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# Thermal Conductivity of Vitreous Silica at Low Temperatures*

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The thermal conductivity of a number of samples of vitreous silica has been measured between 1.5 and 20 K and between 65 and 300 K. The specimens were obtained from a number of manufacturers and were all high-purity optical-quality material. Above 65 K, the thermal conductivities of all the specimens were found to be identical. Below 20 K, the thermal conductivities of four synthetic silicas, Englehard Suprasil and three types of Corning silica were the same, but the thermal conductivities of the samples made by fusing rock quartz were quite different. These differences were found to be as large as 50% at 2 K. Impurities in small concentrations have no significant effect on the thermal conductivity. According to one theory, long-range (∼ 100 Å) spacial correlations in the phonon scattering resulting from the small amount of long-range order remaining in an amorphous material may be the most important factor in determining the thermal conductivity of glasses at low temperatures, and can, at least in principle, account for the difference between the various silicas.

## I. INTRODUCTION

The structure of vitreous silica has been described both as a disordered array of small quartz crystallites and as a random network of $SiO_4$ molecular units. Over the past 40 years experimental results have been interpreted in terms of one or the other of these models without providing any clear decision between them. Very recently Konnert, Karle, and Ferguson[1] discussed the results of x-ray- and neutron-diffraction studies which they showed support the crystallite model for both silica and germania glasses. Yet, only a little more than a year ago Bell and Dean[2] considering the same kind of data concluded that the random-network model will best describe the structure of vitreous silica. With these diffraction experiments the structure can be readily studied over distances of the order of 20 Å or less but little detailed information about the structure over larger distances can be obtained. Measurements of the lattice thermal conductivity supply another probe—lattice waves or phonons with wavelengths of hundreds of angstroms which can be used for studies of structure over distances of the order of these wavelengths. The thermal conductivity is an average over a distribution of wavelengths and the interpretation of thermal-conductivity results in terms of structure is not as direct as x-ray or neutron diffraction but much information can still be obtained.[3]

For amorphous solids, Klemens[4] described the scattering of phonons as being caused by fluctuations in the elastic properties of the material. Spacial correlations due to a small amount of long-range order were shown to markedly affect the thermal conductivity. Most surprisingly, the theory shows that the introduction of a small amount of long-range order should decrease the thermal conductivity of a completely disordered material. This theory might then explain Cohen's[5] measurements which showed the thermal conductivity of a sample of vitreous silica to increase after neutron irradiation. One need only make the natural assumption that the neutron damage reduces the long-range order. Klemens also pointed out that if this theory is correct then one would expect the thermal conductivity of a glass to depend more on how it was prepared than on its chemical composition.

We have measured the thermal conductivity of a number of commercially available vitreous silicas between 1.5 and 20 K and between 65 and 300 K. Samples were obtained from Corning, Englehard, and the General Electric Co. There are basically two ways of making vitreous silica,[6] either by oxidation of $SiCl_4$ or some such compound or by grinding and then fusing natural rock quartz. The structure of the former silicas, which we shall refer to as synthetic silicas, are different from the structure of the materials made from crushed rock quartz, which we shall refer to as fused quartz. By vitreous silica we mean any amorphous $SiO_2$. The measurements reported here show that the thermal conductivity of the synthetic silicas is markedly different from that of the fused-quartz samples. However, differences as large as those between Cohen's[5] and Berman's[7] results were not found.

A different point of view has been taken by Zeller and Pohl[8] who reported results of measurements of the thermal conductivity and specific heat of some glasses and surveyed the results of many other such measurements. They point out the remarkable similarity between the thermal conductivities of a wide variety of vitreous materials including varnishes, polymers, soda-lime glasses, and vitreous silica. According to them a very simple model—Rayleigh scattering by point defects equal in number to the atoms of the solid—will account for the thermal conductivity of all these glasses between about 5 and 20 K. Rayleigh scattering will not explain the values measured at lower temperatures. Also, their theory does not properly take into account the low-frequency divergence of the thermal conductivity if Rayleigh scattering were to be the only resistive mechanism. Zeller and Pohl suggest that another scattering mechanism is operative and speculate that it may be associated with the specific-heat anomalies found in vitreous materials. Phillips[9] and Anderson, Halperin, and Varma[10] have examined this suggestion. Both have constructed a model of a disordered solid that yields a contribution to the specific heat proportional to absolute temperature $T$ and a contribution to the thermal resistivity varying as $T.^{-2}$ This previous work has stressed the great similarities between the thermal conductivities of many different glasses. The results reported here emphasize the differences between the thermal conductivities of different kinds of vitreous silica. Any viable theory of the thermal conductivity of amorphous solids will have to account for these differences.

