperatures or

over only relatively small ranges of temperature. In general, the thermal conductivity is dependent on several factors, and it is not always possible to calculate the relative importance of these from isolated measurements. Several series of experiments have been made to study the temperature variation of thermal conductivity at liquid helium temperatures, but in order to obtain data on the basis of which a detailed comparison with the theories could be made, such experiments should also be made at both higher and lower temperatures. To extend the experiments to higher temperatures an apparatus has been constructed in which thermal conductivity can be measured at any temperature between 2 and 90°K. Of the experiments so far carried out, only those on dielectric solids will be described here.

#### PREVIOUS WORK

Eucken (1911) measured the thermal conductivity of a large number of dielectric crystals and amorphous substances at room and liquid-air temperatures and also made a few measurements in the liquid-hydrogen range. He found that the conductivity of single crystals increases with decreasing temperature, while the conductivity of amorphous solids decreases.

Debye (1914) was able to explain this difference in behaviour by regarding the flow of heat through a dielectric solid as being due to travelling elastic waves, the scattering of which gives rise to a thermal resistance. This scattering can be expressed in terms of a mean free path  $l$ , defined as the distance which a wave travels before its intensity is reduced to  $1/e$  of its initial value. The thermal conductivity,  $K$ , is then given by the relation  $K = \frac{1}{4}lc_vv$ , where  $c_v$  is the specific heat per unit volume and  $v$  is the wave velocity.

For crystals, the mean free path is limited by scattering of the waves by density fluctuations, which arise from the anharmonicity of the lattice vibrations, and is inversely proportional to the absolute temperature. At temperatures where the specific heat is little dependent on temperature the conductivity would be inversely proportional to the temperature, which is in agreement with the general trend of Eucken's measurements.

In a glass, however, the mean free path is limited by the disorder of the structure and would be independent of temperature. According to this theory, the thermal conductivity of a glass should vary with temperature in the same way as the specific heat.

The more recent work on thermal conductivity of dielectric solids can best be discussed under the separate headings of glasses and crystals.

#### *Glasses*

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 from above room temperature down to liquid-air temperature (about 80°K). However, measurements by Bijl (1949), on several glasses, between 1.4 and 3°K, showed that the conductivity varied as  $T^{1.3}$  at temperatures where the specific heat is probably proportional to  $T^3$ . Some measurements by Wilkinson & Wilks (1949) on Phoenix glass indicated that between 10 and 20°K the conductivity varies little

with temperature. The mean free path, calculated from the Debye formula, must therefore increase with decreasing temperature.

While the present experiments were being made, Professor Pryce suggested that the increase of mean free path at low temperatures occurred because the wavelength of the waves dominant in carrying the thermal energy increases as the temperature decreases, with a consequent reduction in the scattering produced by the disorder in the glass. At about the same time Kittel (1949) also put forward this explanation and calculated that this effect should be noticeable below about 200° K. The complete dependence of the mean free path on temperature could not be deduced from these four sets of experiments, since each had been made on different glasses.

### *Crystals*

Peierls (1929) developed a more refined theory of thermal conductivity of crystals than that of Debye. He considered the individual atomic motions, instead of the continuum treated by Debye, and used the concept of phonons in treating the lattice vibrations. According to this theory the conductivity is limited by 'Umklapp' processes; interference processes involving three phonons, in which the total energy is conserved but the direction of the energy current is changed. At high temperatures this leads to a conductivity which is inversely proportional to the absolute temperature. At low temperatures, if only limited by Umklapp processes, the conductivity would increase more rapidly than the inverse of the temperature and would tend to infinity at absolute zero. The presence of impurities or lattice defects will, however, increase the thermal resistance.

At low temperatures, according to Peierls, the thermal resistance can be written

$$W = aT^\nu \exp(-\Theta/2T) + bT,$$

where  $a$ ,  $b$  and  $\nu$  are constants and  $\Theta$  is the Debye characteristic temperature. The first term is the resistance due to Umklapp processes and the second is due to lattice defects. The resistance, given by this formula, tends to zero at absolute zero, corresponding to infinite conductivity.

de Haas & Biermasz (1935) made measurements on a quartz crystal to find whether this relation holds down to the lowest temperatures. They found that in the liquid-helium temperature region the conductivity actually decreases with decreasing temperature, apparently to zero at absolute zero. They estimated that the conductivity would be a maximum at about 10° K, but did not make measurements between 5 and 15° K. They remarked that the ratio  $K_{220}/K_{880}$  was 10.6, in good agreement with the value of 11.7 found by Eucken, but did not apparently calculate how this agreed with the theory of Peierls.

Peierls (see de Haas & Biermasz 1937) suggested that the decrease in conductivity below 10° K might be due to a limit to the mean free path of the phonons being set by reflexion at the walls of the crystal. The effect of this was calculated by Casimir (1938), who showed that at sufficiently low temperatures it would lead to a conductivity proportional to the diameter (or width) of the crystal and proportional to the specific heat of the substance; the dependency on size was later confirmed experimentally by de Haas & Biermasz (1938).

de Haas & Biermasz (1937) also measured the conductivity of two ionic crystals, KCl and KBr. They again found that the conductivity must have a maximum, which for these crystals was estimated to occur at about 7°K. The conductivities of these crystals are considerably less than that of quartz, and are nearly inversely proportional to the absolute temperature between 10 and 90°K.

#### THE PRESENT EXPERIMENTS

##### *Glasses*

The thermal conductivities of quartz glass and Phoenix glass have been measured between 2 and 90°K. On the basis of these experiments a detailed theory of heat conductivity of glasses has been worked out by Klemens (1951).

A similar variation of conductivity with temperature has been found at low temperatures for the thermo-plastic Perspex.

##### *Crystals*

Further measurements have been made on a quartz crystal so that, in conjunction with the measurements of de Haas & Biermasz, the temperature variation of the conductivity is well established over the whole range from 2 to 90°K. It can be deduced that the effect of impurities and lattice defects is small and the resistance above 10°K is mainly due to Umklapp processes. Lattice defects were then produced in this crystal by neutron bombardment and the thermal resistance due to these defects found. From the measurements of conductivity it has been possible to derive some information as to the nature of the defects. After the last irradiation the crystal was heated to various temperatures, and the annealing of the defects has been determined by measuring the increase in the thermal conductivity produced. The effect of the same heat treatment on an unirradiated crystal has also been measured.

