

## Low-Temperature Thermal Conductivity of Amorphous Solids

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(Received January 29, 1962)

The thermal conductivities of five samples of commercial glasses and glass ceramics were measured at liquid helium temperatures. It was found that the conductivity data could be accounted for by an intrinsic structure scattering of phonons as proposed by Klemens combined with an internal boundary scattering. The intrinsic structure scattering of these specimens was less than that calculated by Klemens using Berman's data for vitreous quartz. The mean free path calculated for scattering at internal boundaries was of the order of  $10^{-2}$  to  $10^{-3}$  cm.

### INTRODUCTION

DESPITE the fact that the molecular units in glass have no long-range order, it is possible to analyze the collective motions of these units in terms of normal modes of vibration. The theory of the thermal transport due to the phonons in these normal modes of vibration has been developed by Klemens<sup>1</sup> and found to be in agreement with measurements on vitreous quartz.<sup>2</sup> According to this theory, the thermal conductivity at liquid helium temperatures is due solely to phonons of the longitudinal mode of vibration. In the liquid helium temperature range the predominant scattering mechanisms for these longitudinal phonons are processes not conserving the wave vector of the phonons (we shall call this "intrinsic structure scattering"). The dependence of the phonon mean free path on wave vector is  $l_1 \sim k^{-2}$  for this scattering mechanism. This gives rise to a thermal conductivity proportional to the temperature.<sup>3</sup> At slightly higher temperatures (about  $10^\circ\text{K}$ ) another scattering mechanism—the interaction of longitudinal phonons with transverse phonons—becomes important. In this region the conductivity increases less rapidly with increasing temperature and finally reaches a maximum. Therefore, at low temperatures the measured exponent for the temperature dependence of the conductivity of glasses should be between one and zero if only these two scattering mechanisms are operative.

However, our thermal conductivity measurements and those of Bijl<sup>4</sup> on a number of commercial glasses and glass ceramics have shown an exponent for the temperature dependence of the conductivity greater than one. This suggests that still another scattering mechanism is of importance in these materials. A

plausible guess is that this additional scattering is due to internal boundaries in the specimens since a combination of boundary scattering and the "intrinsic structure scattering" give a temperature dependence intermediate between  $T$  and  $T^3$ . Such a temperature dependence is observed, in fact, and the theoretical expression derived for this combined scattering does account for the data we have taken.

### EXPERIMENTS

During the experiments, one end of the specimen was held in contact with a copper block which was, in turn, in contact with liquid helium. A thin piece of pure indium foil was compressed between the specimen and the block to minimize the thermal contact resistance. An electrical heater was attached to the other end of the specimen to provide the necessary heat current for the experiments, and two 68-ohm,  $\frac{1}{2}$ -w carbon resistance thermometers (Allen-Bradley) were mounted between the heater and the heat sink to measure the temperature gradient down the specimen. The resistances of the thermometers were measured using a bridge circuit with three leads attached to each thermometer. The net effect of the three-lead arrangement was to compensate for the electrical resistance of the leads and provide the minimum heat leak from the thermometer leads.<sup>5</sup>

To ensure that all the heat produced in the heater flowed through the specimen, the entire assembly was mounted in a vacuum can. The copper top of this can formed the holder for the specimen on the vacuum side, and on the other side was in contact with the liquid helium. An annealed gold O-ring and Loctite Sealant<sup>6</sup> were used to seal the can.

The thermometers were calibrated in the manner of Clement and Quinell<sup>7</sup> each time the apparatus was cooled to liquid helium temperatures. In order to

<sup>1</sup> P. G. Klemens, Proc. Roy. Soc. (London) **A208**, 108 (1951).

<sup>2</sup> R. Berman, Proc. Roy. Soc. (London) **A208**, 90 (1951). The thermal conductivity of vitreous quartz has also been measured by A. F. Cohen, J. Appl. Phys. **29**, 591 (1958), who found higher values of conductivity than Berman and a more rapid temperature variation. These measurements, although not treated in detail in this paper, can probably be accounted for by a combination of intrinsic and internal boundary scattering.