## II. EXPERIMENTAL PROCEDURE

The apparatus used to measure the thermal conductivity between 65 and 300 K has been described in detail elsewhere.[11] In brief, a stationary heat-flow method was used with copper-constantan thermocouples for thermometers. The ends of the samples were ultrasonically tinned and soldered between the sink and the sample heater. This heater was guarded to reduce radiative heat losses. Corrections were made for the remaining heat losses which for the samples of fused silica were less than 10% of the total heat generated. A small correction (1% of the total thermal resistance) was made for the thermal resistivity of the solder layers. The accuracy of these measurements is estimated to be 3–4%.

The apparatus used to measure the thermal conductivity between 1.5 and 20 K is similar to those used by others.[12] Figure 1 is a schematic diagram of the sample chamber. $A$ is a chamber that can be filled with liquid He through a valve and capillary (not shown) for measurements at and below 4.2 K. $B$ is the bulb of gas thermometer and $C$ is the vapor-pressure-thermometer bulb. Germanium resistance thermometers $D$ glued to molybdinum mounts which in turn were glued to the sample are used to measure the temperature difference established by the sample heater $E$, a wire wound resistor of 20 kΩ. Each electrical lead was 100 cm of No. 40 constantan wire between its connection to either a thermometer or the heater and the terminal board $F$. From the terminal board No. 40 copper wire was used to carry the leads to room temperature. These wires were first thermally anchored to the sink and then to plugs soldered into the vacuum pumping lines $G$. $H1$, $H2$, and $H3$ were manually set heaters used to raise the temperature. $H4$ was an automatically controlled heater. It was wrapped on a carbon resistor which was one arm of an ac bridge circuit used to control the current in $H4$. The numbers 1 through 4 locate the position of four Au–0.02-at.%-Fe vs Cu thermocouples. No attempt was made to accurately calibrate the thermocouples which were only used to monitor temperature stability. Temperature changes of $5\times10^{-4}$ K could be detected.

Table I describes the samples used in this investigation. The specimens were either right circular cylinders cut from rods or rectangular parallelepipeds cut from plates. The cross-sectional areas $A$ of the specimens ranged from 0.5 to 1 cm$^2$. Initially, the samples were cut 6–7- cm long and mounted in the apparatus as shown in Fig. 2(a). The samples were ultrasonically tinned, soldered to platinum disks which were soldered to the copper heater and to the bottom of the vapor-pressure-thermometer bulb. The separation of the thermometers $l$ was about 3 cm and the width

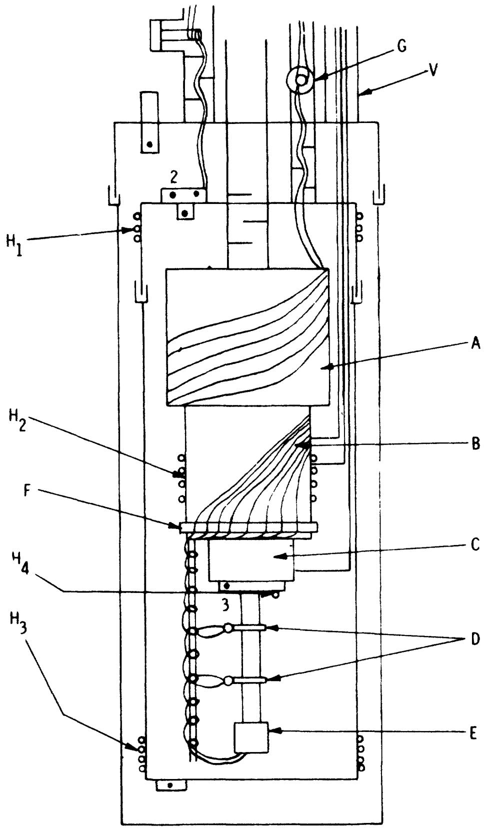

FIG. 1. Schematic drawing of the apparatus.