The thermal conductivity of corundum ( $\text{Al}_2\text{O}_3$ ), a crystal exhibiting some ionic characteristics, was measured between 2 and 90°K. It is deduced that, as in the case of quartz, the resistance at temperatures above the conductivity maximum is mainly due to Umklapp processes. This is in contrast to the two ionic crystals measured by de Haas & Biermasz, in which the resistance due to impurities must be dominant.

Since the maximum conductivity of corundum occurs at about 50°K the boundary resistance is dominant over a larger range of temperature than for quartz and can be studied more fully.

#### APPARATUS

The thermal conductivity is measured by applying heat to one end of a specimen while the other end is kept at any desired temperature. The temperature gradient along the specimen is determined by measuring the temperature difference between two points which are at a known distance apart.

For the present experiments, which extend over a relatively large temperature range, it was considered desirable to use the same method of temperature

measurement throughout the range so that new connexions to the specimen would not have to be made during the course of an experiment. For this reason, although the accuracy of measurement is reduced at both the upper and lower ends of the

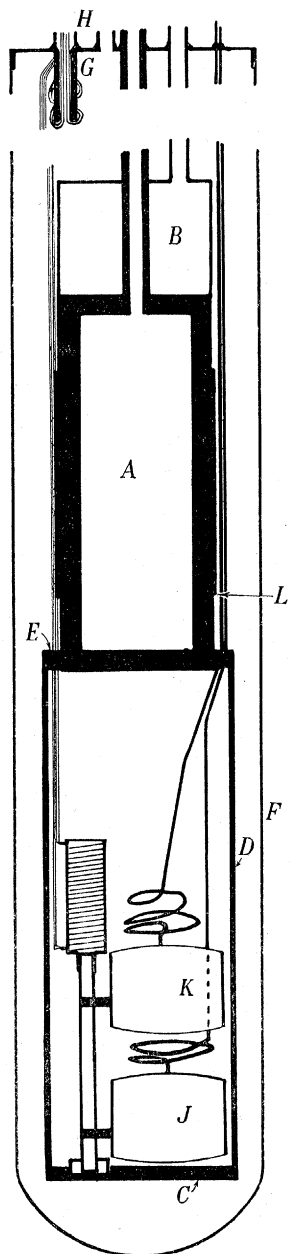


FIGURE 1. Apparatus.

range, gas thermometers were chosen. Gas thermometers were first used in a similar way by de Haas & Rademakers (1940) because they are not affected by magnetic fields.

The apparatus is shown schematically in figure 1. It consists essentially of a Simon expansion helium liquefier with a high-pressure vessel *A* and hydrogen cap *B*. The specimen to be measured is carried on the copper disk, *C*, which is connected to the high-pressure vessel by the radiation shield, *D*. This radiation shield is made in three sections and the base *C* is hard soldered to one of these, which is permanently attached to the collar, *E*, round the bottom of *A*. The other two sections are put in position after the specimen has been mounted and are soldered with Wood's metal to *A* and *C*. The sections of the radiation shield are not soldered to one another so that the gas pressure inside *D* is the same as that inside the vacuum jacket *F*. The edges of the sections overlap, however, so that no radiation reaches the specimen from outside *D*.

The electrical leads (36-gauge insulated constantan) for the heater attached to the specimen pass through small holes in the collar *E* and are wrapped round the high-pressure vessel *A*. They are also wrapped round and varnished to the copper bush *G*, which forms the continuation, below the cap of the vacuum jacket, of the German-silver tube *H*. The leads emerge from the apparatus through four glass tubes attached to the end of *H* which is at room temperature. These tubes are sealed by a little wax. The heater is either wound directly on the specimen or on a light metal former which is attached to the specimen.

The temperatures at two places along the specimen are measured by the two gas thermometers *J* and *K*. Both have a volume of approximately 15 cm.<sup>3</sup> and can be filled with helium gas to any pressure up to atmospheric pressure. The thermometers are connected to the outside by stainless steel capillary tubes (0.6 mm. outer diam., 0.3 mm. inner diam.) which are soldered to the collar *E*, to make good thermal contact, and pass through bushes in the cap of the vacuum jacket. The two capillaries are led to opposite sides of a differential mercury manometer which is read with a katherometer. On one side the differential manometer is connected to a constant-volume mercury manometer so that absolute pressures can also be measured.

*Production of required temperatures*

The temperature drop along the specimen must be kept small if the variation of conductivity with temperature is to be determined in detail. In experiments with bad conductors, as will be shown later, it is also necessary that the thermal resistance of the junction between the specimen and  $C$  should be small. The main factor determining the mean temperature between the two thermometers is therefore the temperature of the vessel  $A$ .

To obtain temperatures from 1.8 to 5°K, helium is liquefied in  $A$  and is allowed to boil at reduced pressure, atmospheric pressure or at a pressure up to the critical pressure. Since there is liquid hydrogen round the vacuum jacket there is always a heat flow into  $A$  down the connecting tubes, even when the helium is above its normal boiling-point.

At temperatures between 5 and 9°K good conductors can be measured by adding a heater to the specimen between the bottom thermometer  $J$  and the point of attachment to  $C$ . For a given temperature gradient along the specimen the heat lost by conduction along the leads and capillary at the top of the specimen is increased by raising the temperature of the specimen as a whole, but for good conductors this is still only a small fraction of the heat which is supplied at the top of the specimen.

For temperatures between 9 and 33°K, hydrogen is condensed into  $A$  and is allowed to boil at reduced pressure, atmospheric pressure or at any pressure up to the critical pressure of 12.8 atm. In the last case it is necessary to put liquid oxygen round the vacuum jacket, after condensing the hydrogen, in order that there should be a heat flow into  $A$  to raise its temperature.

Temperatures between 33 and 55°K are obtained by evacuating  $A$  and  $B$  and placing liquid hydrogen round the vacuum jacket. A suitable current is passed through a heater,  $L$ , wound round  $A$  so that equilibrium is established, at any temperature, between the heat generated in this heater and the heat flowing from  $A$  up to the liquid hydrogen.

For temperatures between 55 and 90°K oxygen is condensed into  $A$  and is allowed to boil at any pressure down to that corresponding to the triple point at 54°K.

Since the equilibrium time for measurements on the worst conductors is over an hour, it is not convenient to keep temperatures above the critical points of helium and hydrogen constant by using a controlled expansion of the gas.