<sup>3</sup> A discussion of the temperature dependence of the conductivity for various scatterers may be found, for example, in an article by P. G. Klemens, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 15.

<sup>4</sup> D. Bijl, *Physica* **4**, 684 (1949).

<sup>5</sup> A description of this method can be found in K. J. Roberts, *Heat and Thermodynamics* (Interscience Publishers, Inc., New York, 1960), 5th ed., p. 34.

<sup>6</sup> American Sealants Company, Hartford, Connecticut. The use of these sealants at low temperatures is described by M. D. Reeber, Rev. Sci. Instr. **32**, 1150 (1961).

<sup>7</sup> J. R. Clement and E. H. Quinell, Rev. Sci. Instr. **23**, 213 (1952).

TABLE I.

Specimen	Cross section	Source
Soda lime glass	0.100 cm×1.588 cm	Ednalite Optical Company, Inc., Peekskill, New York
Crown glass	0.116 cm×1.607 cm	Fish-Schurman Corporation, New Rochelle, New York
Fotoceram	0.105 cm×1.508 cm	Corning Glass Works, Corning, New York
Pyrocera 9606 (a)	0.034 cm×1.666 cm	Corning Glass Works, Corning, New York
Pyrocera 9606 (b)	0.130 cm×1.607 cm	Corning Glass Works, Corning, New York

minimize the error of the temperature measurements and at the same time not average the thermal conductivities over too wide a temperature range, the spacing between the thermometers was adjusted to give a temperature difference from 0.1° to 0.3°K. During the calibration of the thermometers and the measurements of the thermal conductivity, the helium bath was maintained in thermal equilibrium using a bellows-operated manostat and a thermal regulating device similar to that described by Sommers.<sup>8</sup>

The thermal conductivities of five specimens were measured. The sources of the specimens and their geometrical cross sections are listed in Table I. The samples specified as "crown glass" and "soda lime glass" were microscope slides originally intended for use as substrates for thin film superconducting circuitry.

The thermal conductivities of the "crown glass" and "soda lime glass" are shown in Fig. 1 along with a few data points for vitreous silica.<sup>2</sup> As can be seen, a curve drawn through the data points would exhibit a change from a positive curvature to a negative curvature as the temperature increases above 3.5°K. This is believed to be due to the increased importance of the interaction of longitudinal phonons with transverse phonons at the higher temperature. Since the theory we will describe was intended only to represent the combined effects of boundary scattering and nonconservative phonon collisions, we made no attempt to represent the data above 3.5°K with a theoretical expression. It was

felt that the negative curvature of data points was so slight at helium temperatures that no quantitative information could be obtained from these data concerning the strength of the longitudinal phonon-transverse phonon interaction.

The thermal conductivities of three glass ceramic specimens—two of Pyrocera 9606 and one of Fotoceram—are shown in Fig. 2. For comparison with our experimental results and the expression we propose for the thermal conductivity, Bijl's data<sup>4</sup> for a number of glasses are also included in this paper. His results are shown in Fig. 3. The specimens he used were cylinders with a diameter of 0.78 cm.

### THEORY

Expressions for the thermal conductivity may be derived from the well-known expression :

$$\kappa = \frac{1}{3} \int C(\mathbf{k}) v l(\mathbf{k}) d\tau_k, \quad (1)$$

where  $C(\mathbf{k})$  is the heat capacity of a mode having wave vector  $\mathbf{k}$ ,  $v$  is the velocity associated with this mode, and  $l(\mathbf{k})$  the mean free path. Following Klemens, we will assume that only longitudinal modes contribute to the thermal conductivity at low temperatures and integrate over  $\mathbf{k}$  space for longitudinal modes only.