TABLE I. Samples used in this investigation. According to the manufacturers, all the vitreous silica listed here are high-purity amorphous $SiO_2$ containing chemical impurities in concentrations of 200 ppm or less with the exception of Corning's 7971 ULE silica which contains of the order of 5% titania. Infrasil and GE 201 are specially treated to remove $OH^-$ ion contamination and thus have high IR transmisivities. All of the synthetic silicas and Homosil contain $OH^-$ ion impurities and show pronounced IR absorption at $2.7\,\mu$.

| Sample designation | Manufacturer | Number of samples measured | Type of silica |
|---|---|---|---|
| 201 | General Electric | 1 | fused rock quartz |
| Infrasil | Englehard | 2 | fused rock quartz |
| Homosil | Englehard | 1 | fused rock quartz |
| Suprasil | Englehard | 3 | synthetic |
| 7940 Optical | Corning | 2 | synthetic |
| 7940 Schlieren | Corning | 1 | synthetic |
| 7971 ULE | Corning | 1 | synthetic |

of the thermometer mounts at the contact with the specimen was 1 mm, therefore, it was possible to measure accurate values of the factor $l/A$.

The germanium resistance thermometers used to measure the temperature gradient were calibrated against the helium-vapor-pressure temperature scale below 4.2 K and with a helium constant-volume gas thermometer above 4.2 K. The gas thermometer was filled to a pressure of about 12 cm Hg with the bulb at 4.2 K so that temperature changes of the order of 1 part in $10^4$ could be reproducibly measured. A variable-dead-space volume permitted temperature measurements up to 300 K without changing the amount of gas in the thermometer.

Two pairs of germanium resistance thermometers were used. One pair was cut from a compensated single-crystal ingot grown at the Westinghouse Research Laboratories. The other pair was purchased from Cryocal, Inc. of Riviera Beach, Fla. In the usual way, $1/T$ was fit to a polynomial in powers of $\log R$ using about 50 calibration points between 1.2 and 21 K for each thermometer. The calibration runs thus also yielded values of $\delta T = T - T_{\mathrm{cal}}$, where $T_{\mathrm{cal}}$ is the temperature calculated from the polynominal. In the thermal-conductivity measurements, the temperatures were obtained from $T_{\mathrm{cal}} + \delta T$. For our homemade thermometers, a five-parameter fit was found to give excellent results. Unfortunately, these thermometers, unencapsulated and glued (with a layer of fiberglass insulation) to the thermometer mounts, were irreproducible from run to run and had to be abandoned. The Cryocal thermometers required an 8-term polynomial in order to keep $\delta T$ sufficiently small (about $3\times10^{-2}$ K at 20 K). The Cryocal thermometers were extremely stable and showed no significant shift in calibration during 18 months. A sample of Infrasil was measured with both sets of thermometers. Any difference in the thermal conductivities measured in the two runs never exceeded 2% of the measured values.

As mentioned previously, our first samples were cut 6–7-cm long so that they could be used in a "four-probe" thermal potentiometer as shown in Fig. 2(a). However, the thermal equilibrium times were found to be extremely long above 10 K. Not only was this very tiresome, but serious errors can be introduced if the average temperature of the

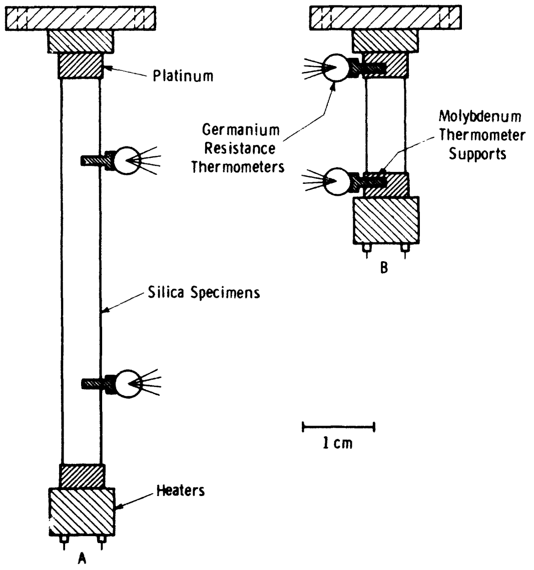

FIG. 2. Two sample mounting arrangements used in these measurements, (A) "four-probe" method, (B) "two-probe" method.