*Measurement of temperature*

The thermometers are filled with the required pressure of helium at the boiling-points of oxygen or hydrogen, depending on the temperature range to be measured. The two thermometers are connected through the differential manometer, and a small pressure of helium gas is in the vacuum jacket as exchange gas.

The connexion is closed after it is seen that the pressure in both thermometers remains unchanged when they are left separated for several minutes. Since, in the process of liquefying helium, the exchange gas is pumped out of the vacuum jacket it is not always convenient to fill the thermometers at liquid-helium temperatures. For a bad conductor it would be some time before the two thermometers were

definitely at the same temperature and pressure. It is occasionally verified, however, that when filled with equal pressures of helium gas at the boiling-point of hydrogen, the pressures in the two thermometers are still equal at liquid-helium temperatures.

For convenience in calculating temperatures from subsequent pressure readings, the ratio of the dead volume of the measuring system to the volume of the gas thermometer itself was made the same for both thermometers. This ratio was determined by measuring the change in pressure on cooling the thermometers from room temperature to liquid-oxygen temperature and from liquid-oxygen temperature to liquid-hydrogen temperature.

For calculating the temperature differences a small correction has to be made at the higher absolute temperatures for the change in the dead volumes produced by the movement of the mercury in the differential manometer.

No correction is made for the fact that part of the dead volume consists of the capillary tubes inside the apparatus at a temperature between that of the thermometers and room temperature. Owing to their small volume this does not affect the calculated temperature or the temperature difference within the accuracy of the measurements.

A small correction has to be made to the calculated absolute temperatures below  $20^{\circ}\text{K}$  to account for the fact that even helium does not behave as an ideal gas at these low temperatures. At the lowest temperatures used the correction to be applied to the measured pressure on account of the thermomolecular pressure effect in the capillaries is about 1%.

The accuracy of temperature measurement is smallest at either end of the temperature range used. At the upper end this is due to the correction to be applied for the external volume and for the change in this volume with the pressure difference. There is also a slight uncertainty in the temperature at which the thermometers are filled, owing to possible superheating of liquid oxygen. At the lower end the accuracy is limited by the pressure which can be used in the thermometers. This pressure must be low enough so that the helium does not condense in the coldest part of the measuring system, which occurs where the capillaries pass through the collar *E*.

Up to about  $30^{\circ}\text{K}$  temperature differences between the thermometers of less than  $0.1^{\circ}$  can be measured with an accuracy of about 1%. The accuracy decreases with increasing absolute temperature, and at about  $90^{\circ}\text{K}$  temperature differences of  $0.5$  to  $1^{\circ}$  can be measured to within about 5%.

#### *Correction for heat losses*

Apart from flowing down the specimen, the heat generated in the heater can be lost by (1) conduction along the electrical leads connected to the heater and along the capillary tube connected to the top thermometer, (2) radiation from the specimen, heater and top thermometer to the radiation shield, and (3) conduction through any residual gas in the radiation shield.

(1) The lengths of the electrical leads and capillary tubes between the specimen and the collar *E* were made about 30 cm. by coiling them. The thermal conductivity



of the constantan wires was measured in a separate experiment, in which over 300 short wires in parallel were used. The conductivity of a stainless-steel rod was measured, and, since the values found were similar to those found for various steels by other authors, they were assumed to apply to the capillaries, to within the necessary accuracy. These measurements are described elsewhere (Berman 1951).

(2) The heat lost by radiation is appreciable only in the liquid-oxygen temperature region. This loss was determined by finding the temperature reached at the top of a thin rod of Perspex when heat was applied. The small amount of heat lost by conduction through the rod and the leads was estimated and the heat lost by radiation could be calculated.

(3) The pressure maintained in the vacuum jacket during measurements is sufficiently low that no correction need be made for heat lost by conduction through the residual gas, even when measuring the worst conductors. It was, however, considered necessary to verify this in the case of the measurements on glass at low temperatures. For this purpose hydrogen was used as exchange gas during the preliminary cooling from room temperature and also prior to the helium liquefaction. If there were any residual gas in this case it would be hydrogen, and this would not conduct any measurable quantity of heat at liquid-helium temperatures owing to its extremely small vapour pressure at these temperatures. No difference in the conductivity measured was found when the measurements were carried out with either helium or hydrogen used to cool the apparatus. Also, no difference was found when the vacuum jacket was disconnected from the pump after the helium expansion had started.

For the measurements on glass, when thin rods were used, the corrections for heat lost by conduction and radiation varied from about 30% at 90°K to about  $\frac{1}{2}$ % in the liquid-helium region. For the measurements on quartz (before irradiation) the correction was about 1% at 90°K and rapidly decreased to a negligible amount below this temperature.

As a check on these corrections, the conductivity of two different lengths of several specimens was measured. For the same temperature difference to be produced between the thermometers the heat inputs are inversely proportional to the lengths. The heat losses are nearly the same for both lengths, and the percentage correction is therefore proportional to the length of the specimen. No difference greater than the experimental uncertainties was found between the calculated conductivities of different lengths of specimens.

The heat generated in the leads was kept small by using heaters with a resistance of about 1000 $\Omega$ , while the leads have a resistance of about 4 $\Omega$ .

It was verified that no heat reached the specimen, from outside the radiation shield, sufficient to produce a measurable temperature gradient along the worst conductors. With the specimen at liquid-hydrogen temperature no temperature difference between the thermometers was found when the liquid hydrogen round the vacuum jacket was replaced by liquid oxygen.

## MEASUREMENTS ON GLASSES

Three different specimens of quartz glass, two of Phoenix glass (a borosilicate glass) and one of Perspex were measured.

The diameters of the glasses varied between 6 and  $9\frac{1}{2}$  mm., and the distance between the points of attachment of the thermometers from 2 to  $4\frac{1}{2}$  cm. For connecting the specimens to the base of the radiation shield and to the thermometers, rings of 'liquid silver' were painted at the appropriate places and heated gently. The resulting metal surfaces were tinned with a thin layer of soft solder. At the two measuring points copper strips were soldered to the glass and the thermometers were connected to these strips with Wood's metal. At the base the glass was soldered into a collar which was connected to the radiation shield.

The Perspex specimen was a  $\frac{1}{2}$  in. rod kindly supplied by I.C.I. Ltd. Connexions to this were made by screwing brass screws in the specimen at the appropriate places and making the Wood's metal joints to these.