We assume there are two scattering mechanisms which determine the mean free path. The first is the intrinsic structure scattering proposed by Klemens.<sup>1</sup> The mean free path for this scattering is dependent upon the magnitude of the wave vector,  $\mathbf{k}$ , through the relation :

$$l_1 = (A/a) k^{-2}, \quad (2)$$

where  $(A/a)$  is a constant with the dimensions of reciprocal length. Klemens chooses to set  $a$  equal to the distance between vibrational units in the glass.  $A$ , then, is a dimensionless constant which has significance in that the mean free path is approximately equal to  $(Aa)$  for phonons with wave vector  $k \cong 1/a$ .

In addition to this scattering mechanism, there appears to be scattering by internal boundaries in the glass. We shall make the usual assumption that this mean free path  $l_2$  is independent of the phonon wave vector. The resultant mean free path is a combination of the two mean free paths :

$$1/l = 1/l_1 + 1/l_2. \quad (3)$$

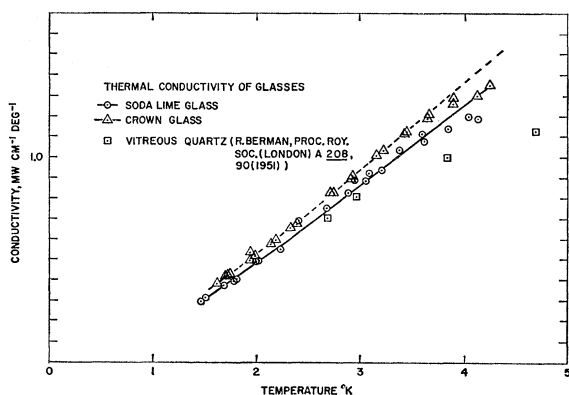


FIG. 1. The thermal conductivities of soda lime glass, crown glass, and vitreous quartz. The lines represent the theoretical expression with constants adjusted to pass through the data points.

<sup>8</sup> H. S. Sommers, Rev. Sci. Instr. **25**, 793 (1954).

Expression (1) may then be evaluated assuming the Debye distribution of longitudinal phonon states:

$$\kappa = \frac{K^2 T}{h 6 \pi^2} (A/a) \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2 x^2 + (A/a l_2) (h v / K T)^2} dx. \quad (4)$$

The definite integral was evaluated by a program written for the IBM 7090 computer.<sup>9</sup>

As a practical procedure for obtaining the constants  $(A/a)$  and  $l_2$  from a set of data, the following equations may be used:

$$\log(\kappa/T) = \log \frac{K^2}{h 6 \pi^2} (A/a) + \log J_2 \left[ (A/a) \frac{1}{l_2} \left( \frac{h v}{K T} \right)^2 \right],$$

and

$$\log(1/T^2) = -\log(A/a) \frac{1}{l_2} \left( \frac{h v}{K} \right)^2 + \log \left[ (A/a) \frac{1}{l_2} \left( \frac{h v}{K T} \right)^2 \right], \quad (5)$$

where

$$J_2 \left[ (A/a) \frac{1}{l_2} \left( \frac{h v}{K T} \right)^2 \right]$$

is the definite integral occurring in Eq. (4). It follows from these equations that the curvature of a plot of  $K/T$  vs  $1/T^2$  on log-log paper should fit the curvature of a log-log plot of  $J_2[(A/a)(1/l_2)(h v / K T)^2]$  vs  $[(A/a)(1/l_2)(h v / K T)^2]$ , if the origin of one of the plots is shifted. The magnitudes of the shifts of origin gives the two parameters,  $A/a$  and  $v^2/l_2$  for each specimen. The approximate values obtained in this way can then be further refined by computing values of

$$J_2[(A/a)(1/l_2)(h v / K T)^2]$$

and comparing the results to the data through the use of Eq. (4).