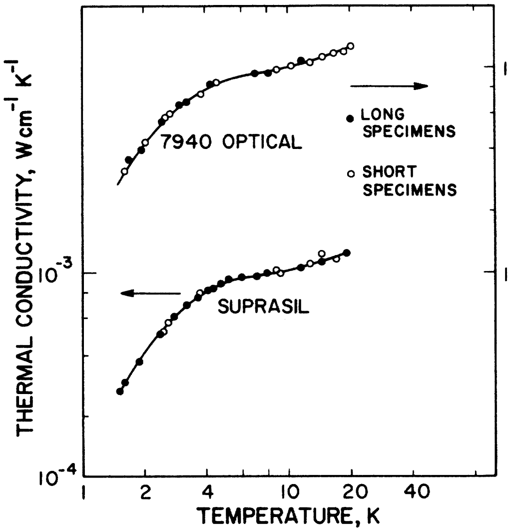

FIG. 3. Measured values of the thermal conductivity of Corning 7940 Optical silica and Englehard Suprasil between 1.3–20 K vs absolute temperature $T$. Measurements made with the four-probe and two-probe arrangements (see Fig. 2) are compared and found to be identical within experimental error.

sample drifts with time (which to some extent is, of course, always the case). The long samples were discarded in favor of the arrangement shown in Fig. 2(a). Two samples were measured in both arrangements. The results of these measurements shown in Fig. 3 demonstrate that the thermal resistance of the solder layer is negligible and that accurate results can be obtained with the "two-probe" method. Using measured values of the thermal time constants, corrections for the drift of the average temperature of the sample were calculated. These corrections (for the short samples) never exceeded 6% of the total heat generated.

Over all, including errors in the measurement of the geometrical form factors, the temperature differences and those resulting from the drift of the average temperature of the sample we estimate that these results are accurate to ± 2% below 4 K and ± 4% above 4 K.

## III. EXPERIMENTAL RESULTS

Figure 4 shows the measured values of the thermal conductivity of five specimens of vitreous silica between 65 and 300 K. Within experimental error, the thermal conductivities of all samples are the same. Many results of measurements in this temperature range have been reported and there are differences between them.[13] Our values agree with those of Ratcliff near 100 K but are about 6% larger than his at 300 K.

For both Infrasil (fused quartz) and Suprasil (synthetic silica) we measured the thermal conductivity of a rod and a sample cut from a plate, in order to see if the pulling or extrusion received by the rod would cause the thermal conductivity to differ from that of the plate specimen. Within 2% the two Infrasil samples had the same thermal conductivity between 1.5 and 20 K. The thermal conductivity of the plate specimen of Suprasil was about 5% smaller than that of the rod sample. However, since this was true throughout the temperature range, 1.5–20 K, it is probably to be attributed to errors in measurement of the form factors.

Figure 5 shows the thermal conductivity of the synthetic silica samples. Within experimental error, these silicas all have the same thermal conductivity between 1.5 and 20 K; these results are tabulated in Table II. There may be a small difference between the conductivity of the Corning silicas and that of the Suprasil. If real, this difference is of the order of the experimental error.

Figure 6 compares all the low-temperature measurements. The results for silicas made from fused rock quartz differ from one another and from the results for the synthetic silicas. The values of the thermal conductivities reported here are much smaller than those of Cohen,[5] for which we have no explanation. As is indicated in this figure, the thermal conductivity is varying faster than linearly with temperature at the lowest temperatures. These results are consistent with those of Zeller and Pohl[8] who find a $T^{1.8}$ dependence below 1 K.