For all these specimens the heating coil consisted of a length of Impag resistance mat (constantan woven with silk) of resistance 750 to 1250  $\Omega$  wrapped directly on the top of the specimen and attached by means of varnish which was then baked.

In order that the thermometers should have the same temperatures as the specimen at the points of attachment the contact resistance between the specimen and the thermometers must be small compared with the thermal resistance of the length of capillary tube between the thermometers and the collar *E*. The contact resistance can be estimated, since the method of attaching the thermometers to the specimen is the same as the method of attaching the specimen to the base of the radiation shield. The resistance of this bottom contact can be calculated by comparing the temperature rise of the thermometers when there is a temperature gradient down the specimen. At liquid-oxygen temperatures the contact resistance is a very small fraction of the resistance of the specimen which, in turn, has a resistance of only a few units per cent of the thermometer capillaries. At liquid-helium temperatures the contact resistance has become equal to about 10 % of the resistance of the specimen, but the resistance of the specimen has become in turn less than 1 % of the resistance of the capillaries. Over the whole temperature range, therefore, the temperature drop along the specimen is measured correctly to within the accuracy of the measurement of the temperature difference between the thermometers themselves.

Since the thermometer attachments extend over a finite length of the specimen it is necessary to determine the length of specimen which corresponds to the measured temperature difference in order to derive the absolute values of the conductivity. One specimen of Phoenix glass was measured at liquid-hydrogen temperature using first 4 cm. between the thermometers and then using 2 cm. The effective length was assumed to be the distance between the insides of the copper bands with an 'end-correction' to be determined. The two conductivities measured could be reduced to the same value by taking as the 'end-correction' half the width of the bands. The same correction was found to apply to two other substances which have been measured and for which the method of attaching the

copper bands was rather different (a quartz crystal and a German-silver rod). For Phoenix glass these two measurements are not included with the other results since they were measured with a pair of thermometers which did not give accurate readings below  $20^{\circ}\text{K}$  owing to the presence of a deposit in one of them which absorbed helium.

The results of the present measurements are shown in figure 2. For both types of glass there is a region of temperature in which the conductivity varies little with the temperature. In the liquid-helium temperature region the conductivity is proportional to the absolute temperature. At the highest temperatures the conductivity is nearly proportional to the specific heat.

To reduce the equilibrium time for the measurements between 15 and  $20^{\circ}\text{K}$ , the shorter and thicker rods of glass were used. The measurements on these are shown by open circles in figure 2. The difference in the absolute magnitude of the conductivity found for these specimens compared with the longer specimens of both glasses may be due, in part, to a slight uncertainty in the true length of specimen to be assumed when calculating the conductivity.

The present measurements agree well with previous values in the temperature regions where they overlap. At  $90^{\circ}\text{K}$  the value found for Phoenix glass is 10% lower than the value found by Stephens for Pyrex glass. At 10, 15 and  $20^{\circ}\text{K}$  the values are about 5% higher than those deduced by Wilkinson & Wilks (1949). In the liquid-helium temperature range the variation of conductivity is, to within the experimental accuracy, the same as that found by Bijl (1949) for several other glasses; the present measurements on Phoenix glass give values of the order of 40% lower, in absolute magnitude, than the lowest values of Bijl. Bijl does not claim great accuracy in the absolute values he reports, owing to uncertainty in the distance to be taken as the length of specimen being measured. Also the glasses he has measured are rather different from Phoenix glass.\* The only previous measurements on quartz glass in the temperature range of the present experiments are those of Eucken. At  $90^{\circ}$  the present measurements give a conductivity 20% lower than that found by Eucken.

In a previous paper (Berman 1949) the variation of apparent mean free path with temperature, below  $90^{\circ}\text{K}$ , was given. This showed a transition from a mean free path independent of temperature to a variation as the inverse square of the temperature at low temperatures. For the calculation of this mean free path the simple Debye relation was used, in which no account was taken of the difference in the mean free path for phonons corresponding to different wave-lengths, nor was any distinction made between the behaviour of transverse and longitudinal waves.

Klemens (1951) discusses the conductivity of glass more rigorously. At high temperatures the conductivity is mainly due to the transverse waves and should be proportional to the specific heat. At low temperatures the contribution from longitudinal waves predominates and gives rise to a component which is

\* More recently measurements between 2 and  $5^{\circ}\text{K}$  have been made on G. E. C. Wembley X8 glass. Of the various glasses measured by Bijl, the nearest to this in composition is Thuringian glass. The present measurements give the same temperature variation of conductivity, but the absolute values are about 30% lower.

portional to the absolute temperature at the lowest temperatures, reaches a maximum and then falls off at higher temperatures.

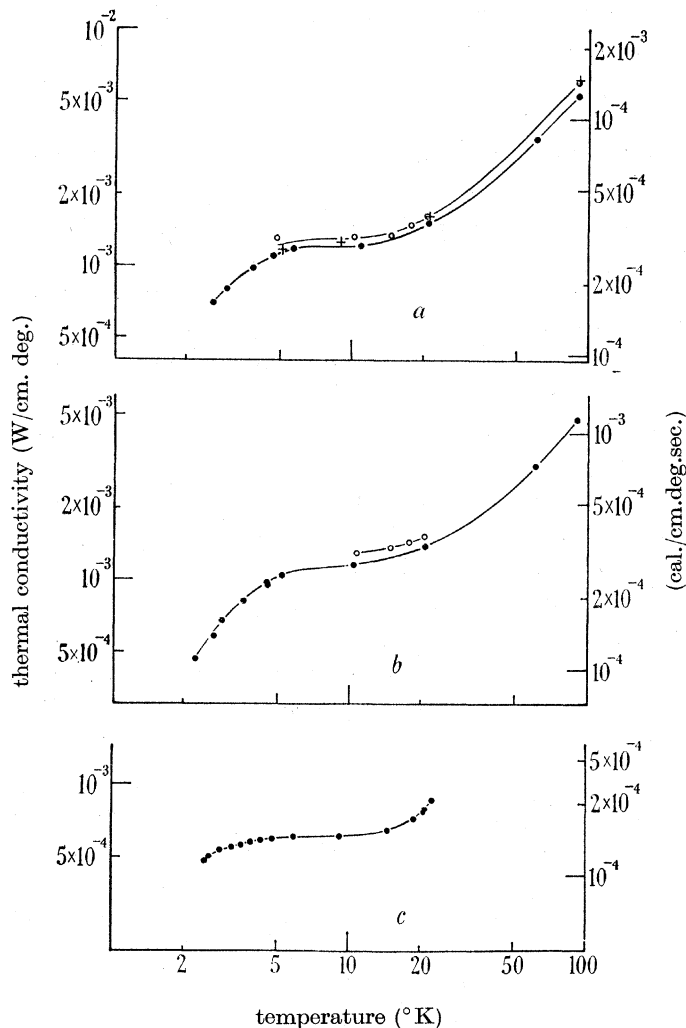


FIGURE 2. Thermal conductivity of quartz glass, Phoenix glass and Perspex.