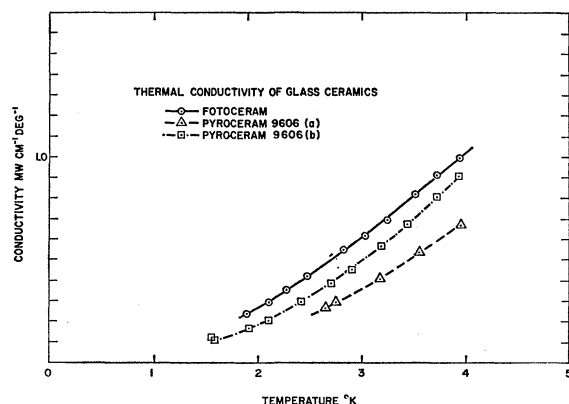


FIG. 2. The thermal conductivities of Pyrocera 9606 (a), Pyrocera 9606 (b), and Fotoceram. The lines represent the theoretical expression with constants adjusted to pass through the data points.

<sup>9</sup> Selected values of this integral may be found in a paper by Joseph Callaway, Phys. Rev. **122**, 787 (1961).

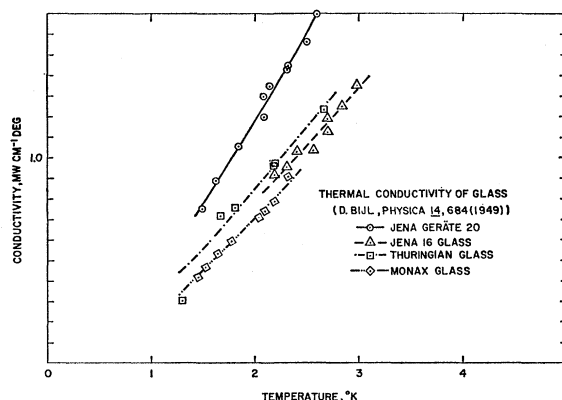


FIG. 3. The thermal conductivities of Jena Geräte 20, Jena 16 glass, Thuringian glass, and Monax glass. The lines represent the theoretical expression with constants adjusted to pass through the data points.

By adjusting the constants in the theoretical expression to give a fit to the experimental data, it is possible to obtain values of  $(A/a)$  and  $v^2/l_2$  for each specimen. However, in order to evaluate  $l_2$ , the mean free path for boundary scattering, it is necessary to determine the velocity of longitudinal waves in each specimen. For isotropic materials this velocity can be evaluated from the formula:

$$\rho v^2 = Y(1 - \sigma)/(1 - 2\sigma)(1 + \sigma), \quad (6)$$

where  $\rho$  is the density,  $Y$  is the adiabatic Young's modulus, and  $\sigma$  is the adiabatic Poisson's ratio. For the Pyrocera and Fotocera specimens, the elastic moduli have been measured<sup>10</sup> at room temperature. The velocities calculated for room temperatures are  $7.4 \times 10^5$  cm sec<sup>-1</sup> for Pyrocera 9606 and  $5.7 \times 10^5$  cm sec<sup>-1</sup> for Fotocera. For the various glasses, the elastic constants have not been measured. However, a value of Young's modulus,  $7.4 \times 10^{11}$  d cm<sup>-2</sup>, and Poisson's ratio, 0.22, are typical of the values measured for glasses. Using these values a velocity of longitudinal waves,  $6.15 \times 10^5$  cm sec<sup>-1</sup>, was calculated. This value was used for all the glass specimens.

The necessary elastic moduli for these specimens have not been measured at low temperatures. However, if the temperature dependence of the longitudinal wave velocity for these specimens is similar to that of vitreous quartz, then the change in this velocity on going to helium temperature is less than the spread of values occurring in glasses of various treatments and compositions. For vitreous quartz the velocity of longitudinal waves decreases about one per cent between room temperature and liquid helium temperatures. Therefore, we have calculated the mean free path for boundary scattering using the room temperature values of the velocity of longitudinal waves calculated from Eq. (6).