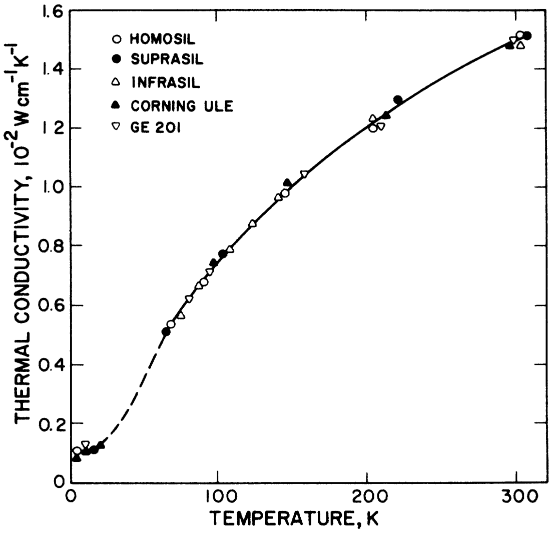

FIG. 4. Measured values of the thermal conductivity of five specimens of vitreous silica between 65 and 300 K vs absolute temperature $T$. The samples are identified in Table I.

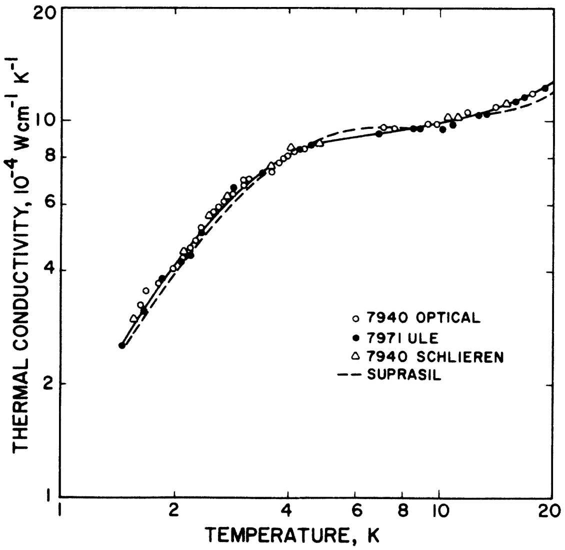

FIG. 5. Measured values of the thermal conductivity of several samples of synthetic silica vs absolute temperature *T*.

## IV. DISCUSSION

Figure 5 shows that the thermal conductivities of the synthetic silicas are the same, and Fig. 6 shows that the thermal conductivities of the specimens of fused quartz differ from each other and from the thermal conductivity of synthetic silica. Of particular interest are the results for the 7971 ULE silica. This is a silica with an exceptionally small coefficient of thermal expansion and contains of the order of 5% titania. The exact composition is not known to us and is of little importance since the thermal conductivity is unaffected. Another significant impurity in vitreous silica is the OH$^-$ ion. The synthetic silicas contain high concentrations of OH$^-$ ions and have low thermal conductivities. The 201 silica and the Infrasil have low OH$^-$ concentrations and higher thermal conductivities. However, Homosil also has a high thermal conductivity and contains a moderate concentration of OH$^-$ ions. There does not seem to be any correlation between the magnitude of the thermal conductivity and the concentrations of chemical impurities. Zeller and Pohl in surveying a far larger number of results reach the same conclusion.

TABLE II. Thermal conductivity of synthetic silica at low temperatures. The values of the thermal conductivity were taken from a smooth curve drawn through all the measured values for four samples of Corning silica (7940 Schlieren, 7971 ULE, and 2 specimens of 7940 Optical), and three samples of Englehard's Suprasil.

| *T* (K) | $10^4$ (W cm$^{-1}$ K$^{-1}$) |
|---|---|
| 1.45 | 2.62 |
| 1.61 | 3.11 |
| 1.84 | 3.71 |
| 2.20 | 4.68 |
| 2.35 | 5.1 |
| 2.79 | 6.2 |
| 3.38 | 7.4 |
| 4.14 | 8.3 |
| 6.92 | 9.3 |
| 8.50 | 9.5 |
| 8.79 | 9.5 |
| 10.1 | 9.8 |
| 12.61 | 10.5 |
| 15.95 | 11.5 |
| 16.24 | 11.6 |
| 19.0 | 12.4 |