	diam. (mm.)	length measured (cm.)
<i>a</i> , quartz glass	•	6.1
	○	7.7
	+	7.4
<i>b</i> , Phoenix glass	•	6.0
	○	9.4
<i>c</i> , Perspex	12.7	3.05

The conductivity of quartz glass has been calculated from this theory by adjusting the absolute values of the two components to fit the experimental results. It can be seen from figure 2 of Klemens (1951) that, with these adjustments, the agreement between the theory and the experiments is very good.

Lyon & Giauque (1949) have measured the specific heat of Pyrex glass below 20°K. The values are close to those for quartz glass determined by Simon (1922) and Simon & Lange (1926). The difference in conductivity of Phoenix glass (a Pyrex-type glass) and quartz glass is therefore probably due to the presence of foreign atoms in the Phoenix glass.

An attempt was made to measure the conductivity of an organic glass—glassy glucose—to see whether the conductivity-temperature relation was similar to that shown by the two inorganic glasses. Several specimens were made, but it was found that, on cooling to liquid-oxygen temperatures, they all developed cracks in the neighbourhood of the contacts.

It was decided to measure the Perspex rod as another example of a disordered organic substance. The results for this rod are shown in figure 2. It can be seen that there is a temperature region in which the conductivity is independent of temperature. It is not possible to compare these results quantitatively with the theory, since the specific heat of Perspex has not been determined at these temperatures.

#### MEASUREMENTS ON QUARTZ

For the measurements on quartz, a crystal 5 cm. long and of square cross-section of side 5 mm. was used. It had been cut so that the length was perpendicular to the principal axis. Contact with the two thermometers was made by fitting on to the crystal two tightly fitting copper bands, each 2.5 mm. wide. These bands were split on one side and could be tightened by small screws. On cooling, the copper contracted more than the quartz so that the fit would be better at low temperatures. A little grease was inserted inside the collars to improve the contact. The contacts at the top and bottom were made by pushing on square collars of copper which were split at the corners. The heater was wound on a light brass former which was soldered to the top collar.

The contact resistance at the bottom of the specimen was estimated by measuring the temperature drop across it. Although at the lowest temperatures the resistance was many times the resistance of the crystal itself, it was still very small compared with the resistance of the leads and capillaries. The heat lost by conduction in the leads was therefore a very small fraction of the heat supplied at all temperatures. On the assumption that the contact resistance between the specimen and the thermometers was of the same order of magnitude as the contact resistance at the bottom, this would also be very small compared with the resistance of the capillaries. The thermometers would therefore give the temperature difference correctly.

Most of the measurements were made using a length of about 3 cm. of the crystal between the thermometers, but in order to verify that the corrections for heat losses were as small as was calculated, a few measurements were made with a length of about 2 cm. No difference was found between the conductivities calculated from these two sets of measurements. The measurements on the shorter length are shown by open circles in the upper curve of figure 3.

The present results agree well with those of de Haas & Biermasz between 15 and 20°K, but the values are about 20 to 30 % lower between 70 and 90°. The agreement with the value given by Eucken at 83°K is very close.

The crystal was then given three periods of irradiation in the Harwell pile, the irradiation doses being in the ratio 1:1.4:16.5. It was measured over the same temperature range after each irradiation; these results are shown in figure 3, in which is also shown the conductivity of quartz glass.

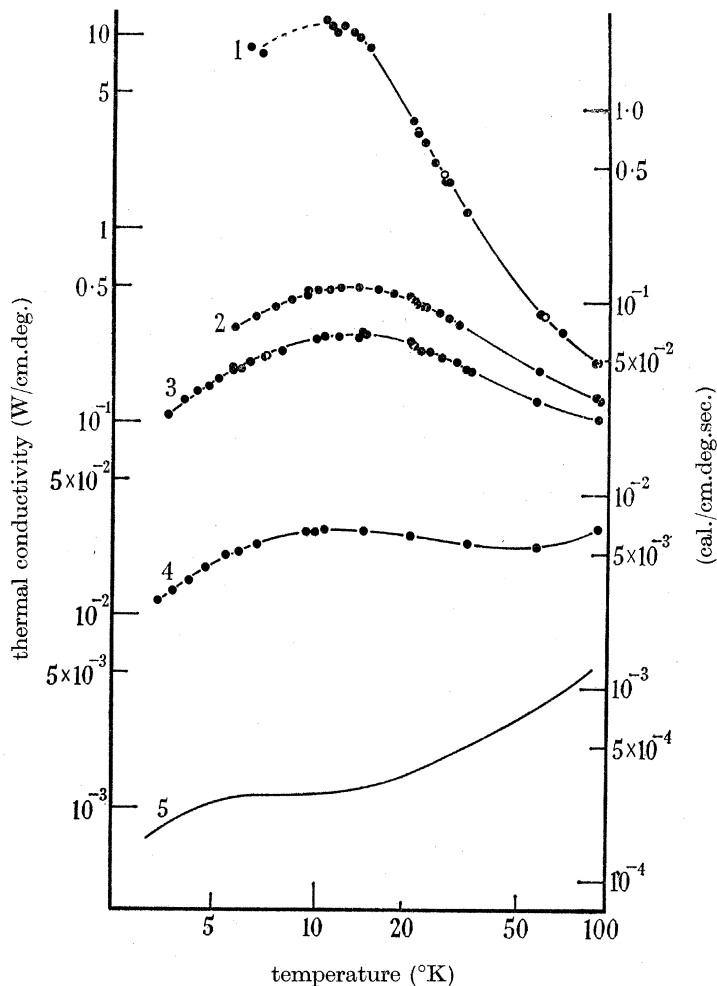


FIGURE 3. Thermal conductivity of quartz crystal, irradiated quartz crystal and quartz glass: (1) Quartz crystal perpendicular to axis 5 mm. square cross-section: • length measured 3.05 cm.; ◦ length measured 2.15 cm. (2) After first irradiation—1 unit. (3) • After second irradiation—1.4 units; ◦ after subsequent heating at 100° C for 3 weeks. (4) After third irradiation—16.5 units. (5) Quartz glass.

The effect of annealing the irradiated crystal at various temperatures and for various periods was studied after the third irradiation. These results are shown in figure 4. In addition, the effect of keeping the crystal at 100° C for 3 weeks after the second irradiation was measured. (These measurements are shown by open circles in figure 3.) As no change in conductivity was found and the crystal had been kept below 100° C while in the pile, it is reasonable to assume that no recovery

took place in the pile during the irradiation and that the effects of successive irradiations will be cumulative.

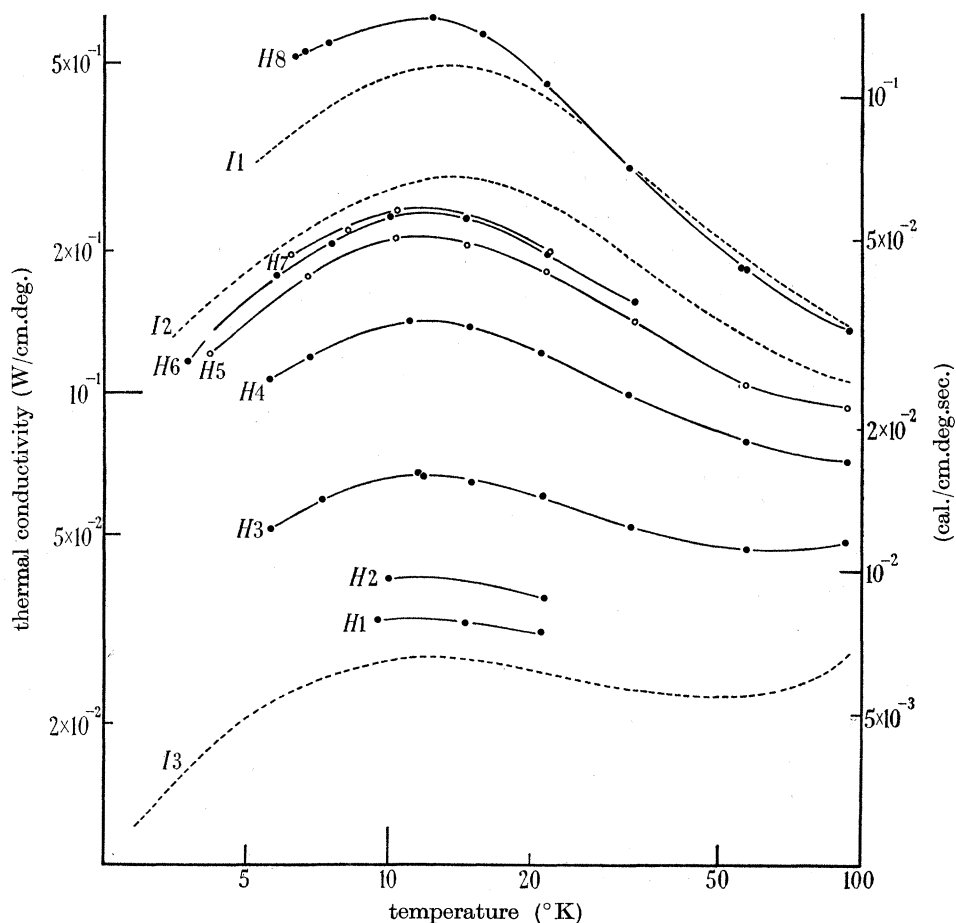


FIGURE 4. Thermal conductivity of quartz crystal after successive periods of heating following the third irradiation.

*I1, I2 and I3, after first, second and third irradiations*

	after heating at (°C)	for (hr.)		after heating at (°C)	for (hr.)
<i>H1</i>	300	8	<i>H5</i>	540	60
<i>H2</i>	400	6	<i>H6</i>	540	677
<i>H3</i>	510	6	<i>H7</i>	600	1
<i>H4</i>	565	6	<i>H8</i>	700	6

Klemens (1951) analyzes the results of de Haas & Biermasz and of the present experiments. The analysis shows that, for the untreated crystal, Umklapp processes are the chief cause of the thermal resistance down to a temperature of about 10°K. This is the only scattering process which produces such a rapid variation of conductivity with temperature as found between 10 and 50°. Below this temperature the boundary scattering is the chief factor. It is only in the neighbourhood of 10°K

that the resistance due to impurities and lattice defects is an appreciable fraction of the total resistance.

Klemens suggests that the effect of impurities on the thermal conductivity is small because their presence in interstitial spaces will not disturb the main silica network appreciably. Measurements by de Haas & Biermasz showed that the conductivities of KCl and KBr were much smaller than that of quartz and varied more slowly with temperature. Klemens suggests that for these substances the presence of impurities is the chief factor determining the thermal resistance between 10 and 90°. Since these are ionic crystals divalent impurities will have associated with them holes in the alkali lattice in order to preserve the electrical neutrality. This will give rise to a defect resistance great enough to swamp the resistance due to Umklapp processes.

To a first approximation the thermal resistance caused by the irradiation can be regarded as additive to the thermal resistance of the natural crystal, and it is possible to calculate this extra resistance after each period of irradiation. This extra resistance is a minimum at about 15°K. Above this temperature it increases roughly linearly with the temperature and, in the case of the first irradiation, then appears to become constant at the highest temperatures measured. Below 15°K the extra resistance increases more rapidly than the inverse of the temperature. The extra thermal resistance can be interpreted as being due, above 15°K, to the presence of numerous lattice defects. Below 15°K the resistance is in the nature of a boundary resistance which can be attributed to clusters of lattice defects. These clusters must be large enough to produce a scattering of phonons which is almost independent of their frequency.

After the third irradiation the form of the temperature dependence of the extra resistance has changed. This extra resistance now decreases with increasing temperature above about 40°K. Owing to the great number of single defects there is interference between neighbouring defects and, as in the case of glass, the scattering becomes less frequency dependent.

As there does not appear to be any annealing during irradiation, the number of defects produced should be in the ratio 1:2.4:18.9. Below about 25°K the induced resistances are in the ratios of approximately 1:1.7:18. It is not clear why there should be the discrepancy between these ratios after the second irradiation, since the agreement after the third irradiation is very close.

The picture of single defects and clusters of defects deduced by Klemens from these conductivity measurements is consistent with the calculations of Seitz (1949) on the effect of the impact of fast massive particles with solids. Since both silicon and oxygen have small cross-sections for any possible nuclear reactions, these defects will be interstitial atoms and vacant lattice points. It is difficult to derive quantitative estimates of the number of defects and the size of clusters from the conductivity measurements. On the assumption that the effect of single-lattice defects on the conductivity is the same as the effect of single-impurity atoms in alkali halides (divalent ions are probably the chief cause of impurity scattering in this case), Klemens has estimated that after the first irradiation the number of single defects is of the order of  $10^{-4}$  per atom. The thermal neutron dose during the



first irradiation is given as  $1.8 \times 10^{18}/\text{cm}^2$ . Since the number of defects produced will depend on the particular spread of neutron velocities, it is not possible to calculate this number with any certainty. The figure of  $10^{-4}$  per atom is not an unreasonable number.

After the crystal had been heated for a considerable time (curve *H8* of figure 4) the conductivity was restored to approximately the value it had after the first irradiation. The variation of conductivity with temperature is, however, different in the two cases. Above  $25^\circ\text{K}$  the two conductivities are nearly equal, but below this temperature the conductivity of the crystal after heating is greater than that after the first irradiation. From the equality of the conductivities above  $25^\circ\text{K}$  it can be deduced that the total number of defects is roughly the same in the two cases. To account for the difference between the conductivities below  $25^\circ\text{K}$  it is necessary to assume that the density of the clusters of defects is less after the heat treatment. Either the defects which were in clusters have annealed more rapidly than the more isolated defects or they have diffused throughout the crystal. The reduction in the density of the clusters which occurs on heating can also be seen, to a lesser extent, by comparing the conductivity after heating at  $540^\circ\text{K}$  for 600 hr. with the conductivity after the second irradiation. Above about  $15^\circ\text{K}$  the ratio of the induced resistance after the heat treatment to that after the second irradiation is 1.3. Below this temperature this ratio falls to about 1.15 at  $5^\circ\text{K}$ . It can be seen from figure 4 that no extra marked change in the conductivity was found after the crystal had been heated above  $573^\circ\text{C}$ , which is the transition temperature from  $\alpha$  to  $\beta$  quartz.

In order to determine the effect of heat treatment alone on the conductivity, an unirradiated crystal was given the same heat treatment, above the transition temperature, as the irradiated crystal. Even after heating to  $800^\circ\text{C}$  no change in the conductivity was found between 10 and  $25^\circ\text{K}$ . This seems to be in disagreement with the measurements of de Haas & Biermasz, who found a reduction of 10 to 15% in the conductivity in the liquid-hydrogen temperature range after heating a quartz crystal to  $570^\circ\text{C}$ .

#### MEASUREMENTS ON CORUNDUM

For the experiments on corundum a single crystal prepared by Salford Electrical Instruments Ltd. was used. This was 6 cm. long and of circular cross-section, with diameter of 3 mm. In a preliminary set of measurements the contacts were made in a similar way to that used for the quartz crystal. It was found, however, that the contact resistance was rather high, probably due to the crystal not being perfectly round. Better contact was obtained by rubbing Wood's metal on the appropriate regions of the crystal. The copper collars were then soldered on. The contact resistance of the bottom junction was  $20\text{ W}^{-1}\text{ deg.}$  at  $20^\circ\text{K}$  and  $100\text{ W}^{-1}\text{ deg.}$  at  $4^\circ\text{K}$ . These values are small compared with the heat resistance of the capillary tubes connected to the gas thermometers which are about  $10^6$  and  $5 \times 10^6\text{ W}^{-1}\text{ deg.}$  at these temperatures. The gas thermometers will then give the true temperature gradient along the crystal.

The thermal conductivity is shown in figure 5. From 95 down to  $50^\circ\text{K}$  the conductivity increases very rapidly with decreasing temperature, so that the thermal

resistance must be mainly due to Umklapp processes. The value of  $\Theta$  derived from this part of the curve is in fair agreement with the value of  $977^\circ\text{K}$  deduced from low-temperature specific heat measurements (Simon & Swain 1935; Kerr, Johnston & Hallett 1950).

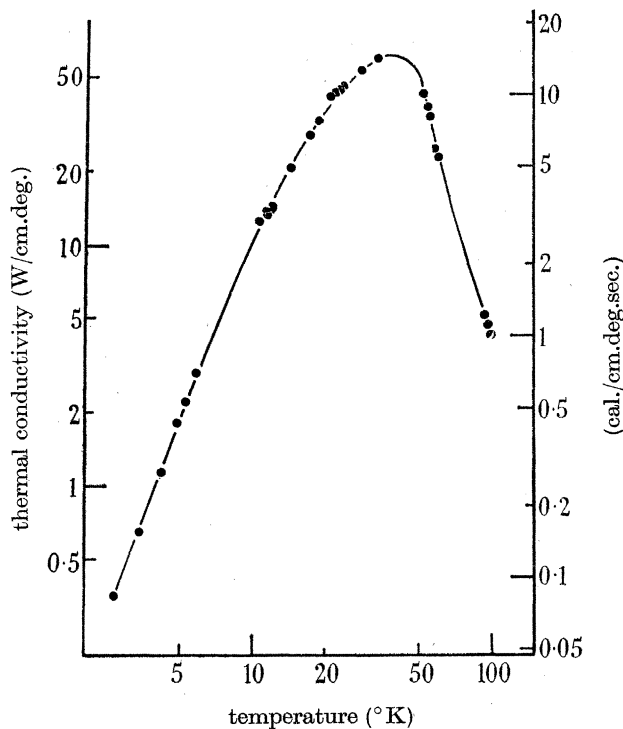


FIGURE 5. Thermal conductivity of corundum (artificial sapphire).  
3 mm. diameter. Length inclined at  $36^\circ$  to axis.

At the lowest temperatures the conductivity is proportional to a power of  $T$  between 2.8 and 3, so that the resistance must be due to scattering by the boundaries of the crystal. From Casimir's formula, the thermal conductivity of a corundum crystal of diameter 3 mm. would be given, at the lowest temperatures by

$$K \simeq 6 \times 10^{-2} T^3 \text{ W/cm.deg.}$$

The actual value found for the constant is  $2.7 \times 10^{-2}$ , which is in reasonable agreement with the calculated value.

The difference between the sum of the calculated resistances due to Umklapp processes and to boundary scattering and the measured resistance between 10 and  $40^\circ\text{K}$  has been calculated. This difference decreases with increasing temperature and cannot, therefore, be attributed to scattering by impurities, but may be due to the mosaic structure. The values of this difference in resistance are nearly the same as those calculated by Klemens for quartz crystals.

#### CONCLUSION

At relatively high temperatures the thermal conductivity of various glasses is proportional to their specific heat. At temperatures below about  $100^\circ\text{K}$  the

conductivities decrease more slowly than the specific heat. Below about  $4^{\circ}\text{K}$  the conductivity is proportional to  $T$ , the absolute temperature, while the specific heat is proportional to  $T^3$ . The present experiments show the way in which the temperature dependence of the conductivity changes in the case of quartz glass and Phoenix glass, and it is found that there is a temperature region in which the conductivity is very little dependent on the temperature.

This is explained by Klemens in terms of the variation of the mean free paths of transverse and longitudinal phonons. At high temperatures the transverse phonons are dominant in heat conduction, and at low temperatures the longitudinal phonons are dominant. The region in which the conductivity is nearly constant occurs where the two contributions are of the same order of magnitude.

For Perspex, a temperature region was also found in which the conductivity is nearly independent of temperature. That this behaviour is associated with great disorder in structure is also confirmed by the measurements on a quartz crystal in which a large number of lattice defects had been produced by subjecting the crystal to neutron irradiation.

The variation of conductivity with temperature of the irradiated crystal has been interpreted by Klemens in terms of single defects and clusters of defects and rough estimates of the numbers can be made.

The measurements of the conductivity of the original quartz crystal, and of a corundum crystal, make it possible for the first time to verify the theory of Peierls in some detail. For both crystals, above the temperature at which the conductivity is a maximum there is a region where the conductivity is determined almost entirely by the Umklapp processes predicted by Peierls. Although both crystals are anisotropic and the theory applies strictly only to isotropic crystals, the exponential variation of conductivity with temperature is verified. The maximum value of the conductivity of corundum is of the same order of magnitude as the maximum value for pure metals.

I should like to thank Professor F. E. Simon, F.R.S., for suggesting the present research and for his continued interest and advice. I am also indebted to Dr P. G. Klemens for valuable discussions and to Mr T. M. Fry for assistance in all matters relating to the irradiations.

The work was carried out during tenure of a Nuffield Research Fellowship and later of a grant from Industrial Distributors Ltd.

#### REFERENCES

- Berman, R. 1949 *Phys. Rev.* **76**, 315.  
 Berman, R. 1951 *Phil. Mag.* **42**, 642.  
 Bijl, D. 1949 *Physica*, **14**, 684.  
 Casimir, H. B. G. 1938 *Physica*, **5**, 495.  
 Debye, P. 1914 *Vorträge über die kinetische Theorie der Materie und der Elektrizität*. Berlin: Teubner.  
 Eucken, A. 1911a *Ann. Phys., Lpz.*, (4) **34**, 185.  
 Eucken, A. 1911b *Phys. Z.* **12**, 1005.  
 de Haas, W. J. & Biermasz, Th. 1935 *Physica*, **2**, 673.  
 de Haas, W. J. & Biermasz, Th. 1937 *Physica*, **4**, 752.

- de Haas, W. J. & Biermasz, Th. 1938 *Physica*, **5**, 47, 320 and 619.  
 de Haas, W. J. & Rademakers, A. 1940 *Physica*, **7**, 992.  
 Kerr, E. C., Johnston, H. L. & Hallett, H. C. 1950 *J. Amer. Chem. Soc.* **72**, 4740.  
 Kittel, C. 1949 *Phys. Rev.* **75**, 972.  
 Klemens, P. G. 1951 *Proc. Roy. Soc. A*, **208**, 108.  
 Lyon, D. N. & Giauaque, W. F. 1949 *J. Amer. Chem. Soc.* **71**, 1647.  
 Peierls, R. 1929 *Ann. Phys., Lpz.*, **3**, 1055.  
 Seitz, F. 1949 *Disc. Faraday Soc.* no. 5, p. 271.  
 Simon, F. 1922 *Ann. Phys., Lpz.*, **68**, 278.  
 Simon, F. & Lange, F. 1926 *Z. Phys.* **38**, 227.  
 Simon, F. & Swain, R. C. 1935 *Z. phys. Chem. B* **28**, 189.  
 Stephens, R. W. B. 1932 *Phil. Mag.* **14**, 897.  
 Wilkinson, K. R. & Wilks, J. 1949 *J. Sci. Instrum.* **26**, 19.

---

## The thermal conductivity of dielectric solids at low temperatures (Theoretical)

BY P. G. KLEMENS,\* *The Clarendon Laboratory, University of Oxford*

(Communicated by F. E. Simon, F.R.S.—Received 18 January 1951)

The statistical equilibrium of phonons in the presence of a temperature gradient is investigated, and a general formula for the thermal conductivity of dielectric solids is obtained. This is applied to quartz glass, giving good agreement with values observed by Berman (1951), and to crystals. Comparison between theory and experiment are made for alkali-halides and quartz, and conclusions are drawn about the defects in neutron-irradiated quartz.

We shall discuss the thermal conductivity of dielectric solids, i.e. solids in which the heat transfer is mainly through the elastic vibrations of the lattice. The solid may be a crystal or it may be amorphous, but each atom has a fixed equilibrium position and the thermal vibrations can thus be resolved into normal modes. For a perfect crystal these normal modes are plane travelling waves. Departures from the perfect lattice result in interactions which are responsible for the statistical equilibrium between the normal modes.

The normal modes of a perfect lattice can be quantized (Peierls 1929, 1935), giving rise to the concept of phonons analogous to the photons of radiation theory. The phonons obey Bose-Einstein statistics. The heat current is determined by the distribution of phonons, which in turn is obtained as a solution of a Boltzmann equation. We shall obtain an approximate solution, and thus obtain an expression for the thermal conductivity. This will be similar, though not quite the same, as expressions given, but without derivation, by Pomeranchuk (1942). The approach here developed can be regarded as a link between the rigorous theory of Peierls and the approach of Pomeranchuk.

\* Now at the Commonwealth Scientific and Industrial Research Organization, Sydney.