<sup>10</sup> S. D. Stookey, Ind. Eng. Chem. **51**, 805 (1959).

## RESULTS

For our glass specimens and those of Bijl<sup>4</sup> the calculated constants which are a measure of the two scattering mechanisms are shown in Table II.

The first point to notice is that the mean free path due to boundary scattering is less than the smallest external dimension of the test specimens. This implies that the boundaries giving rise to scattering are internal boundaries. It is also important to note that all the specimens except vitreous quartz show these internal boundaries. Therefore, the occurrence of these boundaries, whatever their physical origin, is widespread among glasses.

The origin of these internal boundaries cannot be determined from these data alone. They could be the result of inhomogeneities in the composition of the glass, of strains introduced during the heat treatment, or of precipitation of some phase in minute amounts throughout the specimens. However, there is one clue in the relative values of this mean free path for the glasses and glass ceramics. The values of  $l_2$  for Pyroceram and Fotoceram are an order of magnitude smaller than any of the values for glass. It is known that preparation of Pyroceram and Fotoceram involves the formation of a matrix of crystalline material throughout the glass.<sup>10</sup> It is, therefore, possible that the internal boundaries are a result of a formation of planar crystalline regions within the glass. This

"devitrification" is known to be a widespread occurrence in glasses.

Comparing the values of  $A/a$  in Table II, it can be seen that all the specimens have higher value of  $A/a$  and, consequently, a longer mean free path for "intrinsic" scattering than vitreous quartz. This is surprising, since one would expect this mean free path to be much shorter if this intrinsic scattering is primarily associated with chemical impurities or inhomogeneities which frequently occur in glasses. It would appear that these impurities and inhomogeneities are not the dominant causes of the intrinsic scattering. A reasonable hypothesis is to again associate the lessening of the intrinsic scattering with the "devitrification" which presumably causes the boundary scattering. It is possible that this "devitrification" is accompanied by a release of microscopic strains in the specimens and that it is these strains which primarily influence the intrinsic scattering.<sup>11</sup>

To summarize: It has been found possible to fit the low-temperature thermal conductivity of a number of glass specimens with a theoretical expression which represents the combined effects of an intrinsic scattering and an internal boundary scattering. There is reason to think that the occurrence of internal boundary scattering is associated with "devitrification" of the glass. However, before a more certain assignment can be made of the causes for the relative magnitude of the two scattering mechanisms, more measurements must be made with specimens with controlled compositions (obtained, for example, as the result of various heating and aging conditions).

## ACKNOWLEDGMENTS

The authors wish to thank John Peterson and the Corning Glass Works for supplying the specimens of Fotoceram and Pyroceram.

<sup>11</sup> A recent theory developed by P. G. Klemens, *Non-Crystalline Solids*, edited by V. D. Frechette (John Wiley & Sons, Inc., New York, 1960), p. 508, may provide a more fundamental description of the structure changes accompanying such an increase in mean free path. In this analysis the perturbing potential causing phonon scattering is related to a correlation function which is a measure of the degree of order in the structure.

TABLE II.

Material	$A/a$ ( $10^8 \text{ cm}^{-1}$ )	$l_2$ ( $10^{-3} \text{ cm}$ )
Soda lime glass	40.7	14.0
Crown glass	45.3	15.7
Fotoceram	60.4	1.64
Pyroceram 9606 (a)	81.7	0.87
Pyroceram 9606 (b)	100.7	1.27
Jena Geräte 20 <sup>a</sup>	93.2	47.9
Jena 16 glass <sup>a</sup>	58.2	40.8
Thuringian glass <sup>a</sup>	63.2	44.7
Monax glass <sup>a</sup>	60.0	22.1
Vitreous silica <sup>b</sup>	36.0 <sup>c</sup>	...

<sup>a</sup> Data taken from reference 4.

<sup>b</sup> Data taken from reference 2.

<sup>c</sup> Calculation from reference 1.