It is clear that the differences between the various specimens can be associated with differences in the method of manufacture, and, therefore, it is possible to associate these differences in the thermal conductivity with differences in structure. We will, therefore, give a brief resume of Klemen's theory and contrast it to that of Anderson *et al.* At low termperatures in a disordered solid the velocity of sound $\vec{v}$ varies rapidly over distances small compared to the wavelength so that $\vec{v}(\vec{x}) = \vec{v} + \vec{s}(\vec{x})$, where $\vec{s}(\vec{x})$ is the fluctuation of the sound velocity from its average value $\vec{v}$ at the position $\vec{x}$. The phonon wavelengths are large compared to the interatomic spacing and the mean free path is even longer. Therefore, perturbation theory can be used and in scattering rate one finds a factor

$$\int\int d\vec{x}\, d\vec{r}\; \vec{s}(\vec{x})\cdot\vec{s}(\vec{x}+\vec{r})e^{i\vec{p}\cdot\vec{r}}$$

for the scattering of a phonon of wave vector $\vec{q}$ into

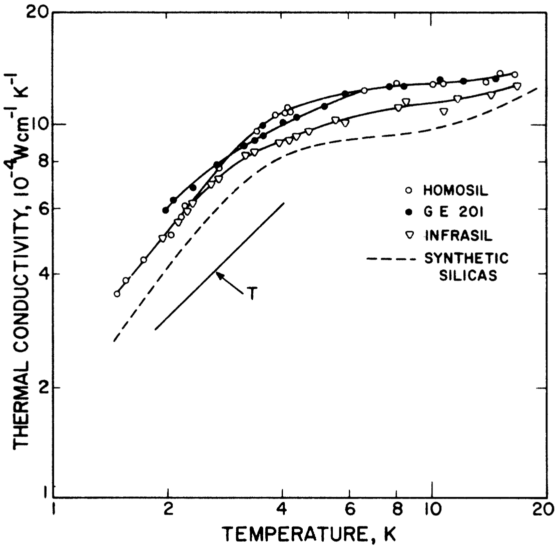

FIG. 6. Measured values of the thermal conductivity of vitreous silica between 1.5 and 20K.

$\vec{q}'$ with $\vec{q}-\vec{q}'=\vec{p}$. Thus, the strength of the scattering depends on the mean square fluctuation and on the spacial correlation function

$$f(\vec{r})=\frac{1}{V\langle s^2\rangle}\int d\vec{x}\,\vec{s}(\vec{x})\cdot\vec{s}(\vec{x}+\vec{r}).$$

The effect of this correlation is that the long-wavelength phonons are more strongly scattered than they would be if this small amount of long-range order were absent. Only when the typical phonon wavelength becomes much larger than the distances over which $f(r)$ has appreciable value will the disorder scattering decrease to the magnitude given by point-defect scattering.

One could now choose a function $f(r)$ and fit the data presented here by using the formulas of Ref. 4. The correlation function would in first approximation, consist of two terms, the larger being a rapidly decreasing function of $r$ and the smaller a very slowly varying function of $r$. The former term would yield the point defect scattering and the latter a scattering rate proportional to the first power of the phonon frequency. At present this would only be a mathematical exercise since we cannot present a model to account for the long-range correlation.

Moreover, the work of Phillips and of Anderson *et al.* provides a scattering mechanism that will yield very nearly the correct temperature dependence of the low-temperature thermal conductivity. The chief assumption of this model is that "there should be a certain number of atoms (or groups of atoms) which can sit more or less equally well in two equilibrium positions." Associated with the different positions are small differences in energy. Averaged over a disordered solid this will provide a nearly continuous (on a scale compared to $kT$) distribution of energy levels over which these groups of atoms will be distributed in thermal equilibrium. The result of this model is a specific heat linear in the absolute temperature and, invoking a resonance scattering, a thermal conductivity varying with the square of the absolute temperature. If these energy differences are to be associated with the positions of the atoms then this author sees no reason to expect, on the basis of this theory, there to be any differences between the thermal conductivities of the various kinds of silica. If, on the other hand, they were to be associated with the positions of larger units (possibly as large as the 20-Å-diam crystallites of Konnert *et al.* ?), then the differences that result from the method of manufacture of these silicas might be understandable in terms of the theory of Anderson *et al.* In any case, this question should be answerable experimentally. If the model of Anderson *et al.* is correct then the differences reported here should also appear in the specific heat. The author knows of no existing data that would settle this question.